### Biomimetic Active Sites in Metal-Organic Framework Catalysts for Hydrocarbon Transformations

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### ABSTRACT

Metal-organic frameworks (MOFs) are a class of crystalline materials featuring uniform distributions of inorganic nodes interconnected within well-defined organic porous environments. For applications in catalysis, the homogeneity of active centers attainable within MOFs enables achieving a level of clarity into structure-catalytic property relationships and reaction mechanisms beyond which can be realized in synthetic catalysts delimited by a high degree of heterogeneity in active site speciation – a feature of particular importance in the development of biomimetic catalysts. Herein, we demonstrate MIL-100 (MIL = *Materials of Institut Lavoisier*), a prototypical MOF featuring mixed-valent trinuclear metal nodes [ $M^{2+}(M^{3+})_2O$ ], features an active site pool which is uniform in structure and catalytic performance.

A combination of in-situ infrared spectroscopic characterization and probe molecule adsorption experiments with H<sub>2</sub>O, NO, and CO evidence the accessibility of the near theoretical density of coordinatively unsaturated divalent and trivalent open-metal sites within the Cr- and Fe-analogues of MIL-100 through facile thermal activation protocols ( $\leq$  523 K, inert or vacuum). Furthermore, we demonstrate the activated catalysts effectuate the gas-phase stoichiometric oxidation of CH<sub>4</sub> with N<sub>2</sub>O to partial oxygenates (methanol and acetaldehyde) through the involvement of every potentially available M<sup>2+</sup> open-metal site. Carbon monoxide is applied as a reductant to further elucidate reaction steps that mediate redox turnovers with N<sub>2</sub>O over MIL-100. Transient, steady-state, and isotopic kinetic analyses provide novel insight into levers for tuning the kinetic relevance of specific reduction and oxidation elementary reaction steps through secondsphere coordination effects and identity of the active metal.

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### **1. Introduction**

#### **1.1. Metal-Organic Frameworks: Prospects in Heterogeneous Catalysis**

Metal organic frameworks (MOFs) are a class of hybrid materials formed by the combination of inorganic nodes linked by organic molecules within crystalline, threedimensional periodic nets.<sup>1–4</sup> Due to the vast diversity of potential node structure and topologies available within MOFs, they offer a unique opportunity to exploit novel structural motifs for advancements in a wide range of applications including gas separation and storage,<sup>5–7</sup> sensing,<sup>8–10</sup> drug delivery,<sup>11,12</sup> and catalysis.<sup>13–18</sup> In relation to applications in catalysis, MOFs allow for heterogenizing active site structures that previously have only been evaluated in homogeneous catalysts.<sup>19</sup> For instance, Dincă and colleagues demonstrated the capability to heterogenize nickel complexes within a MOF framework for the dimerization of ethylene, without encountering penalties in catalytic activity or selectivity,<sup>20–22</sup> exemplifying methodologies which have remained challenges within heterogeneous catalysis research.<sup>23</sup>



**Figure 1.1.** (left) Example of a MOF structure (Cu-BTC) formed by the combination of copper dimer nodes and trimesate linker molecules (BTC = 1,3,5-benzenetricarboxylate). (right) Formation of open-metal sites in Cu-BTC through the desorption of coordinated water ligands.

Active sites within MOFs can arise from several sources, including post-synthetically deposited metal/metal-oxo clusters,<sup>24-26</sup> organic linker functionalities,<sup>27-30</sup> and encapsulated particles.<sup>31–33</sup> Of the various types which can be achieved, structural inorganic nodes serve as promising active sites for catalysis applications as they are inherently uniform and well dispersed throughout the periodic MOF structure.<sup>34–36</sup> Specifically, coordinatively unsaturated sites (or open-metal sites, Figure 1.1)<sup>37-42</sup> can be formed through the removal of labile ligands (*e.g.* water or solvent molecules), by thermal<sup>38,42-45</sup> or chemical activation protocols,<sup>46,47</sup> without comprising the integrity of the structure. It is at these locations where molecules can interact directly with the metal ions, one of the key features which allow MOFs to act as Lewis acidic adsorption<sup>48–52</sup> or catalytic active sites.<sup>53–</sup> <sup>57</sup> Although open-metal sites in MOF catalysts have been tested for a broad range of chemistries, protocols for evaluating atomic structure-property relationships in these materials (e.g. effect of metal oxidation state or coordination environment) and understanding associated reaction mechanisms are often neglected despite being imperative to the prospective application and rational design of MOFs for heterogeneous catalysis applications.

### **1.2. MIL-100 as a Prototypical MOF Structure**

To address gaps in the rigorous evaluation of MOFs as heterogeneous catalysts, the framework MIL-100 is exploited as a platform to demonstrate methodolgy for evaluating open-metal site formation, characterization, and catalytic performance. MIL-100 (MIL = *Materials of Institut Lavoisier*) is an archetypal MOF structure that has attracted consideration for a broad range of applications including gas separation, 58-61 gas storage, 62-

<sup>65</sup> and heterogeneous catalysis.<sup>19,47,66,67</sup> As first discovered by Gérard Férey and coworkers, the inorganic node of this material consists of three octahedrally coordinated metal atoms sharing an oxygen vertex ( $\mu_3$ -O) (Figure 1.2b).<sup>43</sup> By connection through the carboxylate groups of the tridentate organic linker, trimesic acid, each metal node is coordinated into the three-dimensional network with a MTN (Mobil Thirty Nine) topology (Figure 1.2a), delimitating bimodal mesoporous cages with free apertures of 25 and 29 Å, accessible through 5.5 and 8.6 Å windows, respectively.



**Figure 1.2**. (a) MTN topology of MIL-100 (b) Representation of the M<sub>3</sub>O metal node in MIL-100 in the unactivated state and (c) following thermal treatment, leading to coordinatively unsaturated open-metal sites.

The apical coordination position of the metal octahedral in each metal trimer is a water molecule in two positions and a monovalent anion ( $X^- = F^-$ , OH<sup>-</sup>, or Cl<sup>-</sup>) in the third position (Figure 1.2b). Prominently, removal of the labile water molecules can be completed at relatively moderate conditions (T < 523 K) without compromising the integrity of the structure.<sup>42,43,68</sup> This results in coordinatively unsaturated or open-metal sites that are accessible for interaction with guest molecules and is reflected in the application of this MOF for various hydrocarbon transformations including acetalization, hydrogenation, alkylation, and oligomerization chemistries.<sup>66,68–71</sup> For iron-containing MIL-100 it was first documented by Yoon *et al.* that removal of the anionic ligands ( $X^- = F^-$ , OH<sup>-</sup>) could also be achieved under vacuum or inert flow at temperatures of approximately 523 K to

create three open-metal sites per trimer,<sup>42</sup> with the departure of the counter anion resulting in the concurrent reduction of the metal site at that location from  $Fe^{3+}$  to  $Fe^{2+}$ .

### **1.3. Bio-Inspired Applications in Catalysis**

Of the various applications for which MIL-100 has been investigated, its prospective value as a catalyst for the partial oxidation of light alkanes has been of particular interest. Specifically, reduced M<sup>2+</sup> open-metal sites, formed through the elimination of anionic ligands (Figure 1.2b), are suggested to form highly reactive metal(IV)-oxo intermediates by reaction with N<sub>2</sub>O.<sup>72–74</sup> Transition metal-oxo complexes have been identified for their strong reactivity and capability to oxidize hydrocarbons in a range of biological and synthetic materials.<sup>75–79</sup> For instance, oxoiron(IV) species have been long hypothesized as the key oxidizing species in non-heme biological complexes including R2 proteins of ribonucleotide reductase (RNR R2) and soluble methane monooxygenase (sMMO) enzymes.<sup>80–83</sup> Specifically, the conversion of methane to methanol is capitalized with ease for biological processes by bacteria featuring MMO enzymes which are capable of harnessing molecular oxygen for this selective oxidation reaction (Figure 1.3).<sup>84–86</sup>



**Figure 1.3.** Soluble MMO featuring a diiron active center capable of oxidizing the C-H bond in methane (green = iron, red = oxygen, blue = nitrogen, white = carbon). Adapted from Ref. 87.

Inspiration for synthetic catalysts in the activation of light alkanes to value-added chemicals has been strongly inspired by biological materials, such as MMO enzymes. For example, catalytic processes have been demonstrated for Cu-zeolites, which can form methanol from methane and oxygen selectively at low conversions (<1%),<sup>88,89</sup> and isolated iron centers in zeolites have also been found to form active metal-oxo species (Fe<sup>IV</sup>=O) upon reaction with N<sub>2</sub>O that can oxidize methane selectively at ambient conditions.<sup>90-93</sup> Although a spearhead in the advancement of heterogeneous materials for light alkane conversion, several synthetic limitations prevent the improved productivity of both iron and copper zeolites. Specifically, the rigid inorganic framework of the zeolite structure confines architectural tunability and challenges with uniform ion incorporation hinders the production of materials with regular active site properties and limits the abatement of metal cluster or particle formation at high metal loadings.<sup>94-99</sup>

MOFs serve as a potential ideal host for supporting high densities of well-defined and dispersed catalytic sites, which is of significant value in maximizing atomic-level efficiencies for the selective functionalization of light alkanes.<sup>100,101</sup> Moreover, the potential for MOFs to mimic the structural and functional properties of biocatalysts has been considered one of the most appropriate applications of these materials as current synthetic catalysts lack the necessary architectural environment to parallel naturally-occurring compounds.<sup>102–104</sup> For the partial oxidation of light alkanes, a considerable number of MOFs have already been evaluated experimentally, featuring vanadium,<sup>105</sup> iron,<sup>73,106–109</sup> copper,<sup>24,110,111</sup> and chromium<sup>112</sup> active centers either inherent to the MOF structure or post-synthetically incorporated. Theoretical predictions, however, have

contributed to the promise of even a broader range of MOF materials to be viable for light alkane activation.<sup>107,113,114</sup>

As described in this thesis (*vide infra*), the homogeneous nature of open-metal sites in MIL-100, and their uniform participation as redox centers in the partial oxidation of CH<sub>4</sub> with N<sub>2</sub>O, is evaluated. The interpretation of fundamental structure-property relationships of this material is first and foremost dependent on an accurate evaluation of active site formation and quantification, in-situ, and a rigorous understanding of the associated reaction mechanisms. In the studies reported, MIL-100 is utilized as a prototypical metal-organic framework (with details of the individual features evaluated described in the following section) to demonstrate the capability of MOFs to support well-defined active site moieties for redox and Lewis acid catalysis. The methodologies and fundamental insight provided can be broadly applicable to the advancement of metal-organic frameworks as heterogeneous catalysts and the rigorous interpretation of structure-catalytic function relationships more generally.

### **1.4. Outline of Research**

This thesis can be described by three main areas of research: (1) characterization of open-metal site density and speciation, (2) application in the partial oxidation of methane, and (3) kinetic evaluation of the redox catalytic properties of metal-organic frameworks using the structure MIL-100 as an archetypal platform material. The first topic, presenting methods for quantifying and enabling access to open-metal sites within MIL-100 is described in Chapters 2 and 3. The application of sites assessed through these methods in the conversion of methane to partial oxygenates with N<sub>2</sub>O is addressed in Chapter 4. Lastly,

interrogation of the individual elementary reaction steps and catalytic active site properties involved in N<sub>2</sub>O-mediated redox chemistries over MIL-100 is evaluated in Chapters 5 and 6. Detailed summary of the contents of each chapter are provided hereafter.

Chapter 2 is reproduced from a previously published manuscript describing the quantification of open-metal sites in MIL-100 frameworks through irreversible water adsorption measurements (Hall, J.N., Bollini, P., *Langmuir* 36 (2020) 1345-1356). Thermal activation protocols leading to the removal of terminal ligands (*e.g.* H<sub>2</sub>O, OH<sup>-</sup>) in MIL-100 leads to the creation of coordinatively unsaturated open-metal sites, the quantification and characterization of which is essential to evaluating their use for future applications. A wide range of techniques have been developed for analyzing open-metal sites in MOFs; however, a method involving mild adsorption conditions, benign substrates, and providing the ability to directly measure the density of open-metal sites is still lacking. We hypothesized that water adsorption onto open-metal sites is irreversible at room temperature, whereas that elsewhere on the MOF is reversible. Comparison of open-metal site densities determined from irreversible water adsorption on MIL-100 activated at several temperatures with values estimated from infrared spectroscopy measurements evidence the validity and accuracy of this method.

In Chapter 3, characterization of open-metal site speciation, specifically metal oxidation state, is evaluated in correspondence with results presented in Chapter 2. This chapter is reproduced from a previously published manuscript (Hall, J.N., Bollini, P., *ACS Materials Letters* 2 (2020) 838-844). In-situ spectroscopic characterization in the presence of NO as a probe molecule revealed the increasing presence of reduced divalent metal sites

upon dehydroxylation, dissimilar from trivalent metal sites created upon dehydration. Site densities and oxidation states were found to be consistent with trends in the adsorption of carbon monoxide and ethene, both of which exhibit more favorable  $\pi$ -backbonding interactions with M<sup>2+</sup> over M<sup>3+</sup> sites. Results provided that in the hydroxide-containing variant of MIL-100(Cr) evaluated, the near theoretical maximum density of open-metal sites (both M<sup>2+</sup> and M<sup>3+</sup>) could be accessed upon thermal activation up to 523 K, offering potential breakthroughs for related adsorption and catalysis application.

Chapter 4 describes portions of two previously published manuscripts related closely to the application of divalent open-metal sites in MIL-100 for the partial oxidation of methane with N<sub>2</sub>O at low temperatures (423 - 473 K) and sub-ambient reactant partial pressures (Hall, J.N., Bollini, P., Chemistry – A European Journal 26 (2020) 16639-16643; Hall, J.N., Bollini, P., AIChE Journal 67 (2021) e17496). Results of transient kinetic measurements and in-situ active site titration experiments conducted over Fe- and Crcontaining MIL-100 evidence the vital role of M<sup>2+</sup> open-metal sites in the partial oxidation of CH<sub>4</sub>, in which every available site contributes equivalently to the formation of partial oxygenates CH<sub>3</sub>OH or acetaldehyde. Specifically, selectivity for C-C bond formation steps leading to acetaldehyde formation during product extraction steps are significantly enhanced over the chromium variant. Furthermore, results described in this chapter demonstrate the capability to identify clear relationships between metal identity and product selectivity in MOF materials for  $N_2O$ -mediated light alkane oxidation, underlining the value in exploring classes of materials hosting active sites in well-defined coordination environments.
Chapter 5 and Chapter 6 are bipartite components of a kinetic study that is currently in preparation for publication which further aims to obtain clarity into the reaction steps facilitating N<sub>2</sub>O oxidation chemistries over MIL-100. In the oxidation of methane, rigorous mechanistic evaluations are limited by the stoichiometric nature of the oxidation, as partial oxidation products are captured as surface-bound methoxy intermediates. Furthermore, CO is applied as a reductant to further elucidate reaction steps which mediate redox turnovers with N<sub>2</sub>O over MIL-100(Fe) and MIL-100(Cr). Transient, steady-state, and isotopic kinetic analyses provide novel insight into levers for tuning the kinetic relevance of specific reduction and oxidation elementary reaction steps through the identity of the active metal and secondary coordination sphere effects with implications in improving the atomic-level efficiencies of MOFs for light alkane conversion, more broadly.

Lastly, Chapter 7 provides a unique evaluation of MIL-type MOF frameworks in the liquid-phase acetalization of benzaldehyde with methanol, reproduced from a published manuscript (Hall, J.N., Bollini, P., *ACS Catalysis* 10 (2020) 3750 – 3763). In this work, a combination of liquid phase kinetic measurements, in-situ titrations, and in-situ infrared spectroscopy data were used to decipher the identity of active sites responsible for the acetalization of benzaldehyde with methanol. Specifically, Brønsted acid site-selective titrations with 2,6-di-*tert*-butylpyridine (DTBP) and catalyst dehydration experiments support that a significant proportion of the activity is derived from Brønsted acid sites, with infrared spectroscopic experiments revealing that the source of Brønsted acidity is the water and/or hydroxide species coordinated directly to metal atoms. The methodology used in this study to elucidate site requirements is broadly applicable within the burgeoning field

of MOF catalysis, and points to the importance of thoroughly investigating MOF site speciation *under* reaction conditions to more fully exploit this emerging class of materials for catalytic applications.

# 2. Characterization of Open-Metal Site Density in MIL-100 through Irreversible Water Adsorption Measurements

In this chapter, we investigate for the first time the use of room-temperature water adsorption isotherms for the quantification of MOF open-metal site density. We report that the quantity of water adsorbed irreversibly at room temperature on MIL-100 represents the open-metal site density under a given set of activation conditions. We use for this purpose a hydroxyl-containing version of MIL-100(Cr) that enables us to track (using in situ Fourier transform infrared spectroscopy) both dehydration and dehydroxylation events leading to open-metal site creation, providing evidence for site counts measured using irreversible water adsorption. Crucially, this approach circumvents the need for assumptions relating to the identity of open-metal sites and the degree of adsorbate saturation, while also obviating risks associated with the use of hazardous reagents. Given the near-universal presence of water as a labile ligand in the first coordination sphere of possible MOF openmetal sites, we envision that the protocols presented here could represent an approach to counting open-metal sites that is broadly applicable within (and maybe even beyond) the field of MOF research. This section is adapted from the following peer-reviewed article Hall, J.N., Bollini, P., "Quantification of Open-Metal Sites in Metal-Organic Frameworks Using Irreversible Water Adsorption." Langmuir, 36 (2020) 1345-1356.

# **2.1. Introduction**

Accessibility of metal sites in MOF structures, although sometimes entatic,<sup>115</sup> can often be hindered by complete coordination of the metal cations in the structure, and may be unsaturated only in the location of framework defects such as missing organic linkers.<sup>6,116,117</sup> In most cases, however, MOFs contain labile, non-structural ligands within the first coordination sphere of the metal sites, allowing for the creation of coordinatively unsaturated sites (alternatively referred to as open-metal sites),<sup>37–42</sup> through thermal<sup>38,42–45</sup> or chemical activation protocols.<sup>46,47</sup> Open-metal sites (OMSs) are a ubiquitous feature of MOF materials, and central to their ability to act as Lewis acid centers in a range of chemistries<sup>53–57</sup> as well as adsorption sites for both enhanced<sup>48–52</sup> and selective<sup>60,118–120</sup> gas adsorption at low partial pressures. We assert that the ability to accurately measure the density of open-metal sites existing under a given set of experimental conditions can serve as a strong foundation for the rigorous interpretation of adsorption and catalytic data on MOFs, and also aid in their rational design for a variety of applications.

Techniques commonly used in the literature to assess open-metal site density include temperature programmed desorption (TPD), CO and H<sub>2</sub> adsorption, and probe molecule infrared spectroscopy.<sup>121</sup> Despite the widespread use of ammonia TPD in characterizing acid sites in zeolites,<sup>122–124</sup> its use in estimating MOF OMS densities presents two major drawbacks. Firstly, the temperature range for desorption from different types of acid sites (for example, Lewis versus Brønsted acid sites) can often overlap, making peak deconvolution a necessary step in quantifying acid sites.<sup>125,126</sup> Secondly, and even more importantly, temperatures required to desorb strong basic probe molecules such as ammonia may exceed the MOF thermal stability limit, as shown by Kim et al. for MIL-100 and MIL-101.<sup>127</sup>

Probe molecules including pyridine, acetonitrile, carbon monoxide, nitric oxide, and hydrogen have been used in conjunction with infrared spectroscopy to quantify and characterize open-metal sites in MOFs. A unique advantage of this method is that in addition to assessing the density of open metal sites, frequency shifts corresponding to specific adsorbate molecules can serve as a marker for probing the speciation of open-metal sites.<sup>128</sup> A major limitation of this tool, however, is the reliance on accurate molar extinction coefficients, the estimation of which requires the simultaneous measurement of infrared spectra and equilibrium adsorption capacities,<sup>129</sup> with additional complexities in estimating the latter arising in the presence of multiple binding configurations.<sup>130</sup>

 $H_2$  and CO adsorption studies, although commonly used, require the employment of low temperatures ( $\leq 100 \text{ K}$ )<sup>6,131,132</sup> and/or high pressures (~ 30 – 80 bar)<sup>62,133</sup> to saturate open-metal sites. The use of basic probe molecules like pyridine and acetonitrile, on the other hand, do not require extreme temperatures or pressures to saturate open-metal sites, but exhibit complications arising from unselective adsorption. In a study that exemplifies such behavior, Volkringer et al. reported that temperatures in excess of 373 K are needed to evacuate even the most weakly physisorbed pyridine species on MIL-100-Al, thereby, preventing analysis of OMS densities below 373 K.<sup>131</sup>

Given that water removal represents arguably the most common mechanism for MOF open-metal site creation, we hypothesized that the microscopic reverse of this molecular event- adsorption of water onto coordinatively unsaturated metal sites- could provide the molecular level basis for counting these sites. Specifically, we propose that considerations relating to unselective water adsorption can be eliminated by exploiting the fact that while water adsorption onto open-metal sites is irreversible at room temperature, unselective adsorption elsewhere in the MOF material can be reversible. A direct implication of this proposal is that room temperature difference isotherms (total water adsorbed – water

adsorbed reversibly) can serve as a marker for MOF open-metal site density. We report here, using MIL-100 as a prototype, a tool for the measurement of OMS densities that circumvents the need for toxic reagents, sub-ambient temperatures, and high pressures, while also eliminating the need for incorporating considerations relating to unselective adsorption. The methodology presented is analogous to difference isotherms from CO and H<sub>2</sub> chemisorption measurements used routinely in the heterogeneous catalysis literature to determine metal dispersion in supported metal catalysts, but differs in the exclusive use of ambient temperatures and benign reagents as part of the experimental protocol.<sup>134–138</sup> Given the near-universal presence of water as a labile ligand in the first coordination sphere of MOF open-metal sites, we envision that the protocols presented here could represent an approach to counting sites that is broadly applicable within the field of MOF research. In section 3.1 we describe the structure, synthesis, and characterization of MIL-100(Cr)- the material used as a prototype in our study. In section 3.2 we describe our methodology for counting sites, and evidence supporting our use of this methodology. In section 3.3 we assess the effect of activation temperature on OMS density; in Section 3.4 we validate these site counts using in-situ infrared spectroscopy measurements; and in section 3.5 we extend our study to MIL-100(Al), devoid of hydroxyl anions, demonstrating the broader applicability of our approach, independent of metal and anion identity.

# **2.2 Materials and Methods**

#### 2.2.1 MIL-100 Synthesis

MIL-100(Cr) was synthesized by adapting the procedure reported by Mao et al. <sup>139</sup>.9 g of CrCl<sub>3</sub>·6H<sub>2</sub>O (Sigma Aldrich,  $\geq$  98.0%) and 3.55 g of trimesic acid (Alfa Aesar, 98%)

were first ground with a mortar and pestle for 30 minutes at room temperature. The mixture was then transferred to a 45 mL PTFE-lined stainless steel autoclave (Parr Instruments) and heated at 493 K for 15 hours under rotation. The product was washed with approximately 500 mL of deionized water (18.3 MΩ) at 343 K for 3 h and 500 mL of ethanol (Decon Laboratories, Inc., 200 Proof) at 338 K for 3 h in a 500 mL Erlenmeyer flask (Wilmad-LabGlass) fitted with a reflux condenser (Glassco, 200 mm). The sample was collected with fresh ethanol and dried at 343 K overnight. The sample was then transferred to a vacuum oven (MTI Corporation,  $P < 3 \times 10^{-3}$  bar) and maintained at 423 K for 12 hours. Catalyst batches were combined to produce a large enough quantity for the analyses in this work. Samples were stored at room temperature in a desiccator.

MIL-100(Al) was also synthesized according to a previously reported procedure.<sup>140</sup> A mixture of 0.23 g of aluminum nitrate nonahydrate (Sigma-Aldrich, > 98%), 0.104 g of trimethyl-1,3,5-trimesate (Sigma-Aldrich, 98%), and 0.032 mL nitric acid solution (VWR Chemicals, 68-70 wt.%), and 3.538 mL of deionized water (18.3 M $\Omega$ ) were loaded into 45 mL PTFE-lined stainless steel autoclaves (Parr Instruments) and heated to 483 K in 30 minutes, held at 483 K for 3.5 hours, and cooled to room temperature. The resulting powder was collected via filtration, washed five times with approximately 30 mL of deionized water, and dried at room temperature overnight. The resulting solid (from three individual reactions) was separated equally into three autoclaves with 10 mL of N,N-Dimethylformamide, DMF, (Fisher Chemical) each and heated at 423 K for 4 h. The solid was then collected via centrifugation and washed with fresh water twice (4000 rpm, 2 min intervals). The mixture was then transferred into a 500 mL Erlenmeyer flask (Wilmad-

LabGlass) with roughly 500 mL of deionized water and stirred (800 rpm) under reflux at 373 K for 15 hours. The final sample was collected via filtration and dried at room temperature. Thermal treatment in a vacuum oven (MTI Corporation,  $P < 3 \times 10^{-3}$  bar) was completed at 423 K for 12 hours to evacuate residual water and DMF from the pores of the material. The product was stored at room temperature in a desiccator.

# 2.2.2 Material Characterization

Powder X-ray diffraction (XRD) patterns were obtained using an Empyrean Malvern Panalytical diffractometer equipped with a Cu Ka X-ray source ( $\lambda = 1.54$  Å). Approximately 0.02 g of sample was loaded into a glass sample holder (Rigaku, 0.2 mm indentation) prior to diffraction pattern collection  $(2.5 - 20^{\circ})$ , step size of 0.013 °, 23.8 s per step). Nitrogen physisorption experiments (77 K) were completed using a Micromeritics 3Flex Surface Characterization Analyzer. In a typical measurement, approximately 0.05 g of sample was evacuated ( $P \sim 1 \ge 10^{-4}$  bar) at 423 K for 15 hours on a Micromeritics VacPrep degassing system. Thermogravimetric analysis (TGA) was completed using a Tarsus TG 209 F3. Experiments were conducted with approximately 20 mg of sample under a flow of 40 mL min<sup>-1</sup> air (Matheson, zero-grade) at a heating rate of 1 K per minute. Transmission infrared spectroscopy analyses were performed using a Nicolet 6700 FTIR Spectrometer (Thermo Scientfic) with a Harrick High Temperature Cell equipped with CaF<sub>2</sub> windows (32 x 3 mm). Self-supporting wafers (~ 15 mg) were analyzed and thermally treated under dynamic vacuum (pressure  $= 8 - 11 \times 10^{-5}$  bar, Pfeiffer Duo 2.5 Vacuum Pump). Spectra were collected using a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen (77 K) averaging 64 scans at 4 cm<sup>-1</sup>

resolution in the  $4000 - 1100 \text{ cm}^{-1}$  range and an empty cell reference was collected under N<sub>2</sub> flow as the background reference. IR spectra reported here were baseline-corrected and peak areas were integrated using Origin 8.5.

# 2.2.3 Water Adsorption Measurements

Water adsorption measurements were completed using a Micromeritics 3Flex Surface Characterization Analyzer. 10 mL of deionized water (18.3 M $\Omega$ ) within a 25 mL sample cylinder (Swagelok) was used as the vapor source and was held at an external temperature of 308 K during analysis using a heating mantle (Micromeritics). In a typical measurement, approximately 0.05 g of sample was loaded into a quartz flow through sample tube (12 mm, Micromeritics) on a 20 mm bed of quartz wool topped with a quartz frit. Sample pretreatments were completed at elevated temperatures ranging from 303 to 523 K *in vacuo* (P < 6.7 x 10<sup>-5</sup> bar). Following activation, adsorption experiments were conducted at room temperature (296 K). After adsorption up to the saturation pressure (0.028 bar), the sample was evacuated (P < 6.7 x 10<sup>-5</sup> bar) at the analysis temperature (296 K) for 12 hours, immediately after which a repeat adsorption experiment was completed to determine the residual water adsorption capacity.

# **2.3 Results and Discussion**

# 2.3.1 Structure, Open-Metal Site Creation, and Characterization of MIL-100

MIL-100- a porous  $\mu_3$ -oxo centered metal trimesate- has attracted consideration for a range of applications including gas separation,<sup>58–61</sup> gas storage,<sup>62–65</sup> heat pumps,<sup>141–143</sup> and heterogeneous catalysis.<sup>19,47,66,67</sup> Specifically, it has been evaluated in several applications that are part of large-scale industrial processes, for example as a catalyst for methane

hydroxylation<sup>72</sup> and ethylene oligomerization,<sup>70,71</sup> as well as an adsorbent for light olefinparaffin separations  $^{42,60,144}$  – applications that would benefit significantly from rigorously measured open-metal site counts. MIL-100 is an ideal prototype for our study, owing to the significant number of publications dedicated to unraveling conditions for its activation,<sup>42,43,68,131,132,140</sup> providing us with a sound basis for comparing and interpreting our results (detailed discussion in following sections). In addition to being amenable to thermal treatments that eliminate labile ligands while avoiding adverse effects on its structural integrity, MIL-100 is also relatively devoid of missing linker defects that in many cases can complicate interpretation of gas and vapor adsorption data.<sup>145–149</sup> Lastly, the hydroxyl-containing material- key to validating our protocols- is relatively simple to synthesize without the use of hydrofluoric acid, as can be noted from the synthesis protocols described in the Section 2.2 Materials and Methods. We clarify that even though the concepts and methods presented here are applicable regardless of the identity of the anion, the presence of hydroxyl groups and water molecules as exclusive labile ligands in the metal's first coordination sphere enables verification of site counts through the use of in-situ infrared spectroscopy measurements.

MIL-100, first reported by Férey and coworkers,<sup>43</sup> is comprised of  $\mu_3$ -oxo centered metal trimer nodes linked together through trimesate linkers. The inorganic node consists of three octahedrally coordinated metal atoms sharing an oxygen vertex, as shown in Figure 2.1. Each metal atom is further coordinated at the equitorial positions by deprotonated carboxylate groups originating from the trimesic acid linker. These nodes and linkers are arranged to form supertetrahedra with metal nodes as vertices and organic linkers as faces

(Figure 2.1b). Assembly of these supertetrahedra sanctions a 3D network with an MTN (Mobil Thirty Nine) topology (Figure 2.1d), and encompasses a pore system that can be visualized as a combination of two types of mesoporous cages with free apertures of 25 and 29 Å (Figure 2.1c) accessible through 5.5 and 8.6 Å windows, respectively. The apical coordination position of each metal octahedron is occupied by a water molecule for two metal atoms per node and a monovalent anion ( $X^- = F^-$ , OH<sup>-</sup>, Cl<sup>-</sup> etc.) for one metal atom per node. It has been demonstrated in the literature that removal of water molecules can be accomplished under relatively mild conditions (approximately 423 K) without compromising the integrity of the structure,<sup>42,43,68</sup> thereby resulting in coordinatively unsatured sites accessible for interaction with guest molecules.



**Figure 2.1.** Structure of MIL-100 featuring the trimer node (a) linked by trimesic acid to form supertetrahedra (b), which constitute the MOF framework with two cage sizes (c) crystallizing into the MTN topology (d). Adapted with permission from Ref. <sup>4</sup>

Characterization of the physicochemical properties of MIL-100 synthesized in this report are included in Section A1. Material Characterizationof Appendix A. Supporting Information for Section 2. The XRD pattern of MIL-100(Cr) (Figure A1a), consistent with the simulated pattern,<sup>43</sup> suggests crystallization into the MTN topology during hydrothermal synthesis. The broad peaks may reflect smaller crystallite sizes typical of MIL-100 materials synthesized in the absence of HF as a crystallizing agent.<sup>139,150,151</sup> The

shape of the nitrogen physisorption isotherm (Figure A1b) is consistent with literature reports,<sup>139,152,153</sup> and exhibits the majority of its uptake below a relative pressure of 0.4, as expected based on cage diameters of 25 and 29 Å. The estimated BET surface area is approximately 2050 m<sup>2</sup>/g<sub>cat</sub>, close to values previously reported in the literature for MIL-100(Cr).<sup>139,152,153</sup> Furthermore, from the TGA profile of MIL-100(Cr), two weight losses can be observed (Figure A1c): the first weight loss below 523 K can be ascribed to removal of guest molecules and labile ligands, while the second weight loss after 523 K can be attributed to oxidation of the organic ligands. The second weight loss (~ 57 wt.%) is similar to that reported in the literature (58 wt.%),<sup>139</sup> and suggests that the trimesic acid content is close to that of the theoretical material  $(Cr_3O(H_2O)_2(OH)[C_6H_3(CO_2)_3]_2 \cdot nH_2O, n \approx$ 5.5),<sup>43,139</sup> providing a 21 wt.% estimate of the Cr content. Notably, this material exhibits thermal stability in air up to temperatures of 573 K. These characterization experiments were also completed for MIL-100(Al) and point to the expected crystal structure, surface and material composition (Section A1.2. MIL-100(Al) Synthesis area. and Characterization Results, Appendix A).

# 2.3.2. Methodology for Quantifying Open-Metal Sites using Water Adsorption Measurements

Given the presence of chemically bound water molecules in the metal's first coordination sphere, we hypothesized that adsorption of water onto open-metal sites at room temperature is irreversible, whereas that elsewhere onto the MOF material is reversible. Based on our hypothesis, we use an experimental protocol involving four steps (Figure 2.2), the first being activation under vacuum at elevated temperatures. This step eliminates all physisorbed water while also providing conditions aggressive enough to remove a *fraction* of the water chemisorbed onto metal sites. The higher the activation temperature, the lower the fraction of water remaining coordinated to metal sites after activation, and the greater the open-metal site density, as expected based on previous literature.<sup>131,154,155</sup> Specifically, activation was carried out under vacuum ( $P < 6.7 \times 10^{-5}$ bar) at temperatures ranging from 303 to 523 K. In Figure 2.2, we chose to depict the material in a state where half the metal atoms are present as open-metal sites while the other half are coordinated to water after high temperature activation. Dehydration and dehydroxylation are depicted as the two steps leading to open-metal site creation, evidence for which is provided by infrared spectroscopy results included later in this report. We note that the identity of the mechanism involved in the creation of open-metal sites (dehydration versus dehydroxylation) does not alter site counts as long as water adsorption onto openmetal sites constitutes the only irreversible adsorption event in experiments carried out at room temperature- a condition borne out repeatedly in the data reported as part of this study.

The second step involves measuring adsorption isotherms of water onto the MOF containing a specific fraction of open-metal sites created during the high temperature activation in step 1. Figure 2.3 shows the adsorption isotherm for MIL-100(Cr) activated at 523 K (closed symbols) as a function of the absolute pressure of water (saturation pressure = 0.028 bar). The type-V shaped isotherm is characteristic of mesoporous adsorbents, and exhibits three distinct steep regions, consistent with experimental water adsorption isotherms for MIL-100 reported previously.<sup>141,150,156,157</sup> The first of the three

regions lies between approximately 0 and 1 x  $10^{-4}$  bar, with the uptake corresponding roughly to 1 mole water per mole chromium, suggesting that adsorption in this region of



**Figure 2.2**. Representation of the method used for counting OMS density as a function of activation temperature. The OMS density is given by the difference between the amounts of water adsorbed in steps 2 (n1) and 4 (n2).

the isotherm may occur exclusively on chromium sites, all of which are coordinatively unsaturated when activated at 523 K (further evidence provided in following sections). These low values of pressures required to saturate MIL-100 open-metal sites are consistent with Grand Canonical Monte Carlo (GCMC) simulations reported by Maurin and coworkers, in which one water molecule per coordinatively unsaturated iron was found to be adsorbed at a water partial pressure of  $1.5 \times 10^{-5}$  bar (relative pressure =  $5 \times 10^{-4}$ ).<sup>143</sup> The authors also suggest that hydrogen bonding between adsorbate molecules and coordinated water or hydroxide species plays a key role in determining adsorption behaviour in the regime following saturation of OMSs, represented by the region between 1 x  $10^{-4}$  to 0.006 bar (Region I, Figure 2.3), with 2.5 moles water per mole Cr being adsorbed at 0.006 bar. Next, water adsorbs into the pores of MIL-100 through a pore filling mechanism, with simulations indicating the preferential adsorption of water into the 25 Å cages over the 29 Å cages.<sup>143,158,159</sup> Such an interpretation of Region I is also consistent with Monte Carlo simulations on MIL-100(Fe) previously reported by Chen *et al.* in which snapshots of water configurations show the near-absence of water in the large cages and concurrent complete pore-filling of the smaller cages at a relative pressure of 0.4 (water partial pressure = 0.012 bar).<sup>160</sup>



Figure 2.3. H<sub>2</sub>O adsorption isotherm of MIL-100(Cr) evacuated at 523 K for 6 hours ( $\bullet$ ) and the repeat adsorption isotherm obtained immediately after evacuation for 12 hours at the analysis temperature ( $\circ$ ).

Once the smaller, 25 Å cages have been saturated at lower pressures, pore filling at higher pressures should reflect condensation into the larger 29 Å cages, as hinted at by GCMC simulations.<sup>143,160</sup> Such condensation into larger mesopores is responsible for the steep increase in uptake between 0.012 and 0.017 bar (Region III, Figure 2.3). The additional water adsorbed at pressures greater than 0.017 bar, following condensation in the mesopores, is larger in magnitude than that reported previously,<sup>141,161</sup> and may correspond to condensation within inter-particle voids, as suggested by Kaskel and coworkers.<sup>161</sup> These greater inter-particle void volumes may be a consequence of smaller

particle sizes typically obtained using fluoride-free syntheses used in our experiments, in contrast with conventional, fluoride-mediated synthesis procedures.<sup>139,150,151</sup>

Following water adsorption up to near saturation (Step 2, Figure 2.2), evacuation of the sample was completed at the analysis temperature (296 K) for 12 hours (Step 3, Figure 2.2). This is a key step in our protocol, where ideally only water molecules physisorbed in the sample are desorbed, whereas those chemisorbed onto chromium sites are left unaffected. Immediately following this evacuation step, the water adsorption isotherm is remeasured (Step 4, Figure 2.2), represented by the open symbols in Figure 2.3. Consistent with our expectation that water adsorbed onto open-metal sites would not be desorbed upon evacuation at room temperature, the repeat isotherm exhibits lower uptakes compared to the original adsorption isotherm obtained over the material activated at 523 K. Interestingly, although the repeat isotherm lies below the original isotherm in the entire pressure range of the measurement, the difference between the two isotherms is lesser in the low-pressure region (before mesopore filling) compared to the high-pressure region (> 0.016 bar) where MIL-100 mesopores no longer contribute to the water uptake. A possible reason for smaller differences observed at lower pressures is the greater relative preponderance of guest-guest interactions compared to host-guest interactions in the entire pressure range of the repeat isotherm. The increasing importance of guest-guest interactions with water loading for a polar molecule like water has been suggested previously in the literature for MIL-100 materials.<sup>158,160</sup> A clear understanding of the physical basis for the smaller than expected differences between the two isotherms at low pressures requires differentiating between the quantity adsorbed in an adsorption

experiment (represented by the ordinate in Figure 2.3) and the true water density in the MIL-100 material (the ordinate in Figure 2.3 + the OMS density before dosing water as part of Step 4). Whereas the former represents the amount of water transferred from the vapor phase to the surface, the latter represents the degree of hydration of the MOF. We emphasize the fact that even though the amount of water adsorbed in the repeat isotherm is lower than that in the original isotherm, the true water density at any water partial pressure is higher for the repeat isotherm measurement (Step 4, Figure 2.2) compared to the original isotherm (Step 2, Figure 2.2). We propose that the origin of smaller differences between the original and repeat isotherms at lower pressures reflect higher true water loadings for the repeat isotherm at any given partial pressure. Both Papadopoulos and coworkers<sup>159</sup> and Maurin and coworkers<sup>143</sup> have suggested that both hydroxyls and coordinated water can play a key role in promoting hydrogen bonding-mediated guestguest interactions at low pressures (P < 0.01 bar). Such saliency of guest-guest interactions, combined with the higher water loadings prevalent in the repeat isotherm measurements at any given water partial pressure, lead to smaller than expected differences between the two isotherms. The data reported here are consistent with the critical role of pre-adsorbed water on equilibrium adsorption capacities- an aspect that contributes significantly to behavior of MIL-100 in the entire mesopore filling region of the repeat isotherm. This effect of pre-adsorbed water on attenuating differences between the first and second isotherms on MIL-100(Cr) only persists up to water pressures required to saturate the mesopores, with the portions of the isotherm above those pressures being linear in water pressure near complete saturation (P > 0.016 bar), and exhibiting a constant difference

value (Figure A3, Appendix A). We specifically use this high-pressure region of the isotherm to calculate OMS densities, given that both the small and large mesopores have already been completely filled at these pressures. There are two ways of interpreting these constant difference values at higher pressures: the first involves consideration of the fact that in pores of larger sizes water-water interactions would be (on average) less prevalent compared to smaller pores due to larger average water-water distances, and hence the effect of an equivalent amount of pre-adsorbed water is more limited in larger pores compared to smaller pores. The second possibility is that at high enough pressures the difference between the amount of water adsorbed and the true water density becomes negligible, rendering the difference between the original and repeat isotherms to correspond more closely to the OMS density. Specifically, the isotherms in Figure 2.3 exhibit such behavior above an ordinate of approximately 10 mol  $H_2O$  (mol Cr)<sup>-1</sup>- a value an order of magnitude greater than the OMS density under the corresponding activation conditions (approximately 1 mol H<sub>2</sub>O (mol Cr)<sup>-1</sup>). We suggest that in future studies exploiting this technique, difference values be used in pressure regimes high enough where the experimentally measured quantity of water adsorbed approximates to the true water density. Subtraction of the difference between the two isotherms at relative pressures within this range yields a value of  $0.98 \pm 0.02$  moles of H<sub>2</sub>O per total moles Cr for activation at 523 K. This site count was found to be invariant in evacuation time chosen for step 3 (Figure A4), establishing that a 12 hour evacuation treatment is sufficient to effect complete removal of physisorbed water. An open-metal site count close to a value of 1 mol H<sub>2</sub>O per mol Cr suggests that 523 K is a sufficiently high temperature under

vacuum to render the vast majority (if not all) of the chromium in the MIL-100(Cr) material under investigation as open-metal chromium. Next, we present OMS densities assessed using this method as a function of activation temperature.

# 2.3.3. Effect of Activation Temperature on Open-Metal Site Density

Previous studies indicate that MIL-100 OMS density is strongly dependent on activation temperature.<sup>42,132,162</sup> For example, Vimont and co-workers used in-situ IR data in the presence of CO at 100K to report a progressive increase in OMS density in MIL-100-Cr up to 200 °C, at which they could access approximately two-thirds of the Cr sites.<sup>132</sup> In a subsequent study, Volkringer *et al.* utilized the same technique to quantify OMSs on MIL-100(Al) at various activation temperatures between 298 and 623 K. Their results indicated a gradual increase in OMS density up to approximately 0.4 open-metal Al per total Al when activated at 623 K.<sup>131</sup> Similar results were obtained using a combination of <sup>1</sup>H and <sup>27</sup>Al solid state NMR in a follow-up study on MIL-100(Al).<sup>162</sup> Here, the amount of water removed as well as coordinatively unsaturated Al formed upon thermal treatment were tracked quantitatively using <sup>1</sup>H and <sup>27</sup>Al NMR chemical shifts. Although the estimated OMS fraction increased progressively with treatment temperature, the final value corresponded to only approximately 30% of the total Al, low values of which were attributed to occluded organic species that strongly interact with the metal sites.<sup>162</sup> Yoon et al. also reported the effect of activation temperature on OMS density in MIL-100(Fe), with the removal of both water and anionic species (OH<sup>-</sup> and F<sup>-</sup>) leading to OMS fractions greater than 0.70.42 In another extensive infrared study on MIL-100(Fe) activated at different temperatures, the adsorption of several probe molecules including CO, CO<sub>2</sub>,

propane, and propylene was used to demonstrate the importance of activation temperature in controlling OMS density and speciation (*i.e.* Fe oxidation state).<sup>154</sup> Wang and coworkers were able to observe similar trends with activation temperature over both MIL-100(Fe) and MIL-100(Cr) in a series of publications, where increasing fractions of reduced metal sites created through anion removal (OH<sup>+</sup>/F<sup>-</sup>) were detected using x-ray photoelectron spectroscopy.<sup>70,71</sup> Based on these previous observations, it is apparent that being able to quantify OMS densities at different treatment conditions is essential to unraveling the activation process. These data point to differing OMS fractions that can be accessed based on the identity of the MIL-100 metal and the activation conditions used to access these sites but are all consistent with increasing site fractions that can be accessed with progressively higher treatment temperatures. These studies also form the basis for our use of temperatures ranging between 303 and 523 K for the high temperature activation step.

Figure 2.4 shows the original and repeat adsorption isotherms for samples activated between 303 and 523 K. We reemphasize here the fact that the effect of activation temperature on OMS density is observed only in higher pressure region of the isotherm. Original water adsorption isotherms are near-identical in the low-pressure region of the isotherm (Figure 2.4a, <0.016 bar), and differences as a function of activation temperature are sensed fully only at higher pressures (> 0.016 bar), where the amount of water adsorbed in the repeat isotherm approximates to the amount of adsorbate truly present in the material. Repeat adsorption isotherms (Figure 2.4b), on the other hand, are insensitive to activation temperature, owing to the fact that evacuation under vacuum for 12 hours at room

temperature brings MIL-100(Cr) back to a state of hydration corresponding to one mole water per mole chromium (Step 3, Figure 2.2) regardless of the initial activation



**Figure 2.4.** H<sub>2</sub>O adsorption isotherms (296 K) of MIL-100(Cr) evacuated at the specified temperature for 6 hours (a). Repeat adsorption isotherms for MIL-100(Cr) obtained immediately after evacuation for 12 hours at the analysis temperature (b).

temperature. Specifically, adsorption isotherms are identical in the *entire* pressure range of the measurement, since in this case the true water content of the sample differs from the measured amount by the exact same number (roughly one mole water per mole chromium) at every water pressure used in the isotherm measurement, and is independent of activation temperature. We note that apart from trends as a function of activation temperature being qualitatively consistent with our expectations, the insignificant difference between the original and repeat isotherms measured on the sample activated at 303 K suggests that exposure to vacuum at room temperature selectively eliminates *only* physisorbed water without altering the amount of water chemisorbed, the value of which is given by the difference between the two isotherms. This consistency between the original and repeat isotherms for the sample activated at 303 K supports one of the principle postulates underlying our study, namely that room temperature water chemisorption onto open-metal sites is irreversible, whereas that elsewhere in the material is reversible. Also, these water adsorption isotherms were unaffected by stability considerations, as evident from identical isotherms measured in four consecutive analyses on a sample activated repeatedly under the same conditions (Figure A5, Appendix A)- measurements that should in theory be sensitive to relatively minor changes in structural integrity.

MIL-100(Cr) OMS densities were measured using the method discussed in the previous sections at various activation temperatures between 303 and 523K (raw data in Figure A6-Figure A10, Appendix A). Summarized in Figure 2.5, the fraction of chromium present in open-metal form increases monotonically with activation temperature, with almost all of the chromium accessible when activated at 523 K, as discussed previously. As mentioned previously, similar qualitative trends have been reported for MIL-100(Cr) endowed with fluoride anions,<sup>132</sup> albeit with the number of open-metal Cr approaching an upper limit of approximately two-thirds of the total Cr. Access to the entire pool of potential open-metal chromium is made possible herein by the predominance of hydroxide as an anion- a result of the fluoride-free synthesis protocols used in our study. Further evidence of dehydroxylation is provided in the next section using infrared spectroscopy data. In contrast with fluoride-containing MIL-100(Cr), in which significant quantities of the anions persist on the chromium sites even after activation at temperatures as high as 523 K under vacuum,<sup>59,132</sup> we observe that the removal of terminal hydroxide anions occurs under comparatively milder activation conditions, leading to the larger fraction of openmetal sites reported in our study. In the following section, further evidence supporting this

claim, along with verification of total open-metal site counts, is provided using infrared spectroscopy measurements.



**Figure 2.5.** Estimated fraction of open-metal Cr sites in MIL-100(Cr) as a function of activation temperature, determined using difference isotherms with H<sub>2</sub>O as an adsorbate.

# 2.3.4 Open-Metal Site Densities Estimated using Infrared Spectroscopy

In contrast with the fluoride-containing version of MIL-100(Cr), where only metal sites coordinated to water can be tracked using infrared spectroscopy, the hydroxide version used in our study enables tracking *both* dehydroxylation and dehydration processes, allowing for the quantification of all potential open-metal chromium in the sample. Specifically, water species bound to chromium were identified using bands at 3672 and 3649 cm<sup>-1</sup>- indicative of two distinct water species- whereas the presence of Cr-OH was verified using the v(OH) band at 3580 cm<sup>-1</sup> (Figure 2.6).<sup>132</sup> The v(OH) band at 3580 cm<sup>-1</sup>, interpreted as originating from Cr-OH, is close in frequency to hydroxyls previously

assigned at 3585 cm<sup>-1</sup> in MIL-100(Cr) and 3588 cm<sup>-1</sup> in MIL-100(Al).<sup>131,132</sup> Areas corresponding to both sets of hydroxyl vibrations decrease upon activation between 303 - 523 K (Figure 2.6), consistent with increasing OMS densities upon activation at progressively higher temperatures.



**Figure 2.6.** IR spectra of MIL-100(Cr) activated under vacuum ( $P = 8 - 11 \ge 10^{-5}$  bar) for 1 hour at increasing temperature.

The relative quantity of coordinated water species was estimated by comparing the total area of the v(OH) bands at 3672 and 3649 cm<sup>-1</sup> for each activation temperature to that at 303 K, providing an estimate for the fraction of coordinated water removed given by the following as

Fraction of H<sub>2</sub>O··Cr Removed = 1 - 
$$\frac{\text{Area } \nu(\text{H}_2\text{O} \cdot \text{Cr})_{\text{T=x}}}{\text{Area } \nu(\text{H}_2\text{O} \cdot \text{Cr})_{\text{T=303 K}}}$$
, (2.1)

where Area  $v(H_2O\cdots Cr)$  corresponds to the combined area of the v(OH) bands at 3672 and 3649 cm<sup>-1</sup> and *x* is the temperature at which MIL-100(Cr) has been evacuated at for 1 hour. An increase in the  $v(OH\cdots Cr)$  area is observed in our IR data upon elevating the temperature between 303 and 373 K, similar to behavior that has been reported previously by Lillerud and coworkers for UiO-66.<sup>163</sup> The authors noted in their report that the area of the v(OH) band increased upon heating from room temperature to 473 K, and attributed this trend to perturbations resulting from interactions between hydroxyl groups and solvent molecules, the gradual desorption of which could explain the increasing intensity of peaks corresponding to isolated hydroxyl species. To provide the most accurate representation of the fraction of hydroxides removed in MIL-100-Cr upon thermal treatment, the initial area of the v(OH…Cr) band was taken from the spectra of MIL-100(Cr) evacuated at 373 K, which is the temperature at which the maximum area was observed. In our analysis we assume that this area represents the quantity of hydroxide species present in the unactivated material, as described by the following equation

Fraction of OH··Cr Removed = 1 - 
$$\frac{\text{Area } \nu(\text{OH··Cr})_{\text{T=x}}}{\text{Area } \nu(\text{OH··Cr})_{\text{T=373 K}}}$$
. (2.2)

Based on the assumption that each metal timer is terminated in 2 locations by a water molecule and in 1 location by a hydroxide, the total fraction of open-metal Cr after evacuation at a particular temperature, *x*, can be estimated by Equation 2.3, where the second half of the equation applies only to  $T \ge 373$  K, expressed as

Fraction of Open-Metal Cr = 
$$\frac{2}{3}$$
 (Fraction of H<sub>2</sub>O··Cr Removed)  
+  $\frac{1}{3}$  (Fraction of OH··Cr Removed). (2.3)

Open-metal site densities obtained from FTIR absorbance spectra match closely with those measured using the difference of water adsorption isotherms (Figure 2.7), supporting open-metal site counts obtained using the latter method. We note that the consistency between site densities obtained using the two techniques below 373 K supports the assumption that dehydroxylation occurs to an insignificant extent below this temperature,

and that increases in peak intensity with temperature below 373 K may in fact originate from factors like solvent removal, as is the case for UiO-66.<sup>163</sup> FTIR-derived OMS



Figure 2.7. Comparison of the estimated fraction of open-metal Cr obtained using the H<sub>2</sub>O adsorption isotherm method to that estimated from the IR absorption spectra for MIL-100(Cr) (◆). (●) represent H<sub>2</sub>O adsorption experiments repeated using a 1 hour evacuation time.

densities above 373 K on the other hand, although relatively accurate, are consistently lower than those derived from water adsorption measurements. One factor that could explain the underestimation of sites in our infrared spectroscopy measurements is the shorter evacuation time (1 hour) compared to the water adsorption experiments (6 hours). Site densities from water adsorption experiments at 423, 473, and 523 K using an evacuation time of 1 hour instead of 6 hours were in fact found to be lower, and significantly closer to those obtained from infrared spectroscopy measurements (Figure 2.7, circles). The higher sensitivity of site counts to evacuation time at temperatures above 423 K versus below points to its greater saliency in enabling dehydroxylation events to occur relative to dehydration events, with the latter predominating at temperatures below 423 K, and both mechanisms contributing to open-metal site creation above 423 K. Crucially, although our study was focused on MIL-100(Cr) endowed with hydroxyl anions, the method in principle is applicable regardless of the metal and anion identity- a claim that we justify in the next section using MIL-100(Al), which lacks a significant density of hydroxyl groups.

# 2.3.5. Open-Metal Site Densities in MIL-100(Al)

MIL-100(Al) was synthesized using a nitrate precursor, and exhibits porosity, crystal structure, and chemical composition consistent with that expected from previous literature reports (Section A1.2. MIL-100(Al) Synthesis and Characterization Results, Appendix A).<sup>131,140</sup> Open-metal site densities for MIL-100(Cr) and MIL-100(Al) are compared in Table 2.1. OMS densities measured for MIL-100(Al) in our study using water adsorption (raw data in Section A2.2. Irreversible Water Adsorption on MIL-100(Al), Appendix A) are slightly greater than those reported previously,<sup>131,162,164</sup> with such variations being common given the propensity of the material to form defect sites comprised of excess organic molecules coordinated to the aluminum, the prevalence of which has been noted to be highly dependent on the synthesis protocol used.<sup>131,140,162</sup> Analogous to MIL-100(Cr), infrared spectroscopy measurements (Figure 2.8) indicate the presence of a v(OH) band at approximately 3672 cm<sup>-1</sup>, assigned by Volkringer et al.<sup>131</sup> to water coordinated directly to Al<sup>3+</sup>. Unlike the chromium analogue, no significant peak corresponding to hydroxyls bound to  $Al^{3+}$  is present (expected frequency ~ 3588 cm<sup>-1</sup>), presumably due to the predominance of nitrates and deprotonated organic molecules as anions.<sup>131,162</sup> The relative area of the 3672  $\text{cm}^{-1}$  v(OH) band was used to estimate the fraction of open-metal sites created at each activation temperature, assuming no sites are created upon activation at 303 K, expressed as

Fraction of Open-Metal Al = 
$$\frac{2}{3} \left( 1 - \frac{\operatorname{Area} \nu(H_2 O \cdot Al)_{T=x}}{\operatorname{Area} \nu(H_2 O \cdot Al)_{T=303 \text{ K}}} \right)$$
 (2.4)

where *x* is the activation temperature employed. This equation is identical to that used for MIL-100(Cr) (Equation 2.3), with the exception of the term accounting for the removal of hydroxides coordinated to one third of the metal atoms. Comparison of the values obtained from IR absorption spectra of MIL-100(Al) to the fraction of open-metal sites estimated from H<sub>2</sub>O adsorption isotherms (Figure 2.9) show quantitative agreement between values obtained using the two methods (Figure 2.9), suggesting that the method proposed here can be used to estimate open-metal site density regardless of metal and anion identity. We believe that the broad applicability of the methods presented here may reflect the fundamental, universal nature of irreversible room temperature water chemisorption onto coordinatively unsaturated metal sites - which we propose can be exploited in the accurate estimation of open-metal site densities in MOF materials.

Activation Temperature (K)	MIL-100(Cr)	MIL-100(Al)
303	$0.05\pm0.03$	$0.03\pm0.01$
323	$0.17 \pm 0.01$	$0.16\pm0.01$
373	$0.30\pm0.01$	$0.32\pm0.01$
423	$0.64\pm0.02$	$0.37\pm0.01$
473	$0.82\pm0.04$	$0.55\pm0.02$
523	$0.98\pm0.02$	$0.66 \pm 0.01$

**Table 2.1.** Fraction of open-metal sites determined through water adsorption isotherms as a function of activation temperature for MIL-100(Cr) and MIL-100(Al).



**Figure 2.8.** IR spectra of MIL-100(Al) activated under vacuum ( $P = 8 - 11 \ge 10^{-5}$  bar) for 1 hour at increasing temperature.



Figure 2.9. Comparison of the estimated fraction of open-metal Al isotherms show quantitative agreement between values obtained using the  $H_2O$  adsorption isotherm method to that estimated from the IR absorption spectra for MIL-100(Al).

# **2.4 Conclusions**

A new method for counting open-metal sites in MOF materials is presented here. The method uses the fraction of water adsorbed irreversibly at room temperature as a proxy for open-metal site density. Comparison with IR spectroscopy data elucidating dehydration and dehydroxylation events on the hydroxyl-version of MIL-100(Cr) confirms site counts obtained using water adsorption isotherm measurements. The method, when extended to a MIL-100(Al) material devoid of hydroxyl anions, also provides site counts in quantitative agreement between the two methods. This method for counting open-metal sites, which can be carried out at ambient temperatures and pressures using benign reagents, circumvents many of the complications in data interpretation arising from unselective adsorption or incomplete site saturation, and is notably insensitive to metal and anion identity. We envision that these advantages could render it more broadly applicable within the field of MOF research.

# 3. Enabling Access to Divalent Metal Sites in MIL-100 Metal-Organic Frameworks though Choice of Anionic Ligand

MIL-100(Cr) is a prototypical MOF representing the opportunity to exploit open-metal sites having well-defined coordination environments, with  $M^{2+}$  sites offering the potential for breakthroughs not only in the area of selective gas adsorption but also acid and redox catalysis. We report herein, the use of hydroxyl anions in accessing the theoretical maximum density of MIL-100 Cr<sup>2+</sup> sites. It is shown using five complementary characterization techniques, that the use of hydroxyl-endowed MIL-100, unlike the fluoride-containing analogue used extensively in the literature, enables creation of one Cr<sup>2+</sup> site per node. The results point to anion identity being a key synthetic choice, the judicious use of which could enable control over open-metal oxidation state in MOF materials more broadly. This section is adapted from the following peer-reviewed article

Hall, J.N., Bollini, P., "Enabling Access to Reduced Open-Metal Sites in Metal-Organic Framework Materials through Choice of Anion Identity: The Case of MIL-100(Cr)." *ACS Materials Letters*, **2** (2020) 838-844.

# **3.1. Introduction**

Metal organic frameworks offer the opportunity to synthesize, characterize, and assess, from an adsorption and catalysis standpoint, isolated sites, the coordination environments of which tend to be, simultaneously, highly well-defined as well as tunable. One of the most common types of sites in this regard are coordinatively unsaturated sites, or open-metal sites (OMSs).<sup>38,44,165</sup> A key aspect of these unsaturated sites that can in theory be manipulated is their oxidation state, control over which carries significant implications in the fields of adsorption<sup>106,121,166,167</sup> and catalysis science.<sup>6,168–171</sup> The MIL-100(Cr)<sup>43</sup> node

is a prototypical example of the value inherent in controlling open-metal oxidation state in the process of exploiting novel motifs for catalysis and separations applications. The MIL-100 node is comprised of  $\mu_3$ -oxo centered metal trimers bridged by trimesate ligands, two of the apical coordination positions of which are occupied by water molecules, and the third of which is occupied by a monovalent anion (Figure 3.1).<sup>43</sup> As a general rule, the creation of coordinatively unsaturated sites in this class of materials can be achieved upon exposure to high temperature under vacuum or inert flow.<sup>42,43,47,68,131,132,162,172–174</sup> MIL-100(Cr) differs from its Fe-based analogue, however, in that the creation of reduced Cr<sup>2+</sup> sites presents not only a greater incentive from an applications standpoint but also a seemingly greater technical challenge, as reflected by the dearth of studies reporting significant Cr<sup>2+</sup> site densities in MIL-100(Cr).



Figure 3.1. Creation of open-metal  $M^{3+}$  sites through dehydration (left) and  $M^{2+}$  sites through anion departure (right) of  $\mu_3$ -oxo centered trimer nodes in MIL-100(M).

Reports asserting a critical role of  $Cr^{2+}$  sites are ubiquitous in the heterogeneous catalysis literature, a key example of which is the attribution of catalytic activity to their presence in SiO<sub>2</sub> supported Cr catalysts for ethene polymerization.<sup>175–177</sup> Specifically, Cr<sup>2+</sup> sites in carboxylate frameworks like MIL-100(Cr) have been proposed as critical to improved performance in multiple industrially relevant catalysis/separations technologies; for example, achieving high ethene polymerization selectivities,<sup>71</sup> oxidizing light alkanes and CO, <sup>114,178</sup> and selectively adsorbing either O<sub>2</sub> over N<sub>2</sub>.<sup>179</sup> or ethane over ethene.<sup>180</sup> We

emphasize that this potential of  $Cr^{2+}$  sites in MIL-100(Cr) to advance the state-of-the-art in a range of applications remains as-yet unrealized owing to the lack of studies reporting their presence in significant concentrations. For example, Vimont and coworkers noted only a minor change in fluoride anion density (measured using elemental analysis) following outgassing at 573 K (from 0.285 to 0.270 mol%).<sup>132</sup> Additionally, this quantity corresponded directly to the fraction of Cr sites (0.28 mol (mol Cr)<sup>-1</sup>) unavailable for binding to CO (100 K, 266 Pa CO) when activated at 573 K, pointing to the recalcitrance of fluoride anions under conditions typically used to activate MIL-100(M) materials. Yoon et al. reported  $Cr^{2+}$  densities corresponding to less than 2 mol% of the total chromium when MIL-100(Cr) was exposed to vacuum at 523 K, characterized using NO adsorption at 298 K.<sup>59</sup> We note that XPS measurements by Zhang and colleagues indicated occupancy of Cr 2p orbitals attributed to  $Cr^{2+}$  species at evacuation temperatures between 473 and 573 K, but provided no definitive quantitative estimates of the relative ratio of  $Cr^{2+}$  and  $Cr^{3+}$ species.<sup>71</sup> In summary, despite the rather strong incentive to create  $Cr^{2+}$  sites hosted by the MIL-100 framework, the maximum reported density of  $Cr^{2+}$  sites stands at 0.02 mol  $Cr^{2+}$ (mol Cr)<sup>-1\_59</sup> significantly lower than the theoretical maximum density corresponding to one site per trimer node of 0.33 mol  $Cr^{2+}$  (mol  $Cr)^{-1}$ .

We report herein a method for addressing this gap between potential applications of MIL-100  $Cr^{2+}$  sites on the one hand, and their absence in this class of materials on the other. Specifically, we use five complementary characterization techniques to show that the presence, exclusively, of the hydroxyl anion, unlike literature reports in which the

fluoride anion occupies one apical coordination position per node, leads to the ability to access the theoretical maximum density of  $Cr^{2+}$  sites in MIL-100.

# **3.2. Materials and Methods**

MIL-100(Cr) was synthesized according to a previously reported procedure.<sup>55</sup> Detailed discussion of the synthesis protocol and details of material characterization including  $N_2$  physisorption, powder X-ray diffraction, and thermogravimetric analysis are described in Section 2.2 of Chapter 2.<sup>181</sup>

Transmission infrared spectroscopy experiments were conducted using a Nicolet 6700 FTIR Spectrometer (Thermo Scientific) with a Harrick High Temperature Cell with CaF<sub>2</sub> windows (32 x 3 mm<sup>2</sup>). 15 mg self-supporting wafers of MIL-100(Cr) were thermally treated under dynamic vacuum (pressure =  $8 - 11 \times 10^{-5}$  bar, Pfeiffer Duo 2.5 Vacuum Pump). Absorbance spectra were collected by a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen (77K) averaging 64 scans at 4 cm<sup>-1</sup>. The empty cell purged with N<sub>2</sub> was used as a background reference for all spectra. The spectra reported here were baseline-corrected using Origin 8.5.

Volumetric adsorption measurements were completed on a Micromeritics 3Flex instrument. For a typical measurement, 0.05 g of sample was loaded in a quartz flow through sample tube (12 mm, Micromeritics) on a bed of quartz wool (20 mm) topped with a quartz frit. Thermal pretreatments were completed between 202 and 523 K in vacuo ( $P < 6.7 \times 10^{-5}$  bar). Adsorption of CO, ethylene, and ethane were conducted at 303 K.

# **3.3. Results and Discussion**

# **3.3.1.** Total Open-Metal Site Quantification and Spectroscopic Evidence of Dehydroxylation in MIL-100(Cr)

The first of these five techniques quantifies *total* open-metal site (OMS) density using the quantity of water adsorbed irreversibly at room temperature as a proxy for OMS density, the validity of which has been discussed in detail in a previously published study.<sup>182</sup> OMS densities increase monotonically with increasing activation temperature (Figure 3.2a), with the number of sites under activation at 523 K (P < 6.7 x 10<sup>-5</sup> bar, 6 hours) corresponding to the number of chromium atoms present in the material. Crucially, this value is significantly higher than those reported previously for fluoride-containing MIL-100(Cr), where OMS fractions reached a maximum of approximately 2/3 of the total Cr content (Figure B1, Section B1.1), suggesting that only water removal leading to Cr<sup>3+</sup> formation not reduction of the metal through anion elimination, contributes to open-metal



**Figure 3.2.** (a) MIL-100(Cr) open-metal site densities as a function of activation temperature, determined via irreversible room temperature water adsorption. (b) IR spectra of MIL-100(Cr) following activation at the indicated temperature for 2 hours under vacuum.

site creation in the case of fluoride-containing MIL-100(Cr).<sup>59,132,183</sup> Charge neutrality considerations necessitating the presence of one anion per trimer dictate that the creation of one third of the coordinatively unsaturated chromium sites under activation at 523 K likely originate from loss of the anionic ligand, resulting in the formation of  $Cr^{2+}$  sites.

Additionally, use of the hydroxyl version of MIL-100(Cr), unlike the fluoride version, enables us to track, using infrared spectroscopy, the fraction of nodes dehydroxylated under a certain set of activation conditions. Infrared absorption spectra of MIL-100(Cr) exhibit two bands at 3672 and 3649 cm<sup>-1</sup> (Figure 3.2b), indicative of the asymmetric O-H stretching frequency of molecular water coordinated to chromium, and a 3580 cm<sup>-1</sup> band corresponding to hydroxides bound to chromium.<sup>132</sup> The areas of both bands decrease progressively with thermal treatment between 323 and 523 K, and as demonstrated in a previous study, the normalized combined areas of coordinated water and hydroxide species correlate with OMS density estimates using irreversible water adsorption.<sup>182</sup> Although the elimination of hydroxyl anions and the concurrent creation of open-metal chromium can be verified using infrared spectroscopy and water adsorption, respectively, these data provide no *direct* evidence of the formation of Cr<sup>2+</sup> sites, the case for which has so far been made solely based on charge neutrality considerations.

#### 3.3.2. Infrared Spectroscopic Analysis of NO Adsorption

To this end, we use three probe molecules- NO, CO, and ethene- that feature vacant  $\pi^*$  orbitals that can accept electrons from filled d orbitals of the metal. These  $\pi$ -backbonding interactions are more prevalent for Cr<sup>2+</sup> sites than Cr<sup>3+</sup> sites for two reasons: (1) Cr<sup>2+</sup> has a higher number of nonbonding d electrons available for interaction with the ligand and (2)
the higher partial positive charge of the  $Cr^{3+}$  and its  $t_{2g}$  symmetry decreases the radial distance of the electrons from the nucleus, making them less available for interaction with the probe molecule.<sup>184,185</sup> We note that enhanced backbonding interactions for metals in lower oxidation states has been posited repeatedly and extensively in the literature for transition-metal compounds,<sup>186–190</sup> and also specifically in the context of CO<sup>191</sup> and NO<sup>192</sup> adsorption onto silica supported Cr<sup>2+</sup> and Cr<sup>3+</sup> sites.



Figure 3.3. (a) IR spectra following activation at the indicated temperature for 2 hours under vacuum and then exposed to 10 kPa NO in N<sub>2</sub> at 303 K. (b) Comparison of the fractional reduction in hydroxides (3650 cm<sup>-1</sup>) to the relative increase in area of the NO- $Cr^{2+}$  species.

Examination of prior literature indicates that MIL-100  $Cr^{2+}$  densities as low as 2 mol% can be detected using infrared spectroscopy measurements in the presence of NO at room temperature.<sup>59</sup> Consistent with these data, NO-IR spectra in this study exhibit a massif with two bands at 1755 and 1742 cm<sup>-1</sup> that has been previously assigned to the symmetric stretching vibration of NO bound to  $Cr^{2+}$  (Figure 3.3a).<sup>59</sup> Similar assignments have been made for  $Cr^{2+}$  nitrosyl complexes in the range of 1770 – 1747 cm<sup>-1</sup> for  $Cr_2O_3/Al_2O_3$ ,<sup>193</sup>

 $Cr(CO)_6/Al_2O_3$ ,<sup>194</sup> and  $Cr_2O_3/SiO_2$ ,<sup>192,195</sup> in contrast with NO bound to  $Cr^{3+}$  that has been proposed to exhibit bands in the 1900-1950 cm<sup>-1</sup> range for MIL-100(Cr).<sup>59</sup>

Although it is difficult to confirm the oxidation state of Cr solely based on the vibrational frequency of the v(NO-Cr) band, despite consistency with previous literature,<sup>59</sup> results here indicate the Cr sites which are binding NO are most prominent in MIL-100 samples activated at temperatures  $\geq$  423 K, concurrent with the near step-change reduction in intensity of the v(OH) band corresponding to hydroxides (Figure 3.2b). To further emphasize the relationship between the dehydroxylation events occurring upon thermal treatment and the proposed formation of Cr<sup>2+</sup> sites, we directly relate the relative decrease in the area of the hydroxyl band (v(OH) = 3580 cm<sup>-1</sup>) to the comparative increase in the amount of NO adsorbed onto Cr open-metal sites. The fractional reduction in hydroxide density is determined by comparing its area as a function of pretreatment temperature to its area upon activation at 373 K, and is given by equation 3.1 as

Fractional Reduction in area (HO-Cr) = 1 - 
$$\frac{\text{Area}_{T=x}}{\text{Area}_{T=373 \text{ K}}}$$
 (3.1)

where x corresponds to the treatment temperature. This value is compared to the relative increase in area of the v(NO-Cr) band under the same treatment conditions, normalized by the maximum area observed upon treatment at 523 K, expressed as

Fractional Increase in area (NO-Cr) = 
$$\frac{\text{Area}_{T=x}}{\text{Area}_{T=523 \text{ K}}}$$
. (3.2)

An apparent linear correlation between these two values (Figure 3.3b), and the lack of any reasonable relationship between the v(NO-Cr) band area with the amount of coordinated water desorbed (Figure B2, Appendix B), confirms our main hypothesis that solely dehydroxylation events at activation temperatures above 423 K afford the creation of open Cr sites which bind NO under these conditions. Further, the +2 oxidation state can be inferred from the loss of the anionic ligand, analogous to the reduction process distinctively identified for MIL-100(Fe),<sup>42,60,154</sup> and also by their expected heightened interactions with NO over  $Cr^{3+}$  sites, which are present in the majority concentration (Figure 3.1a). Overall, total open-metal site densities obtained by room temperature water adsorption isotherms, in-situ FTIR spectroscopy tracking dehydroxylation, and NO- $Cr^{2+}$ peak areas all evidence formation of significant densities of  $Cr^{2+}$  sites. Accessing openmetal site densities that correspond to the amount of chromium present in the sample (Figure 3.1a) represents a significant advance over prior literature and demonstrates that the theoretical maximum of 0.33 mol  $Cr^{2+}$  (mol  $Cr)^{-1}$  can be achieved under the activation conditions used in this study.

# **3.3.3.** Volumetric CO Adsorption Measurements as a Proxy for Cr<sup>2+</sup> Open-Metal Site Densities

To further characterize and demonstrate the utility of  $Cr^{2+}$  sites in MIL-100, we evaluated its CO adsorption properties. Analogous to the case of NO, CO should exhibit higher binding energies with  $Cr^{2+}$  sites due to enhanced  $\pi$ -backbonding, as suggested by previous studies on supported chromium oxide materials.<sup>176,186,188,191,196,197</sup> Activation temperatures above 373 K result in a step-change in equilibrium CO adsorption capacity (Figure 3.4a), analogous to the non-linear increase in NO-Cr<sup>2+</sup> band area for samples activated at temperatures in the vicinity of 423 K (Figure 3.3a), but in contrast with the more systematic evolution in *total* OMS density as a function of activation temperature (Figure 3.2a). CO adsorption isotherms for MIL-100(Cr) activated between 423 and 523 K

can be described by a dual-site Langmuir adsorption model in which saturation capacities are a function of activation temperature, but affinities are not (details in Section B1.3. CO Adsorption, Appendix B). The overall adsorption isotherm can be interpreted as the combination of adsorption onto site A, which reaches saturation below 0.04 bar owing to a higher affinity, and adsorption onto site B, which remains linear up to at least 0.12 bar owing to its more than 500-fold lower affinity. In the case that site A (exhibiting a higher affinity) corresponds to  $Cr^{2+}$  sites, the ordinate obtained upon extrapolation of the isotherm in the linear region above 0.04 bar to zero pressures should represent the  $Cr^{2+}$  site density at each activation temperature (Figure B4, Appendix B). We note that Kim *et al.* have analogously extrapolated the plateau of the adsorption isotherm to zero pressure to estimate  $Fe^{2+}$  site densities in MIL-100(Fe).<sup>198</sup> Crucially, ordinates obtained upon extrapolation of



**Figure 3.4.** (a) CO adsorption isotherms (303 K) following activation at elevated temperatures. (b) Estimation of the  $Cr^{2+}$  site density based on y-intercept of the fitted line. (c) Comparison of the  $Cr^{2+}$  site density determined by CO adsorption to the area of the  $v(NO\cdots Cr^{2+})$  band.

our overall adsorption isotherm data (exampled in Figure 3.4b) correlate with NO-Cr<sup>2+</sup> areas measured following treatment at the corresponding activation temperatures (Figure 3.4c), consistent with these sites being  $Cr^{2+}$  sites that bind CO with an affinity large enough to ensure saturation below 0.04 bar. Such an interpretation of the isotherm data is consistent with stronger binding onto  $Cr^{2+}$  sites that can result from enhanced  $\pi$ -backbonding interactions. Note that we do not make claims as to the identity of site B, but only present an interpretation of isotherm data consistent with  $Cr^{2+}$  site saturation at low pressures. In contrast with single component adsorption data presented thus far, in the next (final) portion of our study, we extend our analysis to selectivity considerations in ethene-ethane adsorption.

#### 3.3.4. Selective Ethene Adsorption over Ethene by Cr<sup>2+</sup> Open-Metal Sites

In addition to CO and NO, the increased contribution of  $\pi$ -backbonding in Cr<sup>2+</sup> sites compared to Cr<sup>3+</sup> sites has also been proposed in the context of ethene polymerization over supported Cr catalysts,<sup>176,199</sup> and the selective adsorption of ethene over ethane on MOFs containing transition metal sites.<sup>200–202</sup> Room temperature ethene and ethane equilibrium adsorption capacities on MIL-100(Cr) activated at temperatures less than or equal to 373 K are comparable (Figure 3.5a and Figure 3.5b); activation at temperatures greater than 373 K, on the other hand, results in significantly greater increases in uptake of ethene than ethane. Ethene:ethane selectivity increases monotonically from 1 (unselective adsorption) to 4 (selective adsorption) at activation temperatures above 373 K, with the onset of selective adsorption coinciding with the creation of Cr<sup>2+</sup> sites as reflected by dual-site interpretations of the CO adsorption data (Figure 3.5c). Selectivity trends reported here as a function of activation temperature are analogous to those reported by Daturi and coworkers in which improved propene:propane selectivities over MIL-100(Fe) were attributed to adsorption onto  $Fe^{2+}$  open-metal sites.



**Figure 3.5.** (a)  $C_2H_6$  and (b)  $C_2H_4$  adsorption isotherms (303 K) following activation at elevated temperature for 6 hours under vacuum. (b) Comparison of selectivity toward  $C_2H_4$  (P = 0.04 bar,  $C_2H_4$ : $C_2H_6$  = 50:50) to the estimated fraction of  $Cr^{2+}$  sites from CO adsorption results.

#### **3.4.** Conclusions

In summary, we report, using five complementary sets of characterization data, evidence for achieving the theoretical maximum density of  $Cr^{2+}$  open-metal sites (0.33 mol (mol Cr)<sup>-1</sup>) when activating MIL-100(Cr) at 523 K under vacuum (6.7 x 10<sup>-5</sup> bar). Access to this high density of  $Cr^{2+}$  sites, hitherto unreported in the literature, was achieved specifically through exploitation of the hydroxyl variant of MIL-100(Cr)- a strategy that may offer an avenue for accessing reduced open-metal sites in well-defined coordination environments more broadly within the field of MOF research.

### 4. Partial Oxidation of Methane Over Trimer Nodes in MIL-100 and the Role of Metal Identity on Product Selectivity

Clarity as to the role of metal identity and oxidation state in effecting redox and acidcatalyzed turnovers is oftentimes precluded by a high degree of heterogeneity in site speciation, a limitation that can be overcome through the use of well-defined poly-metal clusters hosted by metal organic framework materials- accomplished in the present case using MIL-100 (Fe or Cr) for the low temperature oxidation of methane with N<sub>2</sub>O. Transient kinetic data point to a) methoxy species mediating methane conversion, b) partial and deep oxidation occurring over metal sites distinct in oxidation state, c) chromium clusters amplifying the propensity toward C-C bond formation, and d) the relative velocity of propagation of water and methanol concentration fronts playing a determinative role in maximizing C2 oxygenate selectivity. The study captures the utility of using classes of materials inherently endowed with a high level of definition and uniformity in advancing the elucidation of structure-catalytic property relationships. This section is adapted from the following peer-reviewed articles:

Hall, J.N., Bollini, P., "Low-Temperature, Ambient Pressure Oxidation of Methane to Methanol Over Every Tri-Iron Node in a Metal-Organic Framework Material" *Chemistry – A European Journal*, 26 (2020) 16639-16643.

Hall, J.N., Bollini, P., "Role of Metal Identity and Speciation in the Low-Temperature Oxidation of Methane over Tri-Metal Oxo Clusters," *AIChE Journal*, 67 (2021) e17496.

#### **4.1. Introduction**

The selective, low-temperature oxidation of methane to methanol, if successfully accomplished, could enable valorization of vast reserves of shale gas resources becoming increasingly abundant in the United States and around the world. <sup>203–205</sup> High-valent metaloxo complexes serve as promising active centers for low-temperature methane oxidation, and are exploited in a variety of biological and synthetic systems;<sup>75–79</sup> for instance, iron(IV)-oxo centers have been long hypothesized as the key oxidizing species in nonheme biological complexes including R2 proteins of ribonucleotide reductase (RNR R2),  $Fe^{2+}/\alpha$ -ketoglutarate ( $\alpha KG$ )-dependent hydroxylates, and soluble methane monooxygenase (sMMO) enzymes.<sup>80–83,206,207</sup> Efforts aimed at investigating such active centers have for the most part been focused on iron-zeolites in the heterogeneous catalysis literature<sup>208–212</sup> and homogenous complexes in the bioinorganic chemistry literature,<sup>213–216</sup> with both classes of materials exhibiting unique limitations with respect to low temperature methane oxidation. Homogeneous complexes, on one hand, often display a propensity towards polynuclear aggregation, thereby limiting somewhat their use in catalysis applications.<sup>217–221</sup> Iron-based zeolites, on the other hand, while ideal for investigating iron clusters that do not evolve significantly under reaction conditions, exhibit active site heterogeneity not only greater in degree than that exhibited by homogeneous complexes, but also to an extent that varies significantly with synthesis protocol, thermal treatment, and iron loading.<sup>98,99,222</sup>

Metal-organic framework materials potentially offer a solution to the challenge of synthesizing and evaluating materials that carry well-defined, structurally uniform metaloxo moieties that remain isolated in nature subsequent to their involvement in catalytic

redox cycles, with several copper and iron-containing MOFs having been evaluated for the oxidation of light alkanes including methane,<sup>108,109,111,223</sup> ethane,<sup>106,224,225</sup> and propane.<sup>73</sup> Specifically, MIL-100 (MIL = Materials of Institut Lavoisier) is a MOF that exhibits interesting properties in the partial oxidation of light alkanes.<sup>72–74,109</sup> First discovered by Gérard Férey and coworkers, MIL-100 is comprised of trimetallic clusters  $[(M(III)_3(\mu_3-O)]]$ coordinated by trimesate linkers to form a porous structure featuring an MTN (Mobile Thirty Nine) topology (Figure 4.1a).<sup>43,226</sup> Removal of terminal ligands (H<sub>2</sub>O or X<sup>-</sup>) through thermal activation under inert or vacuum at temperatures below 523 K (Figure 4.1b) creates unsaturated open-metal sites over mixed valence nodes  $[(M(II)M(III)_2(\mu_3-O)]^{42,154,227}$  The propensity of these nodes to convert methane to methanol at low temperatures (423 - 473)K) and ambient pressures has been previously demonstrated,<sup>72,73</sup> including a prior report from our group evidencing participation of every single MIL-100 tri-iron node towards methanol formation,<sup>109</sup> unlike iron-zeolites that typically carry *distributions* of active and inactive multinuclear iron centers.<sup>228-231</sup> In this study, we use a suite of spectroscopic, transient kinetic, and site titration tools to relate metal oxidation state to reactive function. Specifically, the role of  $Fe^{2+}$  and  $Fe^{3+}$  sites in methanol and  $CO_2$  formation are identified. Altering the identity of the metal from iron to chromium enables C-C bond formation events that appear to involve methoxy intermediates that also mediate methanol formation over both MIL-100(M) variants. To this end, (i) we elucidate the identity of sites involved in  $CO_2$  and methanol formation, (ii) identify the role of methoxy intermediates, (iii) demonstrate the propensity towards and methods for controlling the prevalence of C-C bond formation over MIL-100(Cr), before (iv) clarifying the diversity of functionality of Fe<sup>3+</sup>-methoxies. The study captures how precise control over metal identity and oxidation state, combined with manipulation of the relative velocity of water and methanol concentration fronts, enables control not only over the selectivity towards desired partial oxidation products such as methanol (versus CO<sub>2</sub>) but also that towards C2 oxygenates (over C1 oxygenates).



Figure 4.1. (a) Structure of MIL-100 comprised of trimesic acid linkers and  $\mu_3$ -oxo centered trimer nodes, adapted with permission from Ref. 43. (b) Formation of  $M^{2+}$  and  $M^{3+}$  openmetal sites in MIL-100 through thermal activation.

#### 4.2. Materials and Methods

#### 4.2.1. Synthesis and Characterization

MIL-100(Fe) and MIL-100(Cr) were synthesized according to previously reported protocols<sup>66,139</sup> that are described in detail in Sections C1.1. MIL-100(Fe) Synthesis and C1.2. MIL-100(Cr) Synthesis, Appendix C. Comparison of X-ray diffraction patterns, nitrogen physisorption isotherms, and thermogravimetric analysis profiles confirm the

crystal structure, porosity, and composition, respectively, of these materials as being consistent with previous reports (Figure C1 and Figure C2, Appendix C).<sup>66,139</sup> Infrared (IR) spectroscopy measurements were conducted to track the evolution of H<sub>2</sub>O and OH<sup>-</sup> coordinated species in MIL-100(Fe) and MIL-100(Cr) to estimate  $M^{2+}/M^{3+}$  open-metal site densities under various thermal activation conditions (as described in detail in Section C1.6. Infrared Spectroscopy Experiments, Appendix C). Fe<sup>2+</sup> and Fe<sup>3+</sup> open-metal site densities were quantified in-situ using a combination of breakthrough measurements with NO (0.5 kPa, 423 K) and D<sub>2</sub>O (0.9 kPa, 373 K), as described in Sections 2.4 and 2.5 of the SI, respectively.

#### **4.2.2.** Methane Oxidation Experiments

Details of methane oxidation reaction experiments are described in Section C1.4. Procedure for the Oxidation of CH<sub>4</sub> with N<sub>2</sub>O, Appendix C. Briefly, pretreated MIL-100 samples (423 - 523 K, 12 h, He flow (50 cm<sup>3</sup> min<sup>-1</sup>) or vacuum (P < 0.01 kPa) were exposed to CH<sub>4</sub>/N<sub>2</sub>O reactant mixtures at 423 - 473 K with gas-phase product and reactant concentrations determined using a gas chromatograph (Agilent 7890 B). Following reaction, water vapor at various partial pressures (0.35 - 1.1 kPa) and molar flow rates ( $1.54 - 4.61 \times 10^{-6}$  mol s<sup>-1</sup>) were introduced to extract surface-bound intermediates at temperatures between 373 and 473 K, and products formed were measured using an online mass spectrometer (MKS Cirrus 2).

#### **4.2.3. In-situ Titrations**

Titration experiments with NO (10 wt.% NO, balance  $N_2$ , Matheson, Research Purity) and H<sub>2</sub>O (deionized, 18.3 M $\Omega$ ) were conducted at 423 K under constant reaction conditions: 14.5 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, t = 2 h. For NO titration experiments, NO was fed over MIL-100(Fe) prior to the introduction of CH<sub>4</sub> and N<sub>2</sub>O due to the significant time it takes for NO to break through the MOF bed in comparison to the reactants (Section C2.6. CH<sub>4</sub> Oxidation In-Situ NO Titrations, Appendix C). Under titrant co-feeds, inert carrier gas (He, Matheson, Ultra High Purity) concentrations were reduced to maintain constant reactant partial pressures. Total quantities of NO and H<sub>2</sub>O adsorbed by MIL-100 were estimated through breakthrough curves measured using an online mass spectrometer (MKS Cirrus 2) at the outlet of the bed. Molar flow rates were calibrated with respect to those of argon (internal standard) under the assumption that no argon was adsorbed by the sample.

#### **4.3. Results and Discussion**

#### 4.3.1. Active Site Requirements for Methanol and CO<sub>2</sub> Formation

We previously reported the oxidation of methane to methanol and CO<sub>2</sub> at low temperatures (423 - 483 K) and sub-ambient pressures over tri-iron oxo clusters hosted by MIL-100(Fe) nodes.<sup>109</sup> Co-feeding N<sub>2</sub>O and methane at 473 K over MIL-100(Fe) activated at 523 K resulted in transient dinitrogen formation rates that decrease asymptotically toward a constant value and CO<sub>2</sub> formation rates that appear to be invariant in time (Figure 4.2). Extraction with water vapor (0.35 kPa, 473 K) subsequent to exposure to methane and N<sub>2</sub>O resulted in the formation of methanol, the cumulative yield of which asymptotically approaches a maximum value with reaction time (Figure 4.2). Reported N<sub>2</sub> formation to methanol, CO<sub>2</sub> and water based on the reaction stoichiometry (N<sub>2</sub>O + CH<sub>4</sub>  $\rightarrow$  N<sub>2</sub> + CH<sub>3</sub>OH; 4N<sub>2</sub>O + CH<sub>4</sub>  $\rightarrow$  4N<sub>2</sub> + CO<sub>2</sub> + 2H<sub>2</sub>O), as reflected by the close correspondence

between measured cumulative nitrogen yields and those estimated from reaction stoichiometry (Figure 4.2,  $\Box$  symbols). The maximum cumulative methanol yield measured corresponds to the theoretical maximum density of Fe<sup>2+</sup> sites in MIL-100 (0.33 mol Fe<sup>2+</sup>/mol total Fe). Furthermore, Fe<sup>2+</sup> site densities estimated from FTIR signatures of either terminal hydroxyl ligands or NO coordinated to Fe<sup>2+</sup> sites created upon hydroxyl removal serve as proxies for cumulative methanol formation, lending credence to the possible sole involvement of Fe<sup>2+</sup> sites in methanol formation.<sup>109</sup>



**Figure 4.2.** (a) Schematic of the CH<sub>4</sub> oxidation and product extraction steps. (b) Cumulative moles of product formed as a function of reaction time (with N<sub>2</sub>O and CH<sub>4</sub>). Reaction conditions: 2.9 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, 0.35 kPa H<sub>2</sub>O, 473 K, MIL-100(Fe) activated at 523 K.



Figure 4.3. (a) Cumulative moles of methanol and  $CO_2$  formed per total Fe in the absence of titrant and in the presence of NO or H<sub>2</sub>O. (b) Under 0.5 kPa NO, the quantity of H<sub>2</sub>O adsorbed and the cumulative moles of CO<sub>2</sub> formed per total Fe under that condition.

The invariance in CO<sub>2</sub> formation rates with time despite the consumption of Fe<sup>2+</sup> sites converting methane to methanol indicates that Fe<sup>2+</sup> site densities that allow for the rigorous normalization of methanol formation, do not do so for CO<sub>2</sub> formation, and suggests an independence between sites responsible for the formation of these two products. Moreover, unlike methanol formation, which can be completely inhibited by the presence of gas phase NO under reaction conditions, the formation of CO<sub>2</sub> is unaffected by the presence of NO, as reflected by the insensitivity of cumulative CO<sub>2</sub> formation to the presence of NO cofeeds (Figure 4.3a). Reported cumulative moles of CO<sub>2</sub> formed are corrected for those measured when NO was flown over MIL-100(Fe) in the absence of methane and N<sub>2</sub>O (0.0035 mol (mol total Fe)<sup>-1</sup>). Such NO-induced oxidation (presumably of the MIL-100 framework) accounts accurately for the slight increase in CO<sub>2</sub> formation upon introduction of NO with methane and N<sub>2</sub>O (0.0039 mol (mol total Fe)<sup>-1</sup>, Table S4), and suggests that linker oxidation rates are unaffected by the presence of methane and N<sub>2</sub>O. The insensitivity in cumulative CO<sub>2</sub> formation rates to Fe<sup>2+</sup> site densities both in the presence and absence of NO suggest that a significant fraction of CO<sub>2</sub> formation may occur over a distinct set of sites compared to those identified for methanol formation.

Given the near complete absence of NO adsorption onto Fe<sup>3+</sup> sites under reaction conditions and the insensitivity of  $CO_2$  formation rates to the presence of NO in the gas phase, their involvement in CO<sub>2</sub> formation warrants further evaluation- a question that is challenging to definitively address in the absence of titrants that bind exclusively to Fe<sup>3+</sup> sites (and not  $Fe^{2+}$  sites). A clue as to the involvement of  $Fe^{3+}$  sites in CO<sub>2</sub> formation is provided by water titrations (0.9 kPa H<sub>2</sub>O at 423 K) that bind unselectively to open-metal sites regardless of their oxidation state, as indicated by the adsorption of one mole water per mol iron under conditions of interest (Figure C8). Whereas co-feeding NO eliminates (solely) CH<sub>3</sub>OH formation, introduction of H<sub>2</sub>O with methane and N<sub>2</sub>O (14.5 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, 0.9 kPa H<sub>2</sub>O, 423 K) results in the complete elimination of both oxidation products (Figure 4.3a). Additionally, the presence of 0.5 kPa NO in the gas phase causes the introduction of increasing H<sub>2</sub>O partial pressures (0.1 - 0.9 kPa) to result in a systematic increase in the total quantity of water adsorbed, and a concurrent linear decrease in cumulative moles of  $CO_2$  formed with increasing amount of water adsorbed, Figure 4.3b (conditions: 14.5 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, 0.5 kPa NO, 423 K). The linear relationship between the cumulative moles of  $CO_2$  formed and those of water adsorbed reflects a constant ratio between the number of sites that adsorb water and those eliminated from

participation in  $CO_2$  formation. Moreover, the quantity of water adsorption required to completely suppress  $CO_2$  formation was found to be 0.62 mol (total mol Fe)<sup>-1</sup>- a value approximately equal to the concentration of  $Fe^{3+}$  open-metal sites (0.65 mol (total mol Fe)<sup>-1</sup>) measured independently using  $D_2O$  adsorption measurements (Section C2.5). Thermal treatment protocols can be used to access increasing densities of Fe<sup>2+</sup> and Fe<sup>3+</sup> sites,<sup>42,109,181</sup> with activation temperatures below 423 K yielding a majority of Fe<sup>3+</sup> sites, and those above 423 K resulting in the formation of Fe<sup>2+</sup> sites in addition to Fe<sup>3+</sup> sites, Table C3 (activated at temperature for 12 h under He flow). Cumulative CO<sub>2</sub> yields normalized by the density of  $Fe^{3+}$  sites remain nearly invariant in activation temperature. unlike those normalized by total iron content which increase monotonically with activation temperature (Figure 4.4), consistent with the involvement of the former in  $CO_2$  formation. Also consistent with the sole involvement of  $Fe^{3+}$  sites is the monotonically decreasing trend of  $CO_2$  formation rates per Fe<sup>2+</sup> site with activation temperature, expected to result from greater relative contributions of  $Fe^{3+}$  sites to the total open-metal site density at higher temperatures (Figure C9). Overall, (i) CO<sub>2</sub> cumulative yields that increase linearly with time and are unaffected by decreasing  $Fe^{2+}$  site densities, (ii) the insensitivity of CO<sub>2</sub> formation rates to NO pressure, (iii) a linear correlation between the amount of water adsorbed in the presence of NO and cumulative CO<sub>2</sub> yields, (iv) the precise correspondence between the moles of water required to saturate Fe<sup>3+</sup> sites and those required for the complete elimination of  $CO_2$  formation, and (v) the invariance in Fe<sup>3+</sup>-normalized cumulative CO<sub>2</sub> yields with increasing thermal activation temperature are all consistent with and suggestive of the involvement of  $Fe^{3+}$  sites in CO<sub>2</sub> formation, even though these data do not help definitively exclude the possibility that a minute amount of extraframework iron may be responsible for the same.



**Figure 4.4.** Cumulative moles of CO<sub>2</sub> formed normalized by the total iron content (left axis) and per Fe<sup>3+</sup> open-metal site (right axis) with increasing activation temperature (423 - 523 K). Reaction conditions: 473 K, 14.5 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, t = 2 h.

Gagliardi, Snurr, and co-workers have reported density functional theory (DFT)derived energy profiles for the decomposition of N<sub>2</sub>O over M<sup>2+</sup> sites to form M(IV)=O species;<sup>72,73,114</sup> crucially, calculations reported by Barona and Snurr suggest the potential for M<sup>3+</sup> coordinatively unsaturated sites situated in trimeric MOF nodes to participate in methane oxidation with N<sub>2</sub>O.<sup>74</sup> For example, a V<sup>3+</sup> open-metal site in the (Ni<sup>2+</sup>)(V<sup>3+</sup>)<sub>2</sub> mixed-metal node was proposed to be oxidized by N<sub>2</sub>O to Ni<sup>2+</sup>(V<sup>4+</sup>=O)V<sup>4+</sup>, with both of the trivalent vanadium centers donating electrons to form the oxo intermediate. N<sub>2</sub>O activation barriers over Fe<sup>3+</sup> open-metal sites in [(Cr<sup>2+</sup>)(Fe<sup>3+</sup>)<sub>2</sub>] and [(Mn<sup>2+</sup>)(Fe<sup>3+</sup>)<sub>2</sub>] mixedmetal nodes (144 and 146 kJ mol<sup>-1</sup>, respectively) were found to be comparable to those predicted for Fe<sup>2+</sup> open-metal sites on an (Fe<sup>2+</sup>)(Fe<sup>3+</sup>)<sub>2</sub> node (146 kJ mol<sup>-1</sup>). The involvement of Fe<sup>3+</sup> sites in methane oxidation may proceed through the involvement of metal-oxo bond formation steps of such a nature, and a fuller understanding of these steps may require knowledge of changes in formal oxidation states over the entire trimer rather than merely one of three metal atoms constituting the node.

#### 4.3.2. The Key Role of Methoxy Intermediates in Methane Conversion

The absence of gas phase methanol at the reactor outlet during both the methane-nitrous oxide co-feed step as well as the ensuing purge step under inert, but its detection upon exposing the sample to water vapor during the extraction step suggests one of two possibilities: a) water displaces adsorbed methanol through competitive adsorption, or b) reacts with a persistent intermediate formed upon exposure to methane and  $N_2O$  to form gas phase methanol. Exposure to D<sub>2</sub>O (as opposed to H<sub>2</sub>O) allows for a differentiation between these two scenarios. Whereas the displacement of adsorbed methanol by water should result in the exclusive detection of non-deuterated methanol, incorporation of deuterium into the methanol product would be indicative of the formation of a persistent intermediate that undergoes steps involving the exchange of deuterium from water. Exposure to D<sub>2</sub>O was found to result exclusively in the formation of monodeuteromethanol (Figure 4.5a), consistent with the formation of methoxy intermediates that then undergo reaction with water to form methanol and reform the hydroxyl anion that was eliminated to create the Fe<sup>2+</sup> site in the first place (reaction at 1.5 kPa CH<sub>4</sub> and 1.6 kPa N<sub>2</sub>O for 2 h). The fraction of mono-deuteromethanol in the product tracks with the fraction of  $D_2O$  in  $H_2O$ - $D_2O$  mixtures that the methoxy-covered surface is exposed to (Figure 4.5b), suggesting a lack of preferential incorporation of hydrogen versus deuterium into the methanol product. Exposure to  $H_2^{18}O$  yielded exclusively  $CH_3^{16}OH$  (Figure 4.5c),

consistent with the formation of methoxy intermediates that desorb subsequent to bond formation between methoxy oxygens and hydrogens/deuteriums in water. These data suggest that a significant fraction of the methane converted form methoxy intermediates which are then extracted using water vapor, and are inconsistent with the formation of adsorbed methanol that is subsequently displaced by water.



**Figure 4.5**. Formation of different CH<sub>3</sub>OH isotopes (CH<sub>3</sub>OH/CH<sub>3</sub>OD or CH<sub>3</sub><sup>16</sup>OH/CH<sub>3</sub><sup>18</sup>OH) over MIL-100(Fe) when exposed to (a) D<sub>2</sub>O or (b) H<sub>2</sub><sup>18</sup>O at 473 K following reaction. (b) The relative fraction of CH<sub>3</sub>OD formed at different D<sub>2</sub>O/H<sub>2</sub>O molar ratios.

Reaction with water to form methanol from intermediates that are not desorbed from the surface in the absence of water mirrors several observations reported in prior literature. Ethane oxidation over MOF-74(Mg,Fe) to produce ethanol, acetaldehyde, and diethyl ether required extraction with CD<sub>3</sub>CN following reaction at 348 K.<sup>106</sup> Propane/ethane oxidation over MIL-100(Fe) also required oxygenated products to be extracted with D<sub>2</sub>O, with only unsaturated ethene/propene products desorbing into the gas phase in the absence of D<sub>2</sub>O.<sup>73</sup> DFT calculations reported by Vitillo *et al.* evaluating the radical rebound mechanism for methanol formation suggest that the step involving formation of the Fe(IV)=O intermediate over MIL-100(Fe) carries the highest activation barrier (140.5 kJ mol<sup>-1</sup>).<sup>72</sup> The authors suggest that alcohol desorption may not readily occur under reaction conditions due to the high activation barrier for the desorption for methanol (91.5 kJ mol<sup>-1</sup>) in comparison to the heat of adsorption of N<sub>2</sub>O (30 kJ mol<sup>-1</sup>). A competing pathway to radical rebound to form the surface bound methanol product is one in which the radical dissociates from the active center.<sup>232,233</sup> The activation energy for radical desorption from Fe nodes in MIL-100(Fe) MOFs was predicted to be only slightly greater (~ 5 kJ mol<sup>-1</sup> greater) than the barrier for radical rebound.<sup>72</sup> We note in this context that experimental evidence for *catalytic* methane hydroxylation over MIL-100(Fe) has not yet been reported in the literature. Though methoxy intermediates are identified in our study as the predominant species formed prior to exposure to water vapor, the identity of elementary steps that form them remain unclear, and the possibility of minor quantities of methanol being formed is challenging to disprove given the plausibility of methanol reacting with open-metal iron sites, as demonstrated in the discussion that follows.

To test for the plausibility of methoxy formation mediated by either adsorbed or gas phase methanol, thermally-activated MIL-100(Fe) was first exposed to CH<sub>3</sub>OH at 373 K, purged for 6 h under inert flow at 473 K to remove excess CH<sub>3</sub>OH, and then exposed to D<sub>2</sub>O. 0.23 mol CH<sub>3</sub>OD (mol Fe)<sup>-1</sup> were measured upon introduction of D<sub>2</sub>O subsequent to exposure to methanol, a value coinciding closely with that formed following reaction with methane and N<sub>2</sub>O (0.27 mol CH<sub>3</sub>OD (mol Fe)<sup>-1</sup>, reaction conditions: 473 K, 1.6 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, 2 h.)- Figure 4.6 - evidencing the plausibility of methoxy formation through methanol dissociation over Fe<sup>2+</sup> sites. The methanol dissociation observed is analogous to water reacting with open-metal sites to reform hydroxyl anions that have to be eliminated during thermal activations steps in MIL-100(Fe) (Figure C11, Appendix C), as also reported previously over  $Cr^{2+}$  sites in MIL-100(Cr).<sup>227</sup> The susceptibility of methanol towards dissociation over  $Fe^{2+}$  sites suggests that the formation of methanol intermediates in our experiments cannot be excluded. Regardless of the identity of steps mediating methoxy formation, its stoichiometric formation exclusively over  $Fe^{2+}$  sites appears to precede methanol formation upon extraction with water vapor. A 1:1 correspondence between methoxy concentrations and  $Fe^{2+}$  site densities across a range of thermal activation conditions<sup>109</sup> suggests that methoxy formation involves the participation of only one  $Fe^{2+}$ active center, and contrasts with prior reports for iron-exchanged zeolites that propose the involvement of two active ' $\alpha$ -oxygen' sites per methoxy formed (CH<sub>4</sub> + 2(O)<sub> $\alpha$ </sub>  $\rightarrow$  (OH)<sub> $\alpha$ </sub> + (OCH<sub>3</sub>)<sub>6</sub>).<sup>91,234</sup>



**Figure 4.6.** Molar flow rate of CH<sub>3</sub>OD when  $D_2O$  (0.4 kPa) is introduced after the following procedures: (Top) MIL-100(Fe) exposed to CH<sub>3</sub>OH for 1 h at 373 K and then purged with He for 6 h at 473 K; (Bottom) following exposure to CH<sub>4</sub> and N<sub>2</sub>O.

#### 4.3.3. Manipulating Methoxy Reactivity by Controlling Metal Identity

Implicit in the 1:1 correspondence between Fe<sup>2+</sup> site densities and the number of moles of monodeuteromethanol is the lack of secondary reactions between methoxy intermediates and gas phase methanol formed in primary reactions. Over and above this correspondence between active site densities and methanol yield, the absence of C2 oxygenates in the product stream and the fact that all the methane converted can be accounted for (within error) as methanol formed suggests that C2 intermediates, if formed over the MIL-100(Fe) surface under the conditions reported here thus far, may account for a minor fraction of converted methane. Extraction of intermediates formed under identical conditions by methane and N<sub>2</sub>O (473 K, 2.9 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, 2 h) over MIL-100(Cr), however, provides (in addition to the formation of methanol) significant yields of acetaldehyde (fractional molar selectivity = 0.81, Figure 4.7a) during product extraction at 473 K, 0.35 kPa H<sub>2</sub>O, 1.54 x  $10^{-6}$  mol H<sub>2</sub>O s<sup>-1</sup>. Analogous to the case of tri-iron clusters, moles of methane converted over MIL-100(Cr) track with  $M^{2+}$  site densities (Figure 4.7b) estimated using infrared peak areas corresponding to the hydroxyl anion (Figure C12), pointing to their sole involvement in C-H activation (reaction conditions: 423 K, 14.5 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, 2 h). Cumulative moles of methane reacted per mole  $Cr^{3+}$  do not remain invariant in activation temperature but instead increase with the latter (Figure C13, Appendix C) as a consequence of  $Cr^{2+}/Cr^{3+}$  site ratios (*i.e.* active/inactive site ratios) that increase with activation temperature between 423 and 523 K. M<sup>2+</sup> sites therefore participate in the activation of methane over both the iron and chromium variants of MIL-100(M). Although Cr-NO interactions are significantly stronger over  $Cr^{2+}$  sites compared to  $Cr^{3+}$  sites, as

shown using NO adsorption measurements at 303 K reported in our previous work,<sup>227</sup> in contrast with MIL-100(Fe), insignificant NO adsorption occurs onto  $Cr^{2+}$  open-metal sites at reaction temperatures (423 – 473 K), as indicated by NO adsorption breakthrough and IR spectroscopy measurements (Section C2.14. MIL-100(Cr) NO Titrations at Reaction Temperatures, Appendix C). We therefore rely solely on the correspondence between product yields and  $Cr^{2+}$  open-metal site densities to suggest their involvement in methoxy formation, unlike the case of MIL-100(Fe) in which in-situ titrations with NO provided additional corroborating evidence of the same.



**Figure 4.7.** (a) Product selectivity and methane reacted for MIL-100(Fe) and MIL-100(Cr) activated at 523 K under He flow and in vacuum, respectively. (b) Comparison of  $Cr^{2+}$  site densities and the cumulative moles of CH<sub>4</sub> reacted following activation at different conditions.

We hypothesize that secondary reactions of methoxy intermediates with gas phase methanol are responsible for acetaldehyde formation. The presence of these secondary reactions prevent the use of  $D_2O$  for evidencing the prevalence of methoxy intermediates over MIL-100(Cr) upon exposure to methane and N<sub>2</sub>O. Instead, the prevalence of these



**Figure 4.8.** Molar flow rates of CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH when CH<sub>3</sub>OH (0.12 kPa) is fed after CH<sub>4</sub> oxidation at 373 K over (a) MIL-100(Cr) and (b) MIL-100(Fe). MIL-100(Fe) activated at 473 K under inert flow, MIL-100(Cr) activated at 523 K in vacuum.

secondary reactions can be verified through extraction with 0.12 kPa methanol at 373 K (following reaction at 473 K, 2.9 kPa N<sub>2</sub>O, and 1.5 kPa CH<sub>4</sub> for 2 h) which leads to the formation, exclusively, of ethanol in both MIL-100(Fe) and MIL-100(Cr) (Figure 4.8), with the moles of ethanol formed approximating to the M<sup>2+</sup> site density for both materials (Table C6, Appendix C). This result is consistent with the same methoxy-covered surface being prevalent in both MIL-100(M) variants following oxidation of CH<sub>4</sub>, and product distributions detected upon exposure to water vapor being dependent on the differing propensities of Fe and Cr-methoxy intermediates to undergo C-C bond formation steps. It also appears that whereas carbon-carbon bond formation is not predicated on the presence

of water vapor, it seems to be necessary for the formation of acetaldehyde (as opposed to ethanol) in MIL-100(Cr), as indicated by the observation of methanol and acetaldehyde as



**Figure 4.9.** Molar flow rates of CH<sub>3</sub>OH, H<sub>2</sub>O, and C<sub>2</sub>H<sub>4</sub>O at the reactor outlet as a function of time when either (a) 0.12 kPa H<sub>2</sub>O or (b) 0.12 kPa H<sub>2</sub>O and 0.12 kPa CH<sub>3</sub>OH are fed over MIL-100(Cr) at 373 K following the oxidation of CH<sub>4</sub>.

products under aqueous extraction conditions (Figure 4.7a). *Both* water and methanol appear to be necessary for acetaldehyde formation, as evident in experiments involving extraction using equimolar feeds at 373 K. As a reference condition, a temperature of 373 K and a water partial pressure of 0.12 kPa were chosen for the reason that significant water coverages are attained (0.42 mol H<sub>2</sub>O mol Cr<sup>-1</sup>) in the absence of measurable amounts of methanol or acetaldehyde formation (Figure 4.9a and Table 4.1). Co-feeding equimolar mixtures of methanol and water (0.12 kPa each) under these conditions leads to the formation of 0.93 moles acetaldehyde per mole methane reacted (or equivalently, per mol methoxy formed), evidencing near-complete coupling of methoxies with gas phase

methanol. These results suggest that although methoxies can react with methanol in the absence of significant partial pressures of water, the presence of water is necessary for the production of acetaldehyde, rather than ethanol, as the C2 product, and point to water playing a role in acetaldehyde formation over and above (and may be even independent of) their involvement in primary reaction steps that lead to the formation of gas-phase methanol.

**Table 4.1.** Comparison of the cumulative moles of  $CH_4$  reacted and  $C_2H_4O$  formed over MIL-<br/>100(Cr) when the product extraction step is conducted under different pressures of  $H_2O$ <br/>and  $CH_3OH$  at 373 K.

H <sub>2</sub> O Partial Pressure / kPa	CH3OH Partial Pressure / kPa	CH <sub>4</sub> Reacted / mol (mol M) <sup>-1</sup>	C <sub>2</sub> H <sub>4</sub> O Formed / mol (mol M) <sup>-1</sup>	mol C <sub>2</sub> H <sub>4</sub> O (mol CH <sub>3</sub> O) <sup>-1</sup>
0.12	0	0.14		0
0.12	0.12	0.13	0.121	0.93

The role of water in acetaldehyde formation was investigated further by testing the reactivity of ethanol over activated MIL-100(Cr). Stoichiometric conversion of ethanol was observed at 373 K over activated MIL-100(Cr) in quantities consistent with the density of  $Cr^{2+}$  sites (Table 4.2 and Figure C15b). Lower activation temperatures that allow for the concurrent presence of  $Cr^{2+}$  and  $Cr^{3+}$ -OH<sup>-</sup> groups enable acetaldehyde formation in amounts that track with  $Cr^{2+}$  density, but activation under vacuum at 523 K which creates  $Cr^{2+}$  sites far in excess of terminal hydroxyls ( $Cr^{3+}$ -OH<sup>-</sup>) results in a decrease in cumulative acetaldehyde formation (Figure 4.10). Specifically, cumulative moles of acetaldehyde formed (0.07 mol (mol  $Cr)^{-1}$ ) under this activation condition more closely approximate the moles of terminal hydroxides (0.05 mol  $Cr^{3+}$ -OH<sup>-</sup> (mol  $Cr)^{-1}$ ) than the moles of reduced metal sites (0.28 mol  $Cr^{2+}$  (mol  $Cr)^{-1}$ ), suggesting that while methoxy formation is

predicated on the availability of reduced metal sites, terminal hydroxides may be necessary

for the dehydrogenation of ethanol to acetaldehyde.

**Table 4.2.** For MIL-100(Fe) and MIL-100(Cr), the activation condition employed, the corresponding  $M^{2+}$  site density, and the total quantity of acetaldehyde formed when ethanol (0.11 kPa) is fed over the activated material at 373 K.

Material	Activation Condition	M <sup>2+</sup> Site Density / mol (total mol M) <sup>-1</sup>	C <sub>2</sub> H <sub>4</sub> O Formed / mol (total mol M) <sup>-1</sup>
Cr	Inert flow, 523 K	0.16	0.13
Fe	Inert flow, 423 K	0.11	0.12



**Figure 4.10.**  $Cr^{2+}$  open-metal and  $Cr^{3+}$ -OH<sup>-</sup> site densities with increasing extent of activation and the corresponding quantity of acetaldehyde formed when ethanol (0.11 kPa) is fed over MIL-100(Cr) at 373 K following thermal activation in He or vacuum (when indicated).

To further investigate the role of water in methane conversion to methanol/acetaldehyde, methoxy extraction was carried out over MIL-100(Cr) at varying water partial pressures while keeping the total water flow rate constant, and also at varying water flow rates while keeping the water partial pressure constant (Figure 4.11, Table C7)



**Figure 4.11.** Effect of water partial pressure (0.35 - 0.70 kPa) and flow rate  $(1.54 - 3.07 \text{ x } 10^{-6} \text{ mol} \text{ H}_2\text{O s}^{-1})$  on the CH<sub>3</sub>OH and C<sub>2</sub>H<sub>4</sub>O selectivity over MIL-100(Cr) as indicated by the molar flow rates detected for both products at the reactor outlet as a function of time.

following reaction at 473 K, 2.9 kPa N<sub>2</sub>O, and 1.5 kPa CH<sub>4</sub> for 2 h. Regardless of water flow rates and partial pressures, water, methanol, and acetaldehyde break through simultaneously, consistent with methanol formation resulting from primary reactions between surface methoxies and water, and acetaldehyde resulting from secondary reactions between methoxies and gas phase methanol. The primary(/secondary) nature of methanol(/acetaldehyde) is consistent with the water breakthrough time- the time required for the edge of the water concentration front to reach the bottom of the MIL-100(Cr) bedbeing identical to the time required for both methanol and acetaldehyde to elute through the bed. The rank of products in these stoichiometric reactions is also consistent with the relative sharpness of their concentration fronts; methanol, which breaks through with water, exhibits significantly sharper concentration profiles compared to acetaldehyde (the secondary product), and elutes from the bed exclusively during the period when water molar flow rates at the exit of the bed lie between zero and that at the inlet. In fact, acetaldehyde fronts are broad enough that acetaldehyde is produced through methanol-methoxy interactions long after methanol ceases to be detected at the outlet of the bed (Figure 4.11).



**Figure 4.12.** (a) MIL-100 surface following the reaction of CH<sub>4</sub> and N<sub>2</sub>O. (b) Formation of acetaldehyde through the reaction of CH<sub>3</sub>OH molecules formed 'in-situ' (blue) (c) Formation of acetaldehyde exclusively by reaction with CH<sub>3</sub>OH fed at the inlet.

Water partial pressures not only enable us to tune the relative number of primary (methoxy-water) interactions to secondary (methoxy-methanol) interactions as shown in Figure 4.11, but also the possibility of water-methoxy interactions in the first place. The

stoichiometric nature of both these interactions suggests that under conditions where acetaldehyde is the exclusive product the ratio of moles of acetaldehyde formed to methoxies consumed should lie between 0.5 and 1, with a ratio of 0.5 indicating that every molecule of acetaldehyde owes its formation to an interaction between a methoxy species with a methanol molecule that is desorbed into the gas phase subsequent to a primary interaction with water (Figure 4.12b). A ratio of unity, on the other hand, indicates the exclusive participation in methanol-methoxy interactions of methanol molecules fed at the *inlet* of the reactor, and the lack of C-C bond formation contributions from methanol molecules generated 'in-situ' through water-methoxy interactions (Figure 4.12c).

**Table 4.3.** Cumulative moles of CH<sub>4</sub> reacted and C<sub>2</sub>H<sub>4</sub>O formed over MIL-100(Cr) when the product extraction step is conducted under different partial pressures of H<sub>2</sub>O and CH<sub>3</sub>OH at 373 K. C<sub>2</sub>H<sub>4</sub>O to methoxy ratios are determined for 1 mol CH<sub>3</sub>O formed per mol CH<sub>4</sub> reacted.

H2O Partial Pressure / kPa	CH3OH Partial Pressure / kPa	CH <sub>4</sub> Reacted / mol (mol M) <sup>-1</sup>	C <sub>2</sub> H <sub>4</sub> O Formed / mol (mol M) <sup>-1</sup>	mol C <sub>2</sub> H <sub>4</sub> O (mol CH <sub>3</sub> O) <sup>-1</sup>
0.35	0	0.15	0.069	0.46
0.35	0.35	0.14	0.078	0.56

This ratio captures the fraction of methoxies that interact with gas phase methanol of either kind to form acetaldehyde, with larger values indicative of greater relative contributions from methanol fed at the inlet versus those formed in-situ. As expected, acetaldehyde formation:methoxy consumption ratios of 0.5 were observed when the extraction was carried out at 373 K in the presence of 0.35 kPa water due to the absence of co-fed methanol as shown in Table 4.3 (reaction conditions: 473 K, 2.9 kPa N<sub>2</sub>O, and 1.5 kPa CH<sub>4</sub> for 2 h). Interestingly, these ratios were still found to lie in the vicinity of 0.5 when 0.35 kPa methanol was co-fed with 0.35 kPa water, suggesting that fed methanol

contributes negligibly toward acetaldehyde formation, which instead results exclusively from C-C bond formation events involving methanol generated in-situ. A possible reason for the lack of participation of co-fed methanol may be the significantly slower movement of methanol through the MOF bed compared to water due to methanol outcompeting water from the standpoint of its affinity to open metal sites. Co-fed methanol is precluded from participating in secondary reactions due to the slower movement of its front through the MIL-100(Cr) bed, which results in fed methanol accessing only those regions of the bed that have been already been depleted of methoxies through interactions with the more rapidly progressing water concentration front. Such displacement of water by methanol is consistent with the rollover of water to flow rates exceeding those at the inlet (Figure 4.9b)flow rates that likely accelerate the progress of methanol and acetaldehyde fronts generated in-situ. Reducing the water concentration to 0.12 kPa in the absence of co-fed methanol, on the other hand, reduces methanol and acetaldehyde formation rates to values below the detection limit of the mass spectrometer (Figure 4.9a). Introduction of equimolar watermethanol feeds at these pressures (0.12 kPa each) result in approximately the same number of moles of acetaldehyde formed as methoxies consumed, consistent with the lack of water methoxy interactions at these low water pressures (Table 4.1). The reaction of methoxies exclusively with methanol (but not water) at identical pressures of each reactant captures the propensity of MIL-100(Cr) to form C-C bonds, and the resulting prevalence of C-C bond formation steps at water pressures lower than those required for methoxy-water interactions. These interactions are significantly more challenging to deconvolute under conditions where C-C bond formation can also occur between methoxies and methanol

molecules that result from water-methoxy interactions. The data presented in Table 4.3 suggest that exercising precise control over the relative preponderance of water-methoxy and methanol-methoxy interactions is highly non-trivial due to the fact that water-methoxy interactions can increase local methanol concentrations that in turn make secondary reactions of methanol more probable, and may constitute part of the explanation as to why increasing water partial pressures appear to have an outsized effect on methanol-methoxy interactions compared to water-methoxy interactions (Figure 4.11).

#### 4.3.4. Prevalence of Primary Versus Secondary Reactions over Tri-Iron Nodes

The ability of MIL-100(Fe) to convert methane to methanol has been reported by multiple groups. As described above, under identical conditions (0.35-0.70 kPa H<sub>2</sub>O, 373-473 K), MIL-100(Cr) exhibits a propensity to convert methane to C2 oxygenates through secondary interactions of methanol with methoxy species formed on  $Cr^{2+}$  sites. C2 oxygenate formation, however, appears to not necessarily be precluded on MIL-100(Fe) materials, as demonstrated by the formation of ethanol upon product extraction with methanol at 0.12 kPa and 373 K (Figure 4.8b), and by the formation of acetaldehyde upon feeding ethanol over the partially-dehydrated material (0.11 kPa ethanol, 373 K - Figure C15a, Table 4.2).

To test whether C2 oxygenate formation could occur over tri-iron clusters upon extraction with water, the water partial pressure during extraction was increased from 0.35 to 1.0 kPa (Figure 4.13), resulting in the detection of minor amounts of acetaldehyde (fractional molar selectivity = 0.03) following reaction at 473 K, 2.9 kPa N<sub>2</sub>O, and 1.5 kPa CH<sub>4</sub> for 2 h. Analogous to tri-chromium clusters, increasing inlet water partial pressures can be used to 'force' secondary reactions between  $Fe^{3+}$ -methoxies and methanol, but the water partial pressures and/or flow rates required to access meaningful cumulative acetaldehyde selectivities may be much higher on tri-iron nodes than tri-chromium ones. Accessibility to C2 oxygenate production within lower water partial pressure and flow rate regimes enabled by MIL-100(Cr) likely reflect the greater propensity for  $Cr^{3+}-OCH_{3}^{-}$  intermediates to undergo C-C bond formation reactions with gas phase methanol compared to  $Fe^{3+}-OCH_{3}^{-}$  intermediates, and point to metal identity being a reliable lever for tuning product selectivity in the partial oxidation of light alkanes over supported poly-metal oxo clusters.



**Figure 4.13.** Molar flow rates of CH<sub>3</sub>OH, H<sub>2</sub>O, and C<sub>2</sub>H<sub>4</sub>O at the reactor outlet as a function of time when (a) 0.35 kPa H<sub>2</sub>O or (b) 1.0 kPa H<sub>2</sub>O is fed over MIL-100(Fe) at 473 K following the oxidation of CH<sub>4</sub>.

#### 4.5. Conclusions

Tri-metallic nodes on MIL-100 frameworks effectuate the conversion of methane to methanol and acetaldehyde at low temperatures and sub-ambient reactant pressures. In-situ

titrations with NO over MIL-100(Fe), combined with the equivalence between methoxy densities and  $Cr^{2+}$  open-metal site concentrations in MIL-100(Cr) across a range of thermal activation conditions suggest that the formation of both products occurs solely over M<sup>2+</sup> sites.  $CO_2$  transient formation rates that are insensitive to  $Fe^{3+}$ -methoxy coverages, water titrations over surfaces pre-titrated with NO, and cumulative  $CO_2$  yields per  $M^{3+}$  site that remain invariant as a function of activation temperature all point to the involvement of M<sup>3+</sup> sites in deep oxidation. Methoxy intermediates play a key role in both methanol and acetaldehyde formation, with acetaldehyde formation in the absence of co-fed methanol occurring through secondary reactions of methanol molecules formed as a result of primary methoxy-water reactions. Acetaldehyde formation does not occur when purely methanol is fed over a methoxy-covered surface, suggesting that the presence of water is necessary for producing acetaldehyde, not ethanol, as the C2 oxygenate. Relative rates of propagation of water and methanol concentration fronts determine the ratio of cumulative methoxy-water and methoxy-methanol encounters, and hence acetaldehyde selectivity; we show that these encounters can be 'forced' in either direction by varying inlet water partial pressures and/or flow rates. Although tri-chromium and tri-iron nodes both enable C-C bond formation steps, tri-chromium ones do so at significantly lower water extraction pressures, evidencing the potential for tuning C2 oxygenate selectivity merely by varying the identity of the metal atom constituting the oxo-bridged trimer. Elucidation of the role of metal identity and oxidation state in C-H bond scission and C-C bond formation steps is enabled, first and foremost, by the high level of definition, uniformity, and thermal stability of MIL-100 nodes. We assert, in this vein, that the study and use of MOF materials toward catalytic

applications more generally could play a meaningful role in overcoming persistent limitations in the development of structure-property relationships that result at least in part directly from intractable levels of heterogeneity in (in)active site speciation.

## 5. Spectroscopic, Kinetic, and Isotopic Tracer Study of the Mechanism of CO Oxidation with N<sub>2</sub>O over MIL-100 Metal-Organic Frameworks

Metal-organic framework materials offer a unique opportunity for mapping homogeneous molecular catalyst coordination environment onto the surfaces of nanoporous materials. They enable achieving a level of clarity into structure-catalytic property relationships beyond that which can be realized in synthetic catalysts delimited by a high degree of heterogeneity in active site speciation. In this study we use MIL-100, a MOF featuring mixed-valent trinuclear metal nodes  $[M^{2+}(M^{3+})_2O]$ , which effectuates the gas phase oxidation of light alkanes through the involvement of every potentially available  $M^{2+}$  coordinatively unsaturated site. Carbon monoxide is applied as a reductant to elucidate reaction steps that mediate redox turnovers with N<sub>2</sub>O over MIL-100 carrying iron and chromium nodes. A combination of kinetic data, in-situ spectroscopy measurements, isotopic tracer experiments, and in-situ acid site titrations provide novel insight into means for tuning the kinetic relevance of specific reduction-oxidation half cycle elementary steps through control of metal identity.

#### **5.1. Introduction**

The oxidation of light alkanes  $(C - C_3)$  with N<sub>2</sub>O by metal-organic frameworks (MOFs) is an area of research that has developed significantly over the past several years, as reflected by the breadth of experimental studeis<sup>73,106,109,235–237</sup> and density-functional theory (DFT)-led investigations which have emerged.<sup>72,74,107,113,114,224,238,239</sup> Specifically, the regular and uniform nature of MOF structures uniquely allows for achieving high densities of mono- and multinuclear metal centers within organic crystalline architectures, permitting an unprecedented potential to draw direct structure-catalytic property
relationships experimentally which have been identified through theoretical studies. Such evaluations can be often precluded within heterogeneous catalysts in cases where distributions of (in)active sites exist, each contributing differently to steady-state kinetics, or when the primary active metal represents only a minor fraction of the total metal density.

A prototypical example of the high degree of uniformity afforded by MOFs is the family of MIL-type (MIL = Materials of Institut Lavoisier) frameworks established by Férey and colleagues,<sup>43,240</sup> representing one of the most prominently studied classes of MOF materials. Not only have an isoreticular series of MIL-type frameworks been successfully synthesized through variation of organic ligands to yield pores sizes up to approximately 68 Å,<sup>241</sup> they can produced featuring various compositions of single metal (Sc,<sup>47,172</sup> Ti,<sup>242,243</sup> V,<sup>173,244</sup> Cr,<sup>43,240</sup> Mn,<sup>174</sup> Fe,<sup>68,245</sup> Al,<sup>140,246</sup> and In<sup>247</sup>) and mixed-metal<sup>248–</sup> <sup>251</sup> arrangements. As an illustration of the uniform surface structures that can be obtained with this class of MOFs, Han, Zhang, and colleagues used high-resolution transition electron microscopy (HRTEM) measurements to image the periodic, mesoporous structure of MIL-101(Cr) crystals with absolute agreement between experimental and structurallymodeled images.<sup>252</sup> Moreover, the accessibility and uniformity of metal sites in this class of materials can be gauged by their interaction with probe molecules. For example Daturi and coworkers established with MIL-100(Cr) that desorption of coordinated water molecules could be conducted at low temperatures ( $\leq$  523 K) and that the complete density of  $Cr^{3+}$  open-metal sites could be achieved, based on the theoretical structural formula, and as confirmed by CO adsorption IR spectroscopy measurements.<sup>132</sup>

The framework MIL-100 has been previously evaluated for the partial oxidation of light alkanes (methane, ethane, and propane) in our own work,<sup>109,236</sup> and in experiments conducted by Bhan and colleagues.<sup>73,237</sup> It has been demonstrated that divalent metal centers in both iron- and chromium-containing MIL-100, formed through thermal activation protocols, are primarily responsible for the formation of partial oxygenates as well as oxidative dehydrogenation products in the case of ethane and propane, specifically.<sup>73</sup> However, due to the stoichiometric nature of the partial oxidation pathway, it is difficult to attain intrinsic insight into the elementary reaction steps which influence the reaction kinetics or systematically evaluate direct structure-catalytic property relationships. Moreover, in this work we apply CO as a reductant to evaluate the redox properties and catalytic cycles associated with N<sub>2</sub>O-mediated oxidation chemistries in MIL-100, and MOFs featuring isolated divalent active centers more broadly.

The oxidation of CO with N<sub>2</sub>O is a simple reaction, particularly of importance in reaction mechanistic evaluations, as the products (CO<sub>2</sub> and N<sub>2</sub>) are thermodynamically more stable than the reactant molecules and, unlike the case in the partial oxidation of CH<sub>4</sub> to CH<sub>3</sub>OH,<sup>109,236</sup> the products can readily desorb from the catalyst surface (*vide infra*). Nevertheless, as demonstrated in this work, a combination of steady-state, transient, and isotopic kinetic experiments over a broad range of reaction conditions (393 - 498 K, N<sub>2</sub>O: 1.5 - 62 kPa, CO: 1.5 - 32.2 kPa) are required to delineate the microscopic reaction mechanism, a finding which cannot be decided simply on rate laws that govern kinetics measured at steady-state. The results of this work demonstrate the significant role of metal identity (Fe versus Cr) and the coverage of oxidized reaction intermediates (M-O), formed

by the decomposition of N<sub>2</sub>O, to influence the steady-state kinetics of CO oxidation. Moreover, <sup>18</sup>O<sub>2</sub> isotopic exchange rates and in-situ X-ray spectroscopy measurements conducted under steady state redox conditions provide novel insight into the relative concentration and speciation of iron-oxo intermediates formed under reaction conditions. Lastly, isotopic C<sup>18</sup>O oxidation experiments, producing a series of CO<sub>2</sub> isotopologues through CO oxygen exchange reactions, allow for estimating first-order rate constants for individual elementary reaction steps, the magnitudes of which are strongly influenced by the identity of the active metal.

# **5.2. Materials and Methods**

## 5.2.1. MIL-100 Synthesis and Characterization

MIL-100(Fe) and MIL-100(Cr) were synthesized according to previously published procedures.<sup>109,236</sup> The porosity, crystallinity, and composition of the samples were confirmed through N<sub>2</sub> physisorption, X-ray diffraction, and thermogravimetric analysis. Details of material synthesis and characterization are described in Sections C1.1-1.2 and C2.1-2.2, respectively, of Appendix C.

## **5.2.2. Infrared Spectroscopy Measurements**

Infrared spectroscopy measurements conducted in transmission mode were completed with a Nicolet iS50 FT-IR Spectrometer (Thermo Scientific) equipped with a Harrick Dewar Transmission/Reflection accessory featuring ZnSe windows (25 x 2, 32 x 3 mm). Self-supporting wafers of MIL-100 samples (15-20 mg) mixed with KBr powders were prepared and thermally treated under Ar flow (56 cm<sup>3</sup> min<sup>-1</sup>, Matheson, Ultra High Purity). Spectra of the empty IR cell under Ar low was used as a background reference or during

NO adsorption experiments, spectra of the thermally-activated sample prior to the introduction of NO was used as the background at the analysis temperature. For a given set of experimental data, all spectra for the analysis were collected using the same catalyst wafer without any further normalization. Origin 8.5 software was utilized for baseline corrections and integrating peak areas.

## 5.2.3. CO Oxidation Reaction Experiments

Kinetic measurements of the reaction of CO with  $N_2O$  were carried out using the same reactor set-up described previously for the oxidation of CH<sub>4</sub>.<sup>109,236</sup> Briefly, approximately 0.2 g of MIL-100 (pelletized, crushed, and sieved to  $180 - 245 \,\mu m$  particles) was loaded into a stainless steel tube, supported by quartz wool (CE Elantech) and mounted vertically within a single-zone insulated furnace (1060 W/115 V, Applied Test System Series 3210). A K-type thermocouple at the top of the catalyst was used to determine the reaction temperature. Samples were thermally activated at elevated temperatures (423 - 523 K) for 12 hours under either inert flow (50 cm<sup>3</sup> min<sup>-1</sup> He, Matheson, Ultra High Purity) or vacuum (P < 0.01 kPa, Pfeiffer Pascal 2005 SD rotary vane vacuum pump). During steady-state kinetic measurements, gas-phase reactant and product concentrations were measured relative to the internal standard (argon) using a gas chromatograph (Agilent 7890 B) equipped with an HP-PLOT-Q capillary column (30 m x 320 µm x 0.2 µm) and a thermal conductivity detector. Reaction feeds of N2O (Matheson, Research Purity), CO (Matheson, Ultra High Purity), and Ar (Matheson, Ultra High Purity) were balanced with He to produce the desired reactant partial pressures and total flow rate (typically 65 cm<sup>3</sup> min<sup>-1</sup>).

During transient reaction experiments, product and reactant concentrations were estimated using an online mass spectrometer (MKS Cirrus 2).

#### **5.2.4. Isotopic Reaction Experiments**

A series of kinetic measurements were conducted with isotopically enriched reactant and product species. Specifically,  ${}^{13}$ CO<sub>2</sub> (Millipore Sigma, ISOTEC, 99 atom%  ${}^{13}$ C),  ${}^{15}$ N<sub>2</sub> (Millipore Sigma, ISOTEC, 98 atom%  ${}^{15}$ N<sub>2</sub>), and C<sup>18</sup>O (Millipore Sigma, ISOTEC, 96 atom%  ${}^{18}$ O) were used during reaction experiments. During these experiments, isotopic concentrations of CO, N<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub> were monitored using an online mass spectrometer (MKS Cirrus 2). In cases where the calibration data for a specific isotope was unknown (*e.g.*  ${}^{15}$ N<sub>2</sub>O or  ${}^{13}$ CO), it was assumed that the fragmentation pattern and calibration factor (relative to the internal standard: Ar) were identical to the unlabeled compound (*e.g.*  ${}^{14}$ N<sub>2</sub>O or  ${}^{12}$ CO).

#### **5.2.5. In-Situ Titrations**

In-situ titrations with NO were conducted using two-components gas mixtures of NO, either 1000 ppm NO/N<sub>2</sub> or 10% NO/N<sub>2</sub> (Matheson, Research Grade). The quantity of NO adsorbed during in-situ experiments was determined by comparing the breakthrough curve for NO relative to N<sub>2</sub> as a standard, analyzed with an online mass spectrometer (MKS Cirrus 2). Under NO co-feeds, He carrier gas concentrations were reduced to maintain constant reactant partial pressures.

#### 5.2.6. In-Situ X-ray Absorption Spectroscopy

X-ray absorption fine structure (XAFS) spectroscopy measurements were conducted at the Advanced Photon Source (APS) 10-BM beamline (APS/10-BM) at the Argonne National Laboratory. Spectra were collected in transmission mode at the Fe K-edge (7112 eV). Reference spectra of the metal foil was measured simultaneously for use as a reference for energy calibrations, with the inflection point of the K-edge taken as 7110.75 eV for iron.<sup>253</sup> Processing of data including normalization, background subtraction, edge calibration, and alignment were performed using the *Demeter/Athena/Artemis* suite of XAFS analysis software.<sup>254</sup> Complete experimental details and description of the microreactor flow cell and associated equipment used for in-situ measurements is provided in Section D1.1 of Appendix D.

Fitting of the EXAFS portion of the spectra was conducted in the *Artemis* software. The local structure of the catalyst node was obtained from the crystallographic information file for MIL-100(Fe) provided by Horcajada *et al.*<sup>68</sup> Scattering paths for Fe-O, Fe-Fe, and Fe-C (Figure D3) scattering paths were calculated using *feff* version  $6.^{255}$  Fitting was completed in R-space with k<sup>1</sup>, k<sup>2</sup>, and k<sup>3</sup>-weightings all considered over the range in k from 2 - 10.5 Å<sup>-1</sup> and in r from 1 - 3.3 Å.

## **5.3. Results and Discussion**

#### 5.3.1. Evaluation of Steady-State Oxidation Rates

Reaction of CO and N<sub>2</sub>O over MIL-100(Fe) and MIL-100(Cr) produces only N<sub>2</sub> and CO<sub>2</sub> through the oxidation reaction: N<sub>2</sub>O + CO  $\leftrightarrow$  N<sub>2</sub> + CO<sub>2</sub> at all tested conditions between 393 and 498 K, with the formation rates of both products being equivalent at steady state. Based on the gas phase thermodynamic property values obtained from the NIST Chemistry WebBook (Section D2.1, Appendix D),<sup>256</sup> rates measured reflect only the forward oxidation rate, even at significant reactant conversions (~95%), furthermore the approach to equilibrium was not considered in kinetic evaluations. Moreover, oxidation rates measured over both catalysts were invariant in the weight-hourly space velocity and reactant conversion, at low conversions, under the conditions tested (Figure D5 and Figure D6, Appendix D).

# 5.3.2. Active Site Identity, Quantification, and Degree of Site Uniformity in MIL-100(Fe)

In previous analyses of MIL-100(Fe) for the partial oxidation of methane, ethane, and propane,<sup>73,109,236,237</sup> the principal role of divalent iron sites in the partial oxidation reactions with N<sub>2</sub>O has been evidenced by in-situ titrations with NO, a titrant which selectivity binds to reduced  $Fe^{2+}$  sites, and not  $Fe^{3+}$  sites also present under reaction conditions, as indicated by infrared spectroscopic characterization (Figure 5.1, b).<sup>73,109</sup> Further the contribution of Fe<sup>2+</sup> open-metal sites to the overall CO oxidation rate was investigated using the same methodology. Figure 5.1a shows the CO oxidation rate (normalized by the total moles of Fe sites) at 473 K with increasing NO partial pressure (reaction conditions: 1.5 kPa CO, 14.6 kPa N<sub>2</sub>O, 423 K, activated at 523 K under He flow). Approximately 90% of the oxidation rate can be reduced by co-feeding NO at low partial pressures (0.003 kPa) with increasing NO concentrations up to 0.5 kPa leading to no additional reduction in the oxidation rate. Moreover, at 423 K, a majority of the NO adsorbed remains irreversibly bound upon purging NO for 3 hours under reactant flow, further representing the strong interaction between NO and the catalytic active sites contributing most predominantly to the overall oxidation rate under these conditions. In the partial oxidation of CH<sub>4</sub>, selective oxidation to surface-bound methoxy intermediates could be completely eliminated by NO

co-feed under reaction at 423 K, although NO titration led to no inhibition of the deep oxidation product,  $CO_2$ .<sup>236</sup> Similarly to the results presented in this report (Figure 5.1a), there are a fraction of active sites contributing to the oxidation of CO with N<sub>2</sub>O which are not titrated by NO.



Figure 5.1. (a) Reduction in CO oxidation rate as a function of NO partial pressure over MIL-100(Fe). The final set of data points (black) represents the oxidation rate after purging NO for 3 h under He flow. (b) IR spectra of MIL-100(Fe) under NO flow (0.5 kPa) at 423 K.

Given the absence of NO binding to  $Fe^{3+}$  open-metal sites under the tested conditions at 423 K (Figure 5.1), their involvement in the residual oxidation of CO with N<sub>2</sub>O under NO co-feed is further investigated. Previous titration experiments in the oxidation of CH<sub>4</sub> have indicated that water is an unselective titrant with binds to both  $Fe^{2+}$  and  $Fe^{3+}$  openmetal sites under relevant reaction conditions (0.9 kPa H<sub>2</sub>O at 423 K).<sup>236</sup> Moreover, it was observed that under a pressure of NO (0.5 kPa) in which  $Fe^{2+}$  sites are completely titrated, increasing H<sub>2</sub>O partial pressures (0.1 to 0.9 kPa) introduced into the reactant feed resulted in a systematic increase in the equilibrium water coverage (Figure 4.3b). Similarly to NO and H<sub>2</sub>O co-titration experiments in the oxidation of CH<sub>4</sub>, a systematic linear reduction in the CO<sub>2</sub> formation rate was observed with increasing quantity of H<sub>2</sub>O adsorbed, with the quantity of water adsorption required to completely eliminate the residual CO<sub>2</sub> formation rate being 0.62 mol (total mol Fe)<sup>-1</sup> (Figure D7). This value is in close proximity to the concentration of available Fe<sup>3+</sup> open-metal sites (0.65 mol (total mol Fe)<sup>-1</sup>) in MIL-100(Fe) under this condition (Section C2.5, Appendix C). Furthermore, the linear relationship between the quantity of adsorbed  $H_2O$  and the  $CO_2$  formation rate is consistent with the stoichiometric titration of active sites, however, does not unequivocally reflect that every site titrated by H<sub>2</sub>O (*i.e.* every Fe<sup>3+</sup> open-metal site) contributes to the oxidation rate.<sup>257</sup> Therefore, due to the difficulty in excluding the possibility of a minute amount of defect or extraframework iron sites contributing to the oxidation rate under NO co-feed, we only suggest the possibility that Fe<sup>3+</sup> open-metal sites may contribute to the oxidation of CO. In following portions of this work, we focus solely on the catalytic behavior of Fe<sup>2+</sup> openmetal sites, which contribute principally to the overall oxidation rate (Figure 5.1a), and the contributions of which can be easily assessed by conducting selective NO titrations under reaction conditions.

To evaluate the homogeneity of the  $Fe^{2+}$  active centers contributing to the catalytic oxidation of CO, NO titration experiments were conducted at sub-saturation partial pressures of NO to  $Fe^{2+}$  open-metal sites at 488 K. As demonstrated in Figure 5.1a,  $Fe^{2+}$  open-metal sites in MIL-100(Fe) are completely saturated at low NO partial pressures (0.003 kPa) at 423 K. Under this condition, when NO is introduced to the reactant feed, a

linear reduction in the oxidation rate is observed with time and the fraction of NO adsorbed as the titrant passes through the catalyst bed (Figure D8). Results of this titration, however,



Figure 5.2. (a) Equilibrium adsorption coverage of NO as a function of NO partial pressure at 488 K over MIL-100(Fe) activated at 523 K in He flow. (b) Fractional rate as a function of the fraction of Fe<sup>2+</sup> open-metal sites titrated at each condition (14.6 kPa N<sub>2</sub>O, 1.5 kPa CO, 488 K).

cannot rule out the possibility of  $Fe^{2+}$  sites contributing non-uniformly to the overall oxidation rate as the fraction of  $Fe^{2+}$  sites titrated may reflect the fraction of the catalyst bed to which NO has penetrated and adsorption may be unrelated to the binding strength of NO as every site is saturated at this condition. Analysis at 488 K allows for non-complete coverages of NO to  $Fe^{2+}$  open-metal sites, as shown in Figure 5.2a, at NO partial pressures between 0.003 and 0.02 kPa. Moreover, the equilibrium adsorption coverage of NO on the  $Fe^{2+}$  open-metal sites can be well described by a simple Langmuir single-site adsorption model (Figure 5.2a), suggesting the homogeneous nature of the adsorbing sites with equivalent energies of adsorption.<sup>258</sup> Moreover, the fractional oxidation rate measured at each condition depreciates linearly with the fraction of  $Fe^{2+}$  open-metal sites titrated by NO (Figure 5.2b), providing that an equivalent contribution of every  $Fe^{2+}$  open-metal site

to the oxidation rate can be considered under these conditions. After rigorously identifying the homogeneous pool of active  $Fe^{2+}$  open-metal sites, which contribute predominantly to the overall catalytic activity of MIL-100(Fe), we further consider the mechanism of CO oxidation with N<sub>2</sub>O in the following section.

# 5.3.3. Kinetics at Low N<sub>2</sub>O/CO Ratios over MIL-100(Fe)

In order to gain insight into the mechanism by which isolated Fe<sup>2+</sup> open-metal sites oxidize CO with N<sub>2</sub>O in MIL-100(Fe), a series of transient, steady-state, and isotopic kinetic measurements were conducted. Reaction orders (*n*) at 473 K were determined by varying the N<sub>2</sub>O and CO partial pressures independently and measuring the dependence of the oxidation turnover rate (x10<sup>-4</sup> mol (mol Fe<sup>2+</sup>)<sup>-1</sup> s<sup>-1</sup>). Results indicate that at 1.5 kPa CO, the turnover rate increases near linearly (n = 0.91) with N<sub>2</sub>O partial pressure between 1.7 – 15.5 kPa N<sub>2</sub>O (Figure 5.3a). Varying CO partial pressure at 2.9 kPa N<sub>2</sub>O has negligible influence on the turnover rate between 1.4 and 18.3 kPa CO, providing a reaction order of  $n \approx 0$  for CO (Figure 5.3b). Moreover, results of co-feeding the two byproducts (CO<sub>2</sub> and N<sub>2</sub>) independently at 473 K (Figure 5.3c) indicates no rate dependence on product partial pressures under these conditions. Furthermore, within this regime of reactant and product partial pressures (1.7 – 15.5 kPa N<sub>2</sub>O, 1.4 – 18.3 kPa CO, 0 - 18.4 kPa CO<sub>2</sub>, 0 - 18.1 kPa N<sub>2</sub>) at 473 K, the rate per Fe<sup>2+</sup> site can be described as

$$\frac{r}{[Fe^{2+}]} = k_{eff}[N_2 O] \tag{5.1}$$

where *r* is the molar formation rate of N<sub>2</sub> or CO<sub>2</sub>, [Fe<sup>2+</sup>] is the molar concentration of Fe<sup>2+</sup> open-metal sites,  $k_{eff}$  is the first-order effective rate constant (units = kPa<sup>-1</sup> s<sup>-1</sup>), and [N<sub>2</sub>O] is the partial pressure of N<sub>2</sub>O (units = kPa). In the oxidation of propane with N<sub>2</sub>O over

MIL-100(Fe), Bhan and colleagues found that the formation of gaseous products  $N_2$  and propene could be described by the same expression as in Equation 5.1.<sup>73</sup>



Figure 5.3. CO turnover rates as with (a) N<sub>2</sub>O partial pressure (1.5 kPa CO), and (b) CO pressure (at 2.9 kPa N<sub>2</sub>O) at 473 K. (c) CO turnover rate as a function of product (N<sub>2</sub> or CO<sub>2</sub>) partial pressure when co-fed during reaction (1.5 kPa CO, 2.0 kPa N<sub>2</sub>O, 473 K).

# 5.3.4. Consideration of Plausible Reaction Mechanisms

In regards to existing previous proposals for N<sub>2</sub>O-mediated oxidation chemistries over isolated divalent metal sites in MOFs, several research groups have suggested that in alkane hydroxylation pathways, the possibility of a sequential-type or redox mechansim.<sup>72–</sup> <sup>74,114,224,237,238</sup> For instance, Gagliardi and Truhlar groups proposed DFT-derived catalytic cycles for the oxidation of ethane involving two main steps: (1) the formation of a Fe<sup>4+</sup>=O intermediate by the decomposition of N<sub>2</sub>O on a Fe<sup>2+</sup> open-metal site and (2) activation of ethane to form ethanol through radical rebound.<sup>72,224</sup> A similar sequential mechanism for the oxidation of CO with N<sub>2</sub>O has also been proposed through DFT calculations conducted by Limtrakul and colleagues over coordinatively unsaturated M<sup>2+</sup> sites within M<sub>3</sub>(BTC)<sub>2</sub> (BTC = benzene-1,3,5-tricarboxylate) MOF frameworks.<sup>178</sup> Specifically they observed the decomposition of N<sub>2</sub>O over divalent iron centers (N<sub>2</sub>O···Fe  $\leftrightarrow$  Fe-O···N<sub>2</sub>) to occur with activation energy barriers of 82 kJ mol<sup>-1</sup>. The reaction of CO with the oxidized iron intermediate (Fe-O···CO  $\rightarrow$  Fe···CO<sub>2</sub>) was predicted to occur with a significantly lower activation energy barrier of 13 kJ mol<sup>-1</sup>. The energetically-demanding nature of the N-O bond breaking and Fe-O formation step is consistent with other DFT proposals for MIL-100(Fe) in the oxidation of light alkanes,<sup>72,74,224</sup> the results of which were used to describe the first-order dependence of N<sub>2</sub>/propene formation rates on the partial pressure of N<sub>2</sub>O in the experimental oxidation of propane over MIL-100(Fe) by Bhan and coworkers.<sup>73</sup>

In this report, we consider the possibility of the sequential-type oxidation mechanism, as well as additional reaction mechanisms which may accurately describe the observed reaction kinetics and attempt to eliminate various series of elementary reaction steps through additional steady-state, isotopic, and transient kinetic measurements. Here we consider four reaction schemes based on existing proposals for the reduction of N<sub>2</sub>O with CO over a wide range of heterogeneous catalysts (Figure 5.4).<sup>259–270</sup> The sequential "redox" mechanism (Scheme 1, Figure 5.4) is identified as the most commonly published mechanism over several (supported) oxide catalysts for the reaction of N<sub>2</sub>O and CO involving surface oxygen intermediates formed by the decomposition of N<sub>2</sub>O which react with adsorbed of gaseous CO to form CO<sub>2</sub>,<sup>259,260,263-268</sup> consistent with DFT-proposed redox cycles with  $N_2O$  in MIL-type MOF frameworks (as described above).<sup>72,74</sup> Additionally, reactions in which  $CO_2$  and  $N_2$  form in a single elementary step, have been considered, in which one reactant species reacts with the other reactant in adsorbed form or in the gas phase, and is known as a concerted or "associative" mechanism (Figure 5.4, Schemes 2-4).<sup>262</sup> This type of reaction mechanism has been proposed for several catalysts

including Ag/Al<sub>2</sub>O<sub>3</sub>,<sup>260</sup> bulk oxides,<sup>269,270</sup> and Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>.<sup>261</sup> Based on reaction kinetics presented thus far for MIL-100(Fe) catalyzing the oxidation of CO with N<sub>2</sub>O being well described by a first-order rate dependence on the N<sub>2</sub>O partial pressure, with no dependence on CO or any product partial pressure (Equation 5.1), it is not possible to rule out any of the four reaction schemes without additional experimental evidence.

Scheme 1: Sequential	Scheme 2: Concerted (N <sub>2</sub> O binding first)			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			
Scheme 3: Concerted (CO binding first)	Scheme 4: Concerted (two site)			
$1 \qquad CO_{(g)} + M \implies CO \cdots M$	$1 \qquad \qquad \mathbf{N}_2\mathbf{O}_{(g)} + \mathbf{M}_1  \overleftarrow{\qquad}  \mathbf{N}_2\mathbf{O}\cdots\mathbf{M}_1$			
<sup>2</sup> CO···M + N <sub>2</sub> O <sub>(g)</sub> $\implies$ N <sub>2</sub> O···M···CO	$2 \qquad CO_{(g)} + M_2 \implies CO \cdots M_2$			
$3 N_2O\cdots M\cdots CO \implies M\cdots CO_2 + N_{2(\sigma)}$	<sup>3</sup> $N_2O\cdots M_1 + CO\cdots M_2 \implies N_2\cdots M_1 + CO_2\cdots M_2$			
4 $M \cdots CO_2 \implies M + CO_{2(g)}$	4 $N_2 \cdots M_1 \implies M_1 + N_{2(g)}$			
2 2(g)	5 $M_2 \cdots CO_2 \implies M_2 + CO_{2(\sigma)}$			

Figure 5.4. Reaction mechanisms considered in this study for the oxidation of N<sub>2</sub>O with CO.

Isotopic experiments can provide unique insight into the elementary steps mediating a given chemical transformation through the additional layer of information provided from tracing labeled atoms during reaction or isotopic exchange with surface intermediates. For instance, Iglesia and colleagues have demonstrated that  ${}^{18}O_{2}$ - ${}^{16}O_{2}$  isotopic exchange rates measured under steady-state oxidation reaction conditions with CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>,<sup>271</sup> CO,<sup>272,273</sup> or NO<sup>274</sup> can be used to reflect the reversibility of O<sub>2</sub> dissociation steps during catalysis. Here we consider the reactive adsorption of C<sup>18</sup>O under oxidation reaction conditions with N<sub>2</sub>O to probe the reversibility of CO adsorption steps. Carnisio and coworkers demonstrated that oxygen on the surface of ZnO can participate in isotopic mixing with CO.<sup>275</sup> Here, it is observed that replacement of C<sup>16</sup>O with C<sup>18</sup>O in the reactant mixture results in the formation of various CO<sub>2</sub> isotopologues (C<sup>18</sup>O<sup>16</sup>O, C<sup>16</sup>O<sub>2</sub>, and C<sup>18</sup>O<sub>2</sub>) as well as a net

formation rate of  $C^{16}O$  measured at the reactor outlet (Figure 5.5) (details of product analysis and quantification provided in Section D2.6, Appendix D). Although  $C^{16}O_2$  could be associated with the reaction of  $C^{16}O$  impurities in the  $C^{18}O$ -enriched CO gas mixture (95% purity  $C^{18}O$ ), the formation of  $C^{18}O_2$  and  $C^{16}O$  definitively indicates that  $C^{18}O$  can undergo isotopic exchange reactions with surface oxygen intermediates under steady state reaction conditions. Simply, the evolution of  $C^{16}O$  through such isotopic exchange reactions evidences that CO adsorption is reversible under reaction conditions and in later portions of this work (Section 5.3.10) we further analyze the individual steady-state formation rates of each CO<sub>2</sub> isotopologue under a variety of reaction conditions to provide insight into the value of specific rate constants in the overall oxidation mechanism.



Figure 5.5. Net formation rate of various CO<sub>2</sub> isotopologues (C<sup>18</sup>O<sup>16</sup>O, C<sup>18</sup>O<sub>2</sub>, and C<sup>16</sup>O<sub>2</sub>) and C<sup>16</sup>O when CO oxidation is completed with C<sup>18</sup>O with N<sub>2</sub><sup>16</sup>O over MIL-100(Fe) (473 K, 2.5 kPa CO (95% C<sup>18</sup>O), 3.1 kPa N<sub>2</sub><sup>16</sup>O).

To further evaluate the nature of elementary reaction steps involved in the formation of  $N_2$  and  $CO_2$ , additional product co-feeding experiments were conducted with isotopically enriched <sup>15</sup>N<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> gases. In the case of <sup>15</sup>N<sub>2</sub>, the relative concentration of <sup>15</sup>N<sub>2</sub>, <sup>14</sup>N<sub>2</sub>O, and <sup>15</sup>N<sub>2</sub>O in the reactant feed mixture were monitored in a bypassing gas

line and at the reactor outlet when passed over the catalysts at 473 K. Under the concentrations tested (3.4 kPa  $^{15}N_2$ , 3.1 kPa  $^{14}N_2O$ , 1.5 kPa CO), no measurable formation of  $^{15}N_2O$  could be measured above the baseline intensity for the species in comparison to the concentration in the bypassing gas line (Figure 5.6a). Similarly, when co-feed  $^{13}CO_2$  during reaction at 473 K (3.2 kPa  $^{13}CO_2$ , 3.1 kPa  $N_2O$ , 1.5 kPa  $^{12}CO$ ), no measurable formation of  $^{13}CO$  could be indicated. Furthermore, as no enrichment of the reactants (N<sub>2</sub>O and CO) can be observed when co-feeding isotopically labelled  $^{15}N_2$  or  $^{13}CO_2$ , these results suggest that at least one elementary reaction step involved in the formation of both N<sub>2</sub> and CO<sub>2</sub> can be considered irreversible under the tested conditions.



Figure 5.6. Molar flow rates of isotopically labelled product and reactant species when (a) <sup>15</sup>N<sub>2</sub> (3.1 kPa) or (b) <sup>13</sup>CO<sub>2</sub> (3.2 kPa) are co-fed over MIL-100(Fe) during reaction (473 K, 3.1 kPa <sup>14</sup>N<sub>2</sub>O, 1.5 kPa <sup>12</sup>CO).

Under the conditions tested, kinetics measured over MIL-100(Fe) indicate a near firstorder dependence on the N<sub>2</sub>O partial pressure (Figure 5.3a), which for any of the reaction schemes in Figure 5.4, could be described by various sequences of elementary reaction steps (derivations in Section D2.5 of Appendix D). For example, for the sequential oxidation mechanism (Figure 5.4, Scheme 1), a first-order dependence on N<sub>2</sub>O partial 96

pressure could be measured under conditions where the rate-limiting step is either the adsorption or decomposition of N<sub>2</sub>O. Although in the decomposition of N<sub>2</sub>O, the adsorption and desorption of  $N_2O$  is often considered to be quasi-equilibrated,  $^{267,276-278}$ some authors consider the N<sub>2</sub>O adsorption as rate-limiting under certain conditions<sup>279,280</sup> or that the irreversible adsorption and decomposition of N<sub>2</sub>O (N<sub>2</sub>O + \*  $\rightarrow$  N<sub>2</sub> + O\*) can be considered as a single elementary step.<sup>262,264,281</sup> Here, at low temperatures where measurable surface coverages of  $N_2O$  can be obtained, it is demonstrated that  $N_2O$  can be adsorbed and desorbed rapidly in MIL-100(Fe) (Figure 5.7a,b). The corresponding value of the equilibrium adsorption constant at each temperature, estimated from the coverage to  $Fe^{2+}$  open-metal sites, is provided in Table 5.1. Even at temperatures as low as 333 - 363K, it is apparent that some decomposition of the N2O occurs on the timescale of the adsorption/desorption measurement, as indicated by quantities of  $N_2O$  desorbed that systematically decrease with the adsorption temperature (Figure 5.7c). Although  $N_2O$ sorption can be considered reversible at the lower temperatures evaluated (303 - 363 K) in Figure 5.7, this observation does not necessary probe the reversibility of N<sub>2</sub>O adsorption at reaction relevant temperatures (~ 473 K). Specifically, N<sub>2</sub>O adsorption could be considered irreversible if the rate constant for the decomposition step is significantly greater that the rate constant for N<sub>2</sub>O desorption, such that they are treated as one elementary step.<sup>282,283</sup> Herein, we consider possibilities of both N<sub>2</sub>O adsorption being reversible (quasi-equilibrated) and irreversible (dissociative adsorption) when considering plausible reaction mechanisms.



Figure 5.7. (a) Breakthrough adsorption curves and (b) desorption profiles for Ar and N<sub>2</sub>O with MIL-100(Fe) at 303 K. (c) Quantity of N<sub>2</sub>O adsorbed and fraction desorbed with increasing temperature. MIL-100(Fe) activated at 523 K. 2.9 kPa N<sub>2</sub>O at all the tested conditions.

**Table 5.1.** Equilibrium adsorption constants of N2O for MIL-100(Fe) estimated from coverages at303, 333, and 363 K.

Temperature / K	N <sub>2</sub> O Coverage / mol (mol Fe <sup>2+</sup> ) <sup>-1</sup>	K <sub>eq</sub> / (kPa) <sup>-1</sup>
303	0.95	6.53
333	0.36	0.19
363	0.21	0.09

## 5.3.5. Kinetics at High N<sub>2</sub>O/CO Ratios over MIL-100(Fe)

In this section, the range of oxidation conditions tested over MIL-100(Fe) for the oxidation of CO is extended in order to gain further insight into the elementary reaction steps controlling the oxidation rate at steady-state conditions. Figure 5.8 shows the effect of N<sub>2</sub>O partial pressure on the turnover rate for increasing reaction temperatures at 423, 473, and 498 K. At 423 K (Figure 5.8a) the oxidation rate is first-order in N<sub>2</sub>O partial pressure up to 62 kPa N<sub>2</sub>O. At elevated temperature, the N<sub>2</sub>O reaction order at 1.5 kPa CO decreases systematically to 0.89 and 0.79 at 473 and 498 K, respectively, (Figure 5.8b,c) when tested over an extended range of N<sub>2</sub>O partial pressures (1.5 – 62 kPa N<sub>2</sub>O). This negative dependence of the N<sub>2</sub>O reaction order on the reaction temperature is inconsistent

with inhibition from increased coverages of  $N_2O$ , as this would be expected to follow the inverse trend. As shown at low temperatures (303 – 363 K) in Figure 5.7, the equilibrium adsorption coverage of  $N_2O$  decreases systematically with temperature, as expected for an exothermic adsorption process. Furthermore, it is observed at 473 and 498 K, increasing the CO partial pressure has a positive influence on  $N_2O$  rate-dependence, with increasing the CO partial pressure from 1.5 to 5.0 kPa CO allowing for achieving a near first-order dependence on the  $N_2O$  partial pressure at both reaction temperatures. The corresponding CO and  $N_2O$  reaction orders at each condition are described in Table 5.2.



**Figure 5.8.** Effect of N2O pressure on CO oxidation turnover rates at reaction temperatures of 423, 473, and 498 K, from left to right, respectively, for CO partial pressures between 1.5 – 5.0 kPa.

To identify a reaction mechanism and set of elementary reaction steps which describe the oxidation of CO with N<sub>2</sub>O with MIL-100(Fe), the rate expression derived must contain a term which can describe the positive dependence of CO and N<sub>2</sub>O reaction orders on the partial pressure of the other reactant. Results of isotopic kinetic experiments with  $^{15}N_2$ ,  $^{13}CO_2$ , and C<sup>18</sup>O also indicated that at least one elementary step involved in the formation of N<sub>2</sub> and CO<sub>2</sub> is irreversible and that the adsorption of CO is reversible. As described in detail Appendix D, Section D2.5, there are four reaction schemes (Figure 5.9) which can

describe the kinetic behavior of CO oxidation with N<sub>2</sub>O over MIL-100(Fe).

Reaction Temperature	Condition	ConditionReaction Order (n)		
423 K	1.5 kPa CO	N <sub>2</sub> O (n = 1.04)		
473 K	1.5 kPa CO	$N_2O(n = 0.89)$		
473 K	2.5 kPa CO	$N_2O(n = 0.95)$		
473 K	5.0 kPa CO	$N_2O$ (n = 0.98)		
473 K	22 kPa N <sub>2</sub> O	CO(n = 0.06)		
473 K	31 kPa N <sub>2</sub> O	CO(n = 0.16)		
473 K	42 kPa N <sub>2</sub> O	CO(n = 0.34)		
473 K	54 kPa N <sub>2</sub> O	CO(n = 0.38)		
473 K	62 kPa N <sub>2</sub> O	CO(n = 0.41)		
498 K	1.5 kPa CO	$N_2O(n = 0.79)$		
498 K	2.5 kPa CO	$N_2O$ (n = 0.90)		
498 K	2.5 kPa CO	$N_2O$ (n = 0.94)		
498 K	3 kPa N <sub>2</sub> O	CO(n = 0.09)		
498 K	10 kPa N <sub>2</sub> O	CO(n = 0.32)		
498 K	22 kPa N <sub>2</sub> O	CO(n = 0.40)		
498 K	31 kPa N <sub>2</sub> O	CO(n = 0.42)		
498 K	42 kPa N <sub>2</sub> O	CO(n = 0.46)		
498 K	54 kPa N <sub>2</sub> O	CO(n = 0.50)		
498 K	62 kPa N <sub>2</sub> O	CO (n = 0.53)		

**Table 5.2.**  $N_2O$  reaction orders (from 1.5 - 62 kPa  $N_2O$ ) and CO reaction orders (from 1.5 - 5.0 kPa CO) measured over MIL-100(Fe) at 423, 473, and 498 K.

For reaction Scheme 1, representing the sequential CO oxidation mechanism, two series of elementary reaction steps can describe the steady-state kinetics in which either (1) N<sub>2</sub>O decomposition (N<sub>2</sub>O····M  $\rightarrow$  N<sub>2(g)</sub> + M-O) and CO<sub>2</sub> formation (M-O····CO  $\rightarrow$ M···CO<sub>2</sub>) steps are irreversible or (2) N<sub>2</sub>O adsorption (N<sub>2</sub>O<sub>(g)</sub> + M  $\rightarrow$  N<sub>2</sub>O····M) and CO<sub>2</sub> formation steps are irreversible. For Scheme 2, representing the concerted mechanism with N<sub>2</sub>O binding first, a rate expression could be determined which describes the experimental observations under the conditions of N<sub>2</sub>O adsorption and the concerted N<sub>2</sub>/CO<sub>2</sub> formation step being irreversible (N<sub>2</sub>O···M···CO  $\rightarrow$  N<sub>2(g)</sub> + M···CO<sub>2</sub>). For Scheme 3, which is the same as Scheme 2 but with CO binding first (Figure 5.4), no rate expression could be derived which described the kinetic behavior. For Scheme 4, involving the concerted mechanism with two distinct binding sites for CO and N<sub>2</sub>O, a rate expression could be obtained which could accurately represent the experimental data under the conditions that N<sub>2</sub>O adsorption and the N<sub>2</sub>/CO<sub>2</sub> formation steps being irreversible (N<sub>2</sub>O···M<sub>1</sub> CO···M<sub>2</sub>  $\rightarrow$ N<sub>2</sub>···M<sub>1</sub> + CO<sub>2</sub>···M<sub>2</sub>).



**Figure 5.9.** Reaction schemes which provide rate expression which can accurately govern the steady-state kinetics measured over MIL-100(Fe).

To further probe whether the oxidation reaction proceeds through a sequential- or concerted-type mechanism, the catalyst was exposed to  $N_2O$  and CO in discrete steps separated by purging under inter flow, to determine if  $N_2$  and  $CO_2$  can be formed independently. As shown in Figure 5.10a, when MIL-100(Fe) is exposed to  $N_2O$ , in the absence of CO, at 473 K, there is a stoichiometric quantity of  $N_2$  formed, approximately

equivalent to 1 mol N<sub>2</sub> formed per mol Fe<sup>2+</sup> active site. Following exposure to N<sub>2</sub>O, the gas flow was switched to pure He and purged for 30 minutes at 473 K, allowing sufficient time for the N<sub>2</sub>O concentration in the gas phase to be reduced to less than 0.05% of the initial concentration (Figure D11, Appendix D). After this time, CO was introduced to the catalyst bed at reaction temperature, resulting in the generation of CO<sub>2</sub>. Although the total quantity of CO<sub>2</sub> formed represented only a fraction of the N<sub>2</sub> formed, at 0.64 mol (mol Fe<sup>2+</sup>)<sup>-1</sup>, this experiment lends credence to the sequential N<sub>2</sub>O and CO oxidation mechanism as N<sub>2</sub> and CO<sub>2</sub> can be formed within individual reaction steps and in the absence of gas phase CO and N<sub>2</sub>O, respectively.



Figure 5.10. (a)  $N_2$  formation when MIL-100(Fe) is exposed to  $N_2O$  (64 kPa), purged for 30 minutes in He, then (b) exposed to CO (32.2 kPa) to form CO<sub>2</sub> at 473 K. Dashed lines represent the transient formation profiles of  $N_2$  and CO<sub>2</sub> calculated using the lumped kinetic parameters.

With regards to the stoichiometric quantity of  $CO_2$  formed (0.64 mol (mol Fe<sup>2+</sup>)<sup>-1</sup>) being smaller than the quantity of N<sub>2</sub> formed (1.1 mol (mol Fe<sup>2+</sup>)<sup>-1</sup>), it has been evidenced previously in Fe-MOFs for N<sub>2</sub>O-mediated light alkane oxidation, the inability to separate

oxidation and reduction reaction steps.<sup>73,106</sup> Specifically, Long and colleagues demonstrated in the oxidation of ethane by  $N_2O$  over  $Fe_{0.1}Mg_{1.9}(dobdc)$  (dobdc<sup>4-</sup> = 2,5dioxido-1,4-benzenedicarboxylate) that oxidized iron intermediates (proposed to be Fe<sup>4+</sup>=O) may decay rapidly to form Fe<sup>3+</sup>-OH species that is inactive for oxidizing ethane to ethanol, although the source of the H-atom was undetermined.<sup>106</sup> In the oxidation of propane with  $N_2$  over MIL-100(Fe), it was also observed that  $N_2$  could be yielded over the catalyst in the presence of N<sub>2</sub>O only, however, when later exposed to propane after flushing with He, no carbon products were measured.<sup>73</sup> Here, it was also concluded that oxidized intermediates formed by N<sub>2</sub>O decomposition may be unstable over extended periods of time in the absence of a gas-phase reductant to prevent the prevalence of deactivation pathways. In the stepped sequential N<sub>2</sub>O and CO reactions performed in this work, it is also observed that the cumulative moles of CO<sub>2</sub> formed over the catalyst when exposed to CO decreases systematically with the purging time for He used after reaction with  $N_2O$ (Figure D12, Appendix D). Furthermore, consistent with  $N_2O$  oxidation experiments conducted over Fe0.1Mg1.9(dobdc) and MIL-100(Fe) metal-organic frameworks tested previously,<sup>73,106</sup> oxidized intermediates formed by the decomposition of N<sub>2</sub>O may be unstable or undergo deactivation pathways (Fe-O + H  $\rightarrow$  Fe-OH), the nature of which we do not investigate further in this report.

As the stepped reaction experiments with N<sub>2</sub>O and CO over MIL-100(Fe) suggest the possibility of the sequential oxidation mechanism being a possible route for the formation of N<sub>2</sub> and CO<sub>2</sub>, it does not necessarily rule out other reaction mechanisms (*e.g.* concerted mechanisms described in Figure 5.9) being a contributing or primary reaction pathway

under steady-state reaction conditions. To evaluate further, we have fit the reaction model for Scheme 1: Sequential (a,b) to our steady-state kinetic data and determine if the parameters derived can accurately describe the transient production formation of  $N_2$  and  $CO_2$  during stepped reaction experiments (Figure 5.10). As shown in Figure 5.8, with increasing reaction temperature and  $N_2O$  partial pressure, increased dependence of the rate on the CO partial pressure is measured, where the first-order dependence on  $N_2O$  partial pressure can be nearly recovered by increasing the CO partial pressure. Under this consideration, we assume that in the sequential oxidation mechanism involving irreversible  $N_2O$  decomposition and  $CO_2$  formation steps, the rate expression may be reduced to the following simplified rate expression

$$r = \frac{k_2 K_1 [N_2 O]}{1 + \frac{k_2 K_1 [N_2 O]}{\overline{k_3} [CO] \left(1 - \frac{\overline{k_3}}{\overline{k_3} + k_4}\right)}} = \frac{k' [N_2 O]}{1 + \frac{k' [N_2 O]}{k'' [CO]}}.$$
(5.2)

In the sequential oxidation mechanism where the  $N_2O$  adsorption step is considered irreversible (Scheme 1: Sequential (b), Figure 5.9), the rate expression can be reduced to nearly the same form, however, with k' being equivalent to  $k_1$ , instead of  $k_2K_1$  as described in Equation 5.2, as provided by the following expression

$$r = \frac{k_1[N_2O]}{1 + \frac{k_1[N_2O]}{\overline{k_3}[CO]\left(1 - \frac{\overline{k_3}}{\overline{k_3} + k_4}\right)}} = \frac{k'[N_2O]}{1 + \frac{k'[N_2O]}{k''[CO]}}$$
(5.3)

where in both expressions, we assume that surface oxidized intermediates (M-O) are the only relevant surface species, other than vacant metal sites, under steady-state reaction conditions as this produces the only term which can describe the positive dependence of  $N_2O(CO)$  reaction orders on the partial pressure of  $CO(N_2O)$ .



Figure 5.11. (Left column) Comparison of the estimated rate (Equation 5.2) to the experimentally measured rate. (Right column) Measured rate with N<sub>2</sub>O partial pressure and estimated surface fractions of [M] and [M-O]. For reaction at (a) 473 and (b) 498 K, respectively.

**Table 5.3.** Lumped kinetic parameters estimated from fitting steady-state reaction data to the simplified rate expression at 473 and 498 K. The parameter k' can represent k<sub>2</sub>K<sub>1</sub> or k<sub>1</sub> depending on whether the N<sub>2</sub>O adsorption or decomposition step is considered irreversible.

Parameter	Equivalence	Temperature	Value
k'		473 K	1.18 x 10 <sup>-4</sup> (kPa·s) <sup>-1</sup>
	$R_2 K_1$ or $R_1$	498 K	2.82 x 10 <sup>-4</sup> (kPa·s) <sup>-1</sup>
k''	$\overrightarrow{k_3}\left(1 - \frac{\overleftarrow{k_3}}{\overleftarrow{k_3} + k_4}\right)$	473 K	8.05 x 10 <sup>-3</sup> (kPa·s) <sup>-1</sup>
		498 K	9.36 x 10 <sup>-3</sup> (kPa·s) <sup>-1</sup>

As shown in Figure 5.11, this simplified rate expression can accurately describe the oxidation of CO with  $N_2O$  over MIL-100(Fe) over the entire range of reaction conditions

tested at 473 and 498 K. The values of the lumped rate constants, k' and k'', obtained at each reaction temperature are provided in Table 5.3. Based on the expressions derived, it is predicted that with increasing N<sub>2</sub>O partial pressure, the concentration of oxidized surface intermediates become increasingly more prevalent and that this effect is enhanced with increasing reaction temperature. This observation is further investigated in later sections (Section 5.3.6 and 5.3.7), while here we consider if the value of the lumped rate constants can describe the transient formation profiles of N<sub>2</sub> and CO<sub>2</sub> during stepped reaction experiments. Specifically, the rate of N<sub>2</sub> formation should be controlled by the partial pressure of N<sub>2</sub>O and the rate constant k' entirely representing either the sorption and decomposition of N<sub>2</sub>O over MIL-100(Fe). On the other hand, the formation of CO<sub>2</sub> should be entirely represented by the reaction of CO with oxidized surface intermediates (M-O +  $CO_{(g)} \rightarrow M + CO_2$ ) which is related to the relative value of k'' that represents the adsorption (k<sub>3</sub>, k<sub>-3</sub>) and reaction (k<sub>4</sub>) of CO. Moreover, the transient formation rates of N<sub>2</sub> and CO<sub>2</sub> formation can be described by the following expressions

$$(r_{N_2})_{t=x} = k'[N_2 0](1 - N_x)$$
(5.4)

and 
$$(r_{CO_2})_{t=x} = k''[CO](1 - N_x)$$
 (5.5)

where *t* is time, *x* is a given time in seconds, and  $N_x$  represents the cumulative moles of product formed at a given time (t = x). The term  $(1 - N_x)$  represents the residual density of Fe<sup>2+</sup> active centers, assuming that for every mole of product formed, one mole of Fe<sup>2+</sup> active sites is consumed in the formation of N<sub>2</sub>. For CO<sub>2</sub> formation  $(1 - N_x)$  thus would represent the residual density of oxidized intermediates (Fe-O), assuming one mole of CO<sub>2</sub> can form per mole Fe<sup>2+</sup> or mole (Fe-O). As demonstrated in Figure 5.10 by the dashed lines, the transient product formation profiles for N<sub>2</sub> and CO<sub>2</sub>, estimated solely from

reactant partial pressures and the lumped rate constants (k' and k'') regressed from steadystate oxidation experiments, closely represent the experimentally measured profiles. In the case of CO<sub>2</sub>, a finite Fe-O concentration of 0.64 mol (mol Fe<sup>2+</sup>)<sup>-1</sup> was set due to the instability of the intermediates in the absence of the reductant (Figure D12, Appendix D). Moreover, as the formation of N<sub>2</sub> and CO<sub>2</sub> in transient stepped reaction experiments can be accurately characterized by kinetic parameters determined from steady-state oxidation experiments, the results of this exercise further support that the reaction of N<sub>2</sub>O and CO over MIL-100(Fe) proceeds through a sequential oxidation mechanism (Scheme 1: Sequential (a) or (b), Figure 5.9).

# 5.3.6. Evidencing Finite O\* Concentrations under Steady-State Oxidation

As described in the previous sections, results of the steady-state, transient, and isotopic kinetic measurements conducted over MIL-100(Fe) indicate that the oxidation of CO with  $N_2O$  may be interpreted as proceeding through a sequential-type oxidation mechanism, involving the prevalence of a surface-bound oxidized intermediate formed by the decomposition of  $N_2O$ . CO and  $N_2O$  reaction orders measured over MIL-100(Fe) at 473 and 498 K appear to indicate that finite coverages of the oxidized intermediates may exist at steady-state, their concentration of which is dependent on the  $N_2O/CO$  molar ratio (Figure 5.11). In this section, the existence and relative quantity of oxidized intermediates under reaction conditions is further analyzed by isotopic exchange reaction with gaseous  $O_2$  and in the following section (5.3.7), the nature of the oxidized intermediates formed is further assessed through in-situ XAFS measurements.

As discussed in a previous section (Section 5.3.4), Iglesia and colleagues have evidenced that surface oxygen species (O\*), formed under steady-state reaction of O<sub>2</sub> with various substrates, may undergo isotopic exchange with gaseous oxygen, as indicated by  ${}^{18}\text{O}_2{}^{-16}\text{O}_2$  exchange rates under reaction conditions.<sup>271–274</sup> For instance, in the oxidation of ethane with O<sub>2</sub> over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, under  ${}^{16}\text{O}_2{}^{-18}\text{O}_2$  mixtures it was determined that the ratio of isotopic exchange rates, in the presence and absence of ethane, could accurately reflect the ratio of O\* to vacant active site (\*) concentrations over a range of O<sub>2</sub>/ethane ratios.<sup>271</sup> Moreover, it has been observed that oxidized iron intermediates (" $\alpha$ -O") formed by the decomposition over N<sub>2</sub>O over iron centers incorporated into zeolite frameworks may also undergo isotopic exchange reactions with gaseous O<sub>2</sub> as evidenced by reaction of  $\alpha$ -O formed in Fe-ZSM-5 with <sup>18</sup>O<sub>2</sub> in experiments conducted by Panov and colleagues.<sup>284</sup>



Figure 5.12. (a)  $N_2$  and  ${}^{18}O^{16}O$  formation over MIL-100(Fe) and the cumulative moles of  ${}^{18}O^{16}O$  formed under 62 kPa N<sub>2</sub>O and 2.3 kPa 97%  ${}^{18}O_2$  at 473 K. (b) Comparison of the predicted [M-O] fraction and the net  ${}^{18}O^{16}O$  formation rate when  ${}^{18}O_2$  is fed during reaction at 473 K.

Here, it is observed that co-feeding N<sub>2</sub><sup>16</sup>O and <sup>18</sup>O<sub>2</sub> over MIL-100(Fe) at 473 K results in a stoichiometric quantity of N<sub>2</sub> formation as well as the quantitative formation of <sup>18</sup>O<sup>16</sup>O (Figure 5.12a). The quantity of N<sub>2</sub> formed over the catalyst under this condition is approximately 1.07 mol per mol Fe<sup>2+</sup>, consistent with the reaction of N<sub>2</sub>O with each Fe<sup>2+</sup> active site. The net formation rate of <sup>18</sup>O<sup>16</sup>O increases rapidly and tapers off, similarly to the transient N<sub>2</sub> formation profile, however, in this case, the rate does not reduce completely to zero. Specifically, after a reaction time of approximately 700 seconds, the cumulative moles of <sup>18</sup>O<sup>16</sup>O formed continues to increase linearly with reaction time and exceeds more than one mole formed per Fe<sup>2+</sup> active center (~ 1.4 mol <sup>18</sup>O<sup>16</sup>O (mol Fe<sup>2+</sup>)<sup>-1</sup> after 1000 seconds). Linear extrapolation of the cumulative <sup>18</sup>O<sup>16</sup>O formed (from ~ 700 – 1000 s) to a reaction time of zero seconds intercepts the y-axis at a value of 0.99 cumulative moles of <sup>18</sup>O<sup>16</sup>O per mol Fe<sup>2+</sup> (Figure D13, Appendix D). From this analysis, we suggest that the greater initial rates <sup>18</sup>O<sup>16</sup>O formation are primarily due to the reaction between <sup>18</sup>O<sub>2</sub> with oxidized intermediates formed by the decomposition of N<sub>2</sub><sup>16</sup>O, given by the following,

$$N_2{}^{16}O_{(g)} + {}^{18}O_{2(g)} + M \to N_{2(g)} + {}^{18}O_{2(g)} + M - {}^{16}O \leftrightarrow N_{2(g)} + {}^{18}O^{16}O_{(g)} + M - {}^{18}O.$$
(5.6)

If the oxygen gas stream were purely <sup>18</sup>O<sub>2</sub>, the rate of <sup>18</sup>O<sup>16</sup>O formation should reach zero after the surface intermediates have been completely enriched with <sup>18</sup>O if N<sub>2</sub><sup>16</sup>O cannot exchange its oxygen with the surface intermediates (N<sub>2</sub><sup>16</sup>O<sub>(g)</sub> + M-<sup>18</sup>O  $\leftrightarrow$  N<sub>2</sub><sup>18</sup>O<sub>(g)</sub> + M-<sup>16</sup>O). Under the conditions tested, however, there was no measurable formation of N<sub>2</sub><sup>18</sup>O in the gas phase. Furthermore, the non-zero formation rates of <sup>18</sup>O<sup>16</sup>O may be attributed to isotopic exchange reactions between <sup>18</sup>O<sub>2</sub> and <sup>16</sup>O<sub>2</sub> impurities present in the gas steam given the 97 mol% <sup>18</sup>O purity of the oxygen isotopically-enriched gas, given by the following equation

$${}^{16}O_{2(g)} + M {}^{-18}O \leftrightarrow {}^{18}O_{2(g)} + M {}^{-16}O.$$
 (5.7)

It has predicted from the kinetic rate expression (Eq. 5.2-5.3) that measurable concentrations of oxidized intermediates (M-O) may be present under steady-state reaction conditions over MIL-100(Fe) and that the relative concentration of these species is also dependent on the molar ratio of  $N_2O$  to CO (Figure 5.11). Here, we propose that co-feeding <sup>18</sup>O<sub>2</sub> during the oxidation of CO with N<sub>2</sub>O should result in <sup>18</sup>O<sup>16</sup>O formation rates that are proportional to the concentration of M-O intermediates. To evaluate, first the effect of cofeeding O<sub>2</sub> on the rates of N<sub>2</sub> and CO<sub>2</sub> formation in the reaction of N<sub>2</sub>O and CO was considered. As provided in Table 5.4, a minor amount of  $CO_2$  formation occurs over MIL-100(Fe) in absence of N<sub>2</sub>O and CO which could be potentially attributed to oxidation of the organic ligands or occluded species present from the material synthesis. Based on the chemical formula of MIL-100(Fe) used in this study  $[Fe_3O(H_2O)_2(OH)[C_6H_3(CO_2)_3]_2$  $nH_2O$ ,  $n \approx 3.1$ ], 0.22 x 10<sup>-4</sup> mol CO<sub>2</sub> (mol Fe<sup>2+</sup>)<sup>-1</sup>·s<sup>-1</sup> corresponds to approximately 1.22 x  $10^{-6}$  mol CO<sub>2</sub> (mol framework C)<sup>-1</sup>·s<sup>-1</sup>. At this CO<sub>2</sub> formation rate, it would take over 220 hours for all of the framework carbon to be oxidized to CO<sub>2</sub> by reaction with O<sub>2</sub>. Furthermore, we assume that any catalyst deactivation due to framework oxidation over the timescale of a typical experiment (approximately 1-2 hours) is negligible. The CO<sub>2</sub> formation rate measured during the reaction of CO and  $N_2O$  with  $O_2$  co-feed is equivalent, within error, to the formation rate measured in the absence of  $O_2$  co-feed at two different  $N_2O/CO$  molar ratios (Table 5.4), with minor increases being presumably due to the minor quantities of CO<sub>2</sub> formed by framework oxidation or reaction between O<sub>2</sub> and CO.

Moreover, it is concluded that co-feeding  $O_2$  does not inhibit the reaction of  $N_2O$  and CO and has negligible influence on the overall  $CO_2$  formation rate measured.

**Table 5.4.** Comparison of the CO2 formation rate under various reaction conditions with O2, CO,<br/>and N2O demonstrating that CO2 formation occurs in the absence of N2O and N2O/CO<br/>with O2 at 473 K over MIL-100(Fe).

Condition	CO <sub>2</sub> Formation Rate / x10 <sup>-4</sup> mol (mol Fe) <sup>2+</sup> s <sup>-1</sup>	
2.3 kPa O <sub>2</sub>	0.22	
2.3 kPa O <sub>2</sub> + 1.5 kPa CO	0.38	
$2.3 \text{ kPa O}_2 + 1.5 \text{ kPa CO} + 62 \text{ kPa N}_2\text{O}$	41.0	
1.5 kPa CO + 62 kPa N <sub>2</sub> O	40.3	
$2.3 \text{ kPa O}_2 + 1.5 \text{ kPa CO} + 2.9 \text{ kPa N}_2\text{O}$	3.30	
1.5 kPa CO + 2.9 kPa N <sub>2</sub> O	3.23	

Co-feed of <sup>18</sup>O<sub>2</sub> during the reaction of N<sub>2</sub><sup>16</sup>O and C<sup>16</sup>O allows for the measurement of oxygen exchange rates with surface oxidized intermediates present under steady-state reaction conditions. Specifically, it is observed that at a constant partial pressure of <sup>18</sup>O<sub>2</sub>, the net <sup>18</sup>O<sup>16</sup>O formation rate measured at steady-state is strongly dependent on the N<sub>2</sub>O/CO molar ratio employed for reaction (Figure 5.12b). Moreover, the net <sup>18</sup>O<sup>16</sup>O formation rate is proportional to the concentration of oxidized surface intermediates (M-O) predicted at the given N<sub>2</sub>O/CO molar ratio using the kinetic model fit to the steady-state reaction data (Table 5.3). Results of this experiment thus suggest a linear correlation between the oxygen exchange rate and the concentration of oxidized surface intermediates, given by the following rate expression

$$r_{18_0 16_0} \propto [M - {}^{16}0][\,{}^{18}0_2\,] \tag{5.8}$$

where  $[M-^{16}O]$  and  $[^{18}O_2]$  represent the concentrations of  $^{16}O$ -surface intermediates and gaseous  $^{18}O_2$ , respectively. The finite net  $^{18}O^{16}O$  formation rates, and their linear relationship to the predicted M-O surface fraction, evidence that significant concentrations

of these oxidized surface intermediates exist under steady-state reaction conditions and can explain the positive CO reaction orders measured at high  $N_2O$  pressures. In the next section, in-situ X-ray absorption measurements of the catalyst are conducted to further probe the speciation of the oxidized intermediates (M-O) formed in MIL-100(Fe).

# 5.3.7. In-situ X-ray Spectroscopic Analysis under Redox Conditions

XAFS spectra of MIL-100(Fe) were collected to analyze the local structure of the iron atoms under three different states: (1) as-synthesized, (2) thermally activated, and (3) under oxidizing reaction conditions. Analysis of the X-ray absorption near edge structure (XANES) of the as-synthesized sample (Figure 5.13a) reveals that the iron is largely in a



**Figure 5.13.** (a) Fe K-edge XAFS showing the XANES region for MIL-100(Fe) under various conditions. Inset showing an enlargement of the pre-edge features and (c) the shift in the absorption edge at each condition.

+3 oxidation state by qualitative comparison to the spectra of ferric reference compounds (Figure D.14a), consistent with the expected structure of MIL-100(Fe) from  $^{57}$ Fe

Mössbauer spectra recorded previously by Férey and colleagues indicating high-spin Fe<sup>3+</sup> ions in pseudo-octahedral geometries.<sup>42,68</sup> Comparison of the XANES for the thermally-activated sample (523 K, 1.5 h, He flow) shows a resulting shift in the energy of the absorption edge to lower eV. The shift in the absorption edge is consistent with a decrease in the average iron oxidation state. Results of NO titration experiments conducted previously suggest that 30% of the iron in this sample is reduced to a +2 oxidation state following thermal activation at 523 K.<sup>109,236</sup> This quantity is consistent with the theoretical maximum density of divalent iron centers in MIL-100(Fe) (1/3 mol (mol total Fe)<sup>-1</sup>) determined by Yoon *et al.*<sup>42</sup> Direct analysis of the average iron oxidation state from the Fe XANES is not straightforward, as the spectra of Fe<sup>2+</sup> reference compounds are spectroscopically distinct (Figure D.14b), furthermore it assumed that a finite fraction of the iron is reduced from a +3 to +2 oxidation state during the in-situ XAFS experiments, similarly to that determined by independent titration experiments with NO for this catalyst sample.<sup>236</sup>



Figure 5.14. Magnitude of the Fourier transform |X(R)|, k<sub>3</sub>-weighted, characterizing MIL-100(Fe) under various conditions: (i) as synthesized, (ii) thermally activated, (iii) under reactant flow (N<sub>2</sub>O/CO = 3), (iv) under reactant flow (N<sub>2</sub>O/CO = 50), and (v) under N<sub>2</sub>O/O<sub>2</sub> co-feed.

Further analysis of the pre-edge features provides additional evidence of the changes in the coordination environment of the iron atoms during the thermal activation process. Specifically, high-spin Fe<sup>3+</sup> atoms in a pseudo-octahedral coordination geometry will feature pre-edge peaks associated with two 1s  $\rightarrow$  3d electronic transitions (eg and t<sub>2g</sub>),<sup>285</sup> consistent with the experimentally measured spectra of MIL-100(Fe), Figure 5.13b. Following thermal treatment at 523 K, a single, higher-intensity peak can be observed in the pre-edge region. This spectral change is consistent with the expected transition to iron in a primarily square-pyramidal geometry and can be attributed to increased mixing between 4p and 3d orbitals in the iron atom.<sup>285</sup> Analysis of the EXAFS data (Figure 5.14) also indicates a decrease in the magnitude of the Fourier transform,  $|\chi(\mathbf{R})|$ , associated with the first shell average Fe-O coordination number - consistent with the change in coordination geometry indicated from XANES pre-edge features (Figure 5.13b).

Results of kinetic measurements conducted over MIL-100(Fe) at 473 K indicate that at low N<sub>2</sub>O/CO ratios, the concentration of oxidized surface intermediates (Fe<sup>(x+)</sup>-O) under steady-state reaction conditions should be negligeable, as shown in Table 5.5 for an N<sub>2</sub>O/CO molar ratio of 3. Elevated N<sub>2</sub>O/CO molar ratios, however, result in increased concentrations of Fe<sup>(x+)</sup>-O intermediates at steady-state, specifically, for an N<sub>2</sub>O/CO ratio of 50, it is expected that approximately 43% of the divalent iron centers are oxidized, or 13% of the total iron content (Table 5.5). As demonstrated by <sup>18</sup>O<sub>2</sub> oxygen exchange rates and O<sub>2</sub> co-feeding experiments conducted in Section 5.3.6, oxidized reaction intermediates may be maintained in the absence of reductant flow, without being scavenged from the catalyst surface, therefore, the highest density of Fe<sup>(x+)</sup>-O intermediates is expected under this condition. Notably, comparison of the absorption edge measured for MIL-100(Fe) under reaction conditions to the sample immediately following thermal activation, indicates a progressive shift to higher energy (Figure 5.13c) consistent with a fraction of the Fe<sup>2+</sup> actives sites being re-oxidized under reaction conditions. Qualitatively, the absorption edge for the sample measured under an N<sub>2</sub>O/CO molar ratio of 3 is nearly identical to the sample measured prior to reaction at 473 K, consistent with expectations from kinetic measurements that insignificant concentrations of Fe<sup>(x+)</sup>-O exist at this condition (Table 5.5). The shift in the absorption edge to higher energy is more significant under a N<sub>2</sub>O/CO ratio of 50 and most prominent under N<sub>2</sub>O and O<sub>2</sub> co-feed (Figure 5.13c), following the same trend predicted from steady-state kinetic measurements. Further, analysis of the EXAFS data (Figure 5.14) also indicates a gradual increase in  $|\chi(R)|$  associated with the first shell Fe-O coordination number that follows the same relative trend of increasing absorption edge energy.

**Table 5.5.** Fraction of  $Fe^{2+}$  and  $Fe^{(x+)}$ -O intermediates (per total Fe) expected under N<sub>2</sub>O and COreaction conditions, and under N<sub>2</sub>O/O<sub>2</sub> co-feed predicted from the steady-state kineticrate expression (Equation 5.2).

Sample	Fe <sup>2+</sup> Fraction / mol (total mol Fe) <sup>-1</sup>	Fe <sup>(x+)</sup> -O Fraction / mol (total mol Fe) <sup>-1</sup>	
Thermally activated	0.30		
$N_2O/CO = 3$	0.29	0.01	
$N_2O/CO = 50$	0.17	0.13	
$N_2O/O_2$	0	0.30	

EXAFS fitting results are summarized in Table 5.6 and Table 5.7 for all samples. The as synthesized MIL-100(Fe) sample was considered first as it represents the reference state of the catalyst. Specifically, single scattering paths were considered between iron and oxygen in the first coordination sphere (N = 6), the nearest carbon atoms of the organic

ligands (N = 4), and with the iron atoms within the same node (N = 2), as considered previously in XAFS analyses of MIL-100(Fe)<sup>73,286</sup> and as indicated in Figure D3. Results provided that Fe-O and Fe-Fe single scattering paths contribute most significantly to the overall EXAFS fit, with Fe-C scatting paths having a minor contribution to the |X(R)| between 1.5 and 2.5 Å (Figure D17, SI), furthermore, the Fe-C path was not included in the main results reported in Table 5.6. Analysis of the of the as-synthesized sample is consistent with the known local structure of MIL-100(Fe) and with XAFS analyses conducted previously,<sup>68,73,286</sup> featuring iron atoms in a predominantly octahedral coordination environment of oxygen atoms and an Fe-Fe distance within the trimer node of approximately 3.3 Å.

**Table 5.6.** Fe K edge EXAFS fit results (k =  $3.1 - 10.5 \text{ Å}^{-1}$ ),  $\Delta k = 0.1$ ,  $k^N N = 1,2,3$ , R = 1.0 - 3.3 Å,  $S_0^2 = 0.79 \pm 0.11$ ), for the as synthesized sample. Notation: N – coordination number, R – distance to neighboring atom,  $\sigma^2$  – mean square displacement,  $\Delta E_0$  - energy correction.

Sample	Path	Ν	<b>R</b> (Å)	$\sigma^2 (x 10^{-3} \text{\AA}^2)$	$\Delta E_0 (eV)$	<b>R-factor</b>
As Synthesized	Fe-O	6	$1.992 \pm 0.012$	$7.6 \pm 1.7$	$\textbf{-0.91} \pm 1.8$	0.018
	Fe-Fe	2	$3.303 \pm 0.019$	$6.3 \pm 1.1$		

Analysis of the relative change in the Fe-O coordination number, with respect to the as-synthesized catalyst sample was considered by fitting all samples measured at 473 K simultaneously (Table 5.7). As evaluated in the supporting information, Figure D17 and Table D6, adding in the Fe-Fe single scattering path had minor influence on the results for the Fe-O scattering path and was excluded in the fits described in Table 5.7. Results for all samples at 473 K are shown in Figure D18 through Figure D21 of Appendix D. The estimated Fe-O coordination number of approximately 4.5 for the thermally activated MIL-100(Fe) sample is consistent with transition of every iron atom from a pseudo-octahedral
to square-pyramidal coordination geometry during the thermal activation process, as reflected also by the change in the pre-edge feature analyzed in the XANES spectra (Figure 5.13b).

**Table 5.7.** EXAFS fit results for the thermally activated MIL-100(Fe) sample and under all reaction conditions at 473 K ( $k = 3.1 - 10.5 \text{ Å}^{-1}$ ),  $\Delta k = 0.1$ ,  $k^{N} N = 1,2,3$ , R = 1.0 - 2.2 Å. S<sub>0</sub><sup>2</sup> set to 0.79 using the value determined in Table 5.6 to estimate the change in N for the Fe-O path.

Sample	Path	Ν	<b>R</b> (Å)	$\sigma^2 (x 10^{-3} \text{\AA}^2)$	$\Delta E_0 (eV)$	<b>R-factor</b>
Thermally activated	Fe-O	$4.540\pm0.223$	$1.967 \pm 0.004$	$8.6\pm\ 0.5$	$\textbf{-1.9}\pm0.55$	0.0033
$N_2O/CO=3$	Fe-O	$4.551 \pm 0.233$				
$N_2O/CO=50$	Fe-O	$4.661 \pm 0.234$				
$N_2O/O_2$	Fe-O	$4.770\pm0.241$				

Although EXAFS results indicate a qualitative increase in the average Fe-O coordination number under reaction conditions, it is difficult to assess the exact change in coordination number due to the large errors in these values (Table 5.7). Furthermore, we attempt to isolate the feature resulting in the increase in Fe-O coordination number by fitting the difference spectra between the thermally activated sample and the sample under N<sub>2</sub>O/O<sub>2</sub> co-feed, which showed the largest magnitude difference. EXAFS fitting results are provided in Figure D22 and are summarized in Table 5.8. The difference spectra can be characterized by an Fe-O coordination number of approximately 0.18  $\pm$  0.07, with an average Fe-O distance of 1.947  $\pm$  0.041 Å. Notably, this Fe-O bond length is significantly greater than that expected for a double-bonded Fe<sup>4+</sup>=O (1.62 Å) intermediate in MIL-100(Fe), as predicted from DFT simulations conducted by Vitillo *et al.*<sup>72</sup> The value of the coordination number corresponds to approximately 0.18 Fe-O bonds formed per total Fe, or 0.51  $\pm$  0.22 Fe-O bonds formed per Fe<sup>2+</sup> site (assuming that Fe<sup>2+</sup> sites represent 1/3 of the total Fe content).

**Table 5.8.** EXAFS fit results for the difference spectra between the thermally activated MIL-100(Fe) sample and the sample measured under N<sub>2</sub>O/O<sub>2</sub> co-feed at 473 K (k = 3.1 – 9.5 Å<sup>-1</sup>),  $\Delta k = 0.1$ ,  $k^N N = 1,2,3$ , R = 0.9 - 2.2 Å,  $S_0^2$  set to 0.79 in accordance with Table 5.7.

Path	Ν	<b>R</b> (Å)	$\sigma^2 (x 10^{-3} \text{\AA}^2)$	$\Delta E_0 (eV)$	<b>R-factor</b>
Fe-O	$0.177\pm0.073$	$1.947 \pm 0.041$	$4.0\pm~5.9$	$2.8\pm5.9$	0.042

From this result, we further investigate whether  $Fe^{(x+)}$ -O intermediates formed may be more aptly characterized by a single bonded iron oxyl ( $Fe^{3+}-O^{-}$ ) by corresponding analysis of shifts in the absorption edge related to the average change in iron oxidation state. Specifically, changes in the average iron oxidation state from the refence spectra measured following thermal activation at 473 K (containing both Fe<sup>2+</sup> and Fe<sup>3+</sup> atoms) can be estimated through linear combination fitting at each reaction condition using the assynthesized MIL-100(Fe) catalyst sample as an accurate representation of every iron atom being in a + 3 oxidation sate and pseudo-octahedral coordination geometry. Results of the fitting are provided in Table 5.9. Specifically, the sample measured under a N<sub>2</sub>O/CO molar ratio of 3 is fit with no contribution from the as-synthesized MIL-100(Fe) reference spectra, however, its contribution to the linear combination fit is 10% and 23% for the catalyst samples measured under an N2O/CO ratio of 50 and under N2O and O2 co-feed, respectively. Figure 5.15 displays a comparison between the spectra for the sample measured under N<sub>2</sub>O/O<sub>2</sub> co-feed and the linear combination fit, showing agreement in the absorption edge, pre-edge feature, and white line intensity.

**Table 5.9.** Results of linear combination fitting of the MIL-100(Fe) sample under each reaction condition using the spectra of the thermally activated and as synthesized catalyst sample as the reference standards. Fitting range = -20 - 30 eV,  $X_r^2$ : reduced  $X^2$ .

	Standard Weight				
Sample	Thermally Activated	As Synthesized	<b>R-factor</b>	$X_r^2$	
$N_2O/CO = 3$	1.0	0.0	0.00002	0.0009	
$N_2O/CO = 50$	0.90	0.10	0.00004	0.0017	
$N_2O/O_2$	0.77	0.23	0.0002	0.0091	

Interpretation of the results obtained for the sample under N2O/O2 reaction suggests that the approximate increase in Fe-O coordination number (0.51  $\pm$  0.22, Table 5.8), estimated from the EXAFS fit of the difference spectra, corresponds reasonably well with the results of the linear combination fit (Table 5.9), which indicate a portion of the reduced iron is oxidized under reaction conditions. In correspondence with the average bond distance associated with the Fe-O species formed under this condition (R = 1.947  $\pm$  0.041 Å), it can be interpreted that the nature of the oxidized intermediates sensed during the steady-state reaction experiments by XAFS analysis are best represented as single-bonded



**Figure 5.15.** Linear combination fitting results for the spectra of MIL-100(Fe) under N<sub>2</sub>O and O<sub>2</sub> co-feed at 473 K using the as-synthesized and thermally activated samples as the refences spectra.

Fe<sup>3+</sup>-O<sup>-</sup> species. Results of DFT simulations conducted by Rosen, Notestein and Snurr suggest that oxidized intermediates (M-O) formed by the decomposition of N<sub>2</sub>O over divalent metal sites in a series of M<sub>2</sub>X<sub>2</sub>(BBTA) (M=metal,X=bridging anion, H<sub>2</sub>BBTA=1H,5H-benzo(1,2-d:4,5-d')bistriazole) MOF frameworks can feature a varying degree of oxo (M<sup>4+</sup>=O) or oxyl (M<sup>3+</sup>-O<sup>-</sup>) character, depending primarily on the extent of electron donation from the active metal.<sup>287</sup> Moreover, the more radical-like character of the oxygen atom may aid in explaining the fleeting/unstable nature of the intermediates formed as demonstrated in this work (Figure D12) and in N<sub>2</sub>O-mediated oxidation chemistries conducted over iron MOFs previously.<sup>73,106</sup>

Here, it is noted that there is a discrepancy between the fraction or iron expected to be re-oxidized to at least a +3 oxidation state from steady-state kinetic measurements (Table 5.5) and that which is characterized by in-situ XAFS measurements. Specifically, under N<sub>2</sub>O/O<sub>2</sub> co-feed it is expected that every Fe<sup>2+</sup> open-metal site formed reacts with N<sub>2</sub>O to form a Fe<sup>(x+)</sup>-O intermediate, however, XAFS results estimate this quantity is roughly 50%. Nevertheless, it can be observed that there is a linear trend in the change in the XANES spectra (associated with the reoxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>) estimated from the linear combination fitting results and the expected fraction of Fe<sup>2+</sup> sites oxidized to Fe-O estimated from independent kinetic measurements (Figure D23). Therefore, although the quantitative change probed during in-situ XAFS experiments is less than the expected value, the trends observed across the range of conditions tested are qualitatively consistent.

#### 5.3.8. Common Set of Kinetic Parameters in CO and CH4 Oxidation

Within previous sections, it has been established that the oxidation of CO with N<sub>2</sub>O over MIL-100(Fe) is primarily controlled by the rate of N<sub>2</sub>O adsorption/desorption and decomposition over vacant Fe<sup>2+</sup> active centers. In N<sub>2</sub>O-mediated oxidation of light alkanes over MIL-100(Fe), various DFT-based predictions have suggested that N<sub>2</sub>O activation barriers may also significantly exceed those associated with C-H activation.<sup>72,74</sup> For example, in the oxidation of methane with N<sub>2</sub>O, Vitillo *et al* provided the calculated activation enthalpy for the decomposition of N<sub>2</sub>O over an Fe<sup>2+</sup> active center (Fe<sup>2+</sup>...ON<sub>2</sub>  $\rightarrow$  Fe<sup>4+</sup>=O····N<sub>2</sub>) within an Fe<sub>3</sub>O node to be 141 kJ mol<sup>-1</sup>, whereas the corresponding activation enthalpy for C-H activation was only 63 kJ mol<sup>-1.72</sup> Furthermore, here it is considered if the stoichiometric yield of CH<sub>3</sub>OH over MIL-100(Fe) in the oxidation of CH<sub>4</sub> can be described by rate constants governing the adsorption and decomposition of N<sub>2</sub>O which have been regressed from steady-state CO oxidation measurements.

During the reaction of CO with  $N_2O$  over MIL-100(Fe), the oxidation turnover rate is first-order dependent on the  $N_2O$  partial pressure (at  $N_2O/CO$  molar ratios less than approximately 20, Figure 5.8) and can be described by to following equation

$$r = k'[N_2 0] (5.9)$$

where, as discussed further in Section 5.3.5, k' is the lumped rate constant (in units of kPa<sup>-1</sup>·s<sup>-1</sup>) associated with N<sub>2</sub>O adsorption/desorption (N<sub>2</sub>O<sub>(g)</sub> + M  $\leftrightarrow$  M···N<sub>2</sub>O) and decomposition (M···N<sub>2</sub>O  $\rightarrow$  M-O + N<sub>2(g)</sub>). For the stoichiometric oxidation of methane (CH<sub>4</sub> + N<sub>2</sub>O  $\rightarrow$  CH<sub>3</sub>O + H + N<sub>2</sub>), the product formation rate may equal the steady-state CO oxidation turnover rate if kinetically-limited and the oxidation rate is also first-order dependent on the N<sub>2</sub>O partial pressure. To provide an estimate, we can assume that at zero

reaction time (t = 0 s), the cumulative moles of CH<sub>3</sub>OH formed (N<sub>x</sub>) is zero and the fraction of  $Fe^{2+}$  sites available (per total  $Fe^{2+}$  sites), or M<sub>x</sub>, is equal to one as in the following expressions:

$$r_{CH_3OH} = r_{CO_2}$$
 at t = 0 s, (5.10)

$$N_x = 0 \text{ at } t = 0 \text{ s},$$
 (5.11)

and 
$$M_x = 1$$
 at  $t = 0$  s. (5.12)

At a time  $(t_1 = 0 + \delta)$ , we can assume that  $r_{CH_3OH}$  is equal to  $r_{CO_2}$  if the fraction of Fe<sup>2+</sup> sites available  $(M_x)$  remains close to 1, therefore we choose a time step size  $(\delta)$  that is sufficiently small so that the cumulative moles of product formed per total Fe<sup>2+</sup> sites is much less than one at t = t<sub>1</sub>. Here, a step size of 1 s was chosen, which is significantly shorter than the minimum timescale (~ 3080 s) for a single turnover under the conditions evaluated (473 K, 2.9 kPa N<sub>2</sub>O,  $r_{CO_2}$ =3.25 x 10<sup>-4</sup> mol (mol Fe<sup>2+</sup>)<sup>-1</sup> s<sup>-1</sup>). From the cumulative moles of product formed per total Fe<sup>2+</sup> sites, the remaining fraction of Fe<sup>2+</sup> sites (M<sub>x</sub>) can be estimated and used to calculate a corrected rate (r<sub>x</sub>) which accounts for the consumption of Fe<sup>2+</sup> sites with increasing reaction time as given by the following equations

$$M_x = 1 - N_{x-1} \tag{5.13}$$

and 
$$r_x = r_{CO_2} * M_{x-1}$$
 (5.14)

where  $r_x$  represents the reaction rate at a given time ( $t_x = t_{x-1} + \delta$ ). For any reaction time, the cumulative moles of product formed (per total Fe<sup>2+</sup> sites) can be estimated by the following expression

$$N_{\chi} = \frac{\delta(r_{\chi-1}+r_{\chi})}{2} + N_{\chi-1}.$$
(5.15)



**Figure 5.16.** Measured cumulative yield of CH<sub>3</sub>OH with reaction time during the oxidation of CH<sub>4</sub> with N<sub>2</sub>O (2.9 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, 473 K), ref. <sup>236</sup>, and the predicted cumulative yield of CH<sub>3</sub>OH estimated from the kinetic parameters (k<sub>2</sub>K<sub>1</sub>) for CO oxidation.

As shown in Figure 5.16, the transient yield of CH<sub>3</sub>OH calculated through this method follows the same trend as the experimentally measured values from our previous work, at a low N<sub>2</sub>O to CH<sub>4</sub> molar ratio (2.9 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>) at 473 K.<sup>236</sup> Furthermore, it has been demonstrated that the stoichiometric yields of CH<sub>3</sub>OH in the oxidation of CH<sub>4</sub> with N<sub>2</sub>O can be accurately described by the simplified rate expression (Equation 5.2) which is only dependent on the value of k' (regressed from steady-state CO oxidation experiments) and the partial pressure of N<sub>2</sub>O. We emphasize that the CH<sub>3</sub>OH yield measured is determined by stopping the reaction (N<sub>2</sub>O + CH<sub>4</sub>) at a given time, purging with He, and then introducing H<sub>2</sub>O to measure the cumulative moles of CH<sub>3</sub>OH formed over that given time. It is important to note that under these conditions, timescales associated with the activation of CH<sub>4</sub> to form surface-bound methoxy intermediates cannot be sensed, as CH<sub>3</sub>OH yields are not measured until after reaction. Furthermore, these results can be interpreted simply as the decomposition of  $N_2O$  in the presence of  $CH_4$  versus CO following the same kinetic behavior in both transient and steady-state reaction experiments.

#### **5.3.9.** CO Oxidation Mechanism over MIL-100(Cr)

In N<sub>2</sub>O-mediated oxidation chemistries over MIL-100, we have demonstrated previously in the activation of CH<sub>4</sub> that the identity of the active metal can have significant influences on the selectivity for different partially oxygenated products.<sup>236</sup> Specifically, in comparison of iron and chromium-containing MIL-100 samples, it was found that chromium active centers had an increased propensity for forming the C<sub>2</sub>-oxygenate, acetaldehyde, over methanol which was formed near exclusively over MIL-100(Fe). Here we further investigate the role of metal identity in the oxidation of CO with N<sub>2</sub>O to garner further insight into differences in the reaction mechanism and degree of rate control of individual elementary reaction steps.

The catalytic oxidation of CO with N<sub>2</sub>O over MIL-100(Cr), tested under comparable conditions as MIL-100(Fe), shows nearly the inverse dependence on the reactant partial pressures in comparison to the iron analogue (Figure 5.17). Specifically, at 2.9 kPa N<sub>2</sub>O, turnover rates measured over MIL-100(Cr) increase nearly proportionally with CO pressure, whereas at 1.5 kPa CO, there is no influence of the partial pressure of N<sub>2</sub>O on the reaction rate. Notably, the oxidation rate measured over MIL-100(Cr) exhibits a very dynamic dependence on N<sub>2</sub>O and CO partial pressures, as indicated in Figure 5.18 over a range of reaction temperatures between 393 and 473 K with no dependence being measured on product partial pressures at the temperature extremes (Figure D24, Appendix D). Trends measured under these conditions indicate that CO reaction orders are both positively



Figure 5.17. Dependence of the turnover rate on the partial pressure of (a) CO and (b) N<sub>2</sub>O at 2.9 kPa N<sub>2</sub>O and 1.5 kPa CO, respectively, measured over MIL-100(Fe) and MIL-100(Cr) at 473 K.



**Figure 5.18.** (a) CO and (b) N<sub>2</sub>O reaction orders measured over MIL-100(Cr) during CO oxidation with N<sub>2</sub>O (reaction conditions: 1.5 – 8.7 kPa N<sub>2</sub>O, 3.5 – 32.2 kPa CO, 120 – 200 °C).

dependent on reaction temperature and N<sub>2</sub>O partial pressure, whereas N<sub>2</sub>O reaction orders are positively dependent on CO pressure but decrease with increasing reaction temperature. It can be noted that these exact trends were also measured over MIL-100(Fe) (Figure 5.8 and Table 5.2), although requiring higher ranges of reaction temperatures (473 – 498 K) and N<sub>2</sub>O/CO molar ratios (approximately  $\geq$  20) in order to sense dependence on the rate on CO partial pressures. Similarly to MIL-100(Fe), isotopic experiments conducted over MIL-100(Cr) cofeeding <sup>15</sup>N<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> during reaction yielded no isotopic enrichment of the gaseous N<sub>2</sub>O or CO reactant species, respectively (Figure D25, Appendix D). These results indicate that an elementary step involved in the formation of N<sub>2</sub> and CO<sub>2</sub> can be considered irreversible under the reaction conditions tested. Moreover, the reaction of C<sup>18</sup>O with N<sub>2</sub><sup>16</sup>O over MIL-100(Cr) also indicates isotopic exchange between gaseous CO and oxidized surface intermediates (M-<sup>16</sup>O + C<sup>18</sup>O<sub>(g)</sub>  $\leftrightarrow$  M-<sup>18</sup>O + C<sup>16</sup>O<sub>(g)</sub>), as evidenced by the formation of mixed CO<sub>2</sub> isotopologues (C<sup>18</sup>O<sup>16</sup>O, C<sup>18</sup>O<sub>2</sub>, and C<sup>16</sup>O<sub>2</sub>) and a positive net rate of C<sup>16</sup>O formation (Figure 5.19). Notably, under the same N<sub>2</sub><sup>16</sup>O and C<sup>18</sup>O pressures tested over MIL-100(Fe), provided in Figure 5.5, C<sup>18</sup>O<sub>2</sub>/C<sup>16</sup>O<sub>2</sub> isotopologues represent increased fractions of the total quantity of CO<sub>2</sub> formed (Figure 5.19). Further evaluation of the CO<sub>2</sub> isotopologue distributions under various reaction conditions is discussed in the following Section 5.3.10.



Figure 5.19. Net formation rate of various  $CO_2$  isotopologues ( $C^{18}O^{16}O$ ,  $C^{18}O_2$ , and  $C^{16}O_2$ ) and  $C^{16}O$  when CO oxidation is completed with  $C^{18}O$  with  $N_2^{16}O$  over MIL-100(Cr) (473 K, 2.5 kPa CO (95%  $C^{18}O$ ), 3.1 kPa  $N_2^{16}O$ ).



Figure 5.20. Parity plots comparing the  $CO_2$  turnover rate estimated from the rate expression in Equation 5.2 to the experimentally measured turnover rate over MIL-100(Cr) at four reaction temperatures (393 – 473 K).

Despite MIL-100(Cr) showing enhanced rate sensitivity to the N<sub>2</sub>O to CO molar ratio under the same conditions tested over MIL-100(Fe), results of isotopic and kinetic measurements indicate strong similarities between the two materials regarding the reversibility of elementary reaction steps involved in the formation of N<sub>2</sub> and CO<sub>2</sub> as well as the dependence of N<sub>2</sub>O(CO) reaction orders on temperature and the partial pressure of the other reactant. Further evaluation indicates that CO oxidation turnover rates measured over MIL-100(Cr) between 393 and 473 K can be well described by the same rate expression (Eq. 5.2 or 5.3), derived from the sequential CO oxidation mechanism (Scheme 1, Figure 5.9), which represented the steady-state kinetics over MIL-100(Fe). Here, it is observed that the lumped rate k' is more sensitive to the reaction temperature than k'', which can accurately describe the increasing dependence of the oxidation rate on the CO partial pressure with increasing temperature (Figure 5.18a). Although the simplified rate expression can accurately describe the kinetics under this condition, it is noted that this does not evidence the nature of the mechanism or that this is the only plausible rate expression which may be fit to the experimental data.

**Table 5.10.** Lumped kinetic parameters for MIL-100(Cr) estimated from fitting steady-statereaction data to the simplified rate expression at 393, 423, 448, and 473 K.

Parameter	Equivalence	Temperature	Value
k'	$k_2 K_1 \text{ or } k_1$	393 K	1.40 x 10 <sup>-5</sup> (kPa·s) <sup>-1</sup>
		423 K	5.84 x 10 <sup>-5</sup> (kPa·s) <sup>-1</sup>
		448 K	1.40 x 10 <sup>-4</sup> (kPa·s) <sup>-1</sup>
		473 K	3.20 x 10 <sup>-4</sup> (kPa·s) <sup>-1</sup>
1-11	$\overrightarrow{k_3}\left(1 - \frac{\overleftarrow{k_3}}{\overleftarrow{k_3} + k_4}\right)$	393 K	1.09 x 10 <sup>-5</sup> (kPa·s) <sup>-1</sup>
		423 K	1.39 x 10 <sup>-5</sup> (kPa·s) <sup>-1</sup>
ĸ		448 K	1.98 x 10 <sup>-5</sup> (kPa·s) <sup>-1</sup>
		473 K	2.93 x 10 <sup>-5</sup> (kPa·s) <sup>-1</sup>

Stepped reaction experiments involving the sequential exposure of MIL-100(Cr) to first  $N_2O$  then subsequently CO after intermittent purging with He were conducted under the same conditions tested over MIL-100(Fe) in Figure 5.10 to probe the (un)concerted nature of the product formation steps. As shown in Figure 5.21,  $N_2$  and CO<sub>2</sub> formation over MIL-100(Cr) can occur through distinct reaction steps. We note that the MIL-100(Cr) catalyst used in this experiment has been diluted in silica in order to reduce the effect of initial catalyst bed temperature rise do the exothermic adsorption/decomposition of  $N_2O$ . Moreover, although the timescales for the complete reaction of  $N_2O$  with the  $M^{2+}$  open-

metal sites are comparable for MIL-100(Fe) and MIL-100(Cr), the timescale for all the oxidized intermediates formed to react with CO to form  $CO_2$  is significantly extended (> 3000 s) in comparison to that measured over MIL-100(Fe) (< 500 s).



Figure 5.21. (a) N<sub>2</sub> formation under N<sub>2</sub>O (64 kPa) flow, purged for 30 minutes under He, and then (b) exposed to CO (32.2 kPa) to form CO<sub>2</sub> at 473 K over MIL-100(Cr) in silica (1:5 interparticle dilution ratio). Dashed lines represent values estimated from the lumped kinetic parameters.

It can also be observed that the cumulative moles of  $CO_2$  formed in CO reaction steps approximates well the total cumulative moles of N<sub>2</sub> formed and the Cr<sup>2+</sup> site density in the catalyst at this activation condition. Therefore, unlike for MIL-100(Fe), where approximately 38% of the oxidized intermediates had deactivated/decomposed upon purging in He for 30 minutes (Figure 5.10), all of the Cr-O intermediates are still active during this stage. The relative stability/instability of oxo-intermediates formed by the decomposition of N<sub>2</sub>O over divalent metal sites in MOF nodes has been investigated extensively in the literature. In a series of high-throughput screening studies of MOFs for the partial oxidation of methane published by Rosen, Snurr, and Notestein, it was shown over a broad range of MOF structures that the thermodynamic favorability (given as  $\Delta E_0$ =  $E_{M=0} - E_M - 0.5E_{02}$ ) to form a reactive metal-oxo intermediate (M +  $\frac{1}{2}$  O<sub>2</sub>  $\leftrightarrow$  M=O) becomes increasingly endothermic with increasing d-electron density for first-row transition metals.<sup>113,114</sup> It was also demonstrated that metal-oxo sites providing the highest values of  $\Delta E_0$ , were more reactive toward C-H bond activation, due to their lower stability. Moreover, DFT studies have commonly predicted N<sub>2</sub>O activation barriers over Fe<sup>2+</sup> active sites to exceed that of Cr<sup>2+</sup> sites within a given MOF structure.<sup>74,114,178</sup> For instance, Barona and Snurr predicted the energy barrier for N<sub>2</sub>O activation to be 114 and 141 kJ mol<sup>-1</sup>, in MOF nodes akin to MIL-100(Cr) and MIL-100(Fe), respectively, with the C-H activation barrier for chromium being approximately 10 kJ mol<sup>-1</sup> higher than that for iron.<sup>74</sup> Moreover, it is possible to consider that the metal-oxo species formed over MIL-100(Cr) in this study may be more stable than those formed in MIL-100(Fe), the nature of the latter which is expected to be closer to an Fe<sup>3+</sup>-O<sup>-</sup> as evidenced from in-situ XAFS measurements in Section 5.3.7.

In the evaluation of MIL-100(Fe), isotopic exchange rates between  ${}^{18}O_{2(g)}$  with oxidized intermediates present under steady-state reaction conditions with N<sub>2</sub><sup>16</sup>O and C<sup>16</sup>O provided supporting evidence of the finite concentrations of Fe-O intermediates, the relative values of which, can be tuned by the N<sub>2</sub>O/CO molar ratio (Figure 5.12). When the effect of O<sub>2</sub> co-feed on the oxidation of CO with N<sub>2</sub>O was evaluated over MIL-100(Cr) it was observed that O<sub>2</sub> had a significant inhibitory effect on the reaction between N<sub>2</sub>O and O<sub>2</sub> (Table D.7, Appendix D), and co-feeding  ${}^{18}O_2$  with N<sub>2</sub><sup>16</sup>O over the catalyst resulted in no measurable formation of  ${}^{18}O_{16}O$  under the conditions tested. Furthermore, we present here an alternative method for evaluating the steady-state concentration of oxidized surface intermediates under a range of reaction conditions for cases in which oxygen-exchange measurements cannot be conducted.



**Figure 5.22.** Estimated fraction of [Cr-O] intermediates compared to the quantity of CO<sub>2</sub> formed when MIL-100(Cr) is (i) first exposed to N<sub>2</sub>O/CO under steady-state reaction conditions, (ii) purged under He flow for 30 min, (iii) and then exposed to CO (32.2 kPa) at 423 or 473 K.

As demonstrated in Figure 5.21, 1 mol of  $CO_2$  can be formed per  $Cr^{2+}$  active center during stepped N<sub>2</sub>O and CO reaction experiments, where in this case, it can be assumed that Cr-O intermediates following exposure to N<sub>2</sub>O represent the entirety of the Cr<sup>2+</sup> active centers. Therefore, we postulate that under the reaction of N<sub>2</sub>O and CO, the steady-state concentration of Cr-O intermediates may be preserved upon purging with He and their relative density can be quantified by the cumulative moles of CO<sub>2</sub> formed upon subsequent exposure to CO. Over varying CO/N<sub>2</sub>O molar ratios at 423 and 437 K, a linear relationship can be observed between the cumulative moles of CO<sub>2</sub> formed per mol Cr<sup>2+</sup> and the Cr-O surface fraction predicted from the kinetic model at each reaction condition. Results of this analysis suggest that the concentration of Cr-O intermediates under steady-state reaction  $(N_2O + CO)$  can be preserved upon purging the reactants with He, and then measuring the total quantity of CO<sub>2</sub> formed upon exposure to CO.

# 5.3.10. Estimating Individual Elementary Rate Constants from the C<sup>18</sup>O Isotopic Experiments

In previous sections, it has been demonstrated that CO can undergo oxygen exchange reactions with M-O intermediates formed by the decomposition of N<sub>2</sub>O over both MIL-100(Fe) and MIL-100(Cr) as indicated by reaction experiments with C<sup>18</sup>O-isotpicallly enriched reactant steams (Figure 5.5 and Figure 5.19). Here we demonstrate that the formation of mixed CO<sub>2</sub> isotopologues (C<sup>18</sup>O<sup>16</sup>O, C<sup>18</sup>O<sub>2</sub>, and C<sup>16</sup>O<sub>2</sub>), as well as C<sup>16</sup>O formation through the isotopic exchange reaction (C<sup>18</sup>O<sub>(g)</sub> + M-<sup>16</sup>O  $\leftrightarrow$  C<sup>16</sup>O<sub>(g)</sub> + M-<sup>18</sup>O), provide direct insight into the elementary rate constants controlling the sorption of CO,

$$1 \qquad N_{2}^{16}O_{(g)} + M \qquad \longleftrightarrow \qquad N_{2}^{16}O \cdots M \qquad K_{1}$$

$$2 \qquad N_{2}^{16}O \cdots M \qquad \longrightarrow \qquad N_{2(g)} + M^{-16}O \qquad k_{2}$$

$$3 \qquad M^{-16}O + C^{18}O_{(g)} \qquad \longleftrightarrow \qquad M^{-16}O \cdots C^{18}O \qquad k_{3}, k_{.3}$$

$$4 \qquad M^{-16}O \cdots C^{18}O \qquad \longrightarrow \qquad M^{-16}O^{-16}O^{18}O \qquad k_{4}$$

$$5 \qquad M^{-16}O \cdots C^{18}O \qquad \bigoplus \qquad M^{-16}O^{-16}O \qquad k_{5}$$

$$6 \qquad M^{-16}O \cdots C^{18}O \qquad \bigoplus \qquad M^{-18}O \cdots C^{16}O \qquad k_{6}, k_{.6}$$

$$7 \qquad M^{-18}O \cdots C^{16}O \qquad \bigoplus \qquad M^{-18}O \cdots C^{16}O \qquad k_{4}$$

$$8 \qquad M^{-18}O \cdots C^{16}O \qquad \bigoplus \qquad M^{-18}O \cdots C^{16}O \qquad k_{3}, k_{3}$$

$$9 \qquad M^{-18}O + C^{16}O_{(g)} \qquad \bigoplus \qquad M^{-18}O \cdots C^{18}O \qquad k_{3}, k_{3}$$

$$10 \qquad M^{-18}O \cdots C^{18}O \qquad \bigoplus \qquad M^{-18}O \cdots C^{16}O \qquad k_{3}, k_{.3}$$

$$10 \qquad M^{-18}O \cdots C^{16}O \qquad \bigoplus \qquad M^{-16}O \cdots C^{16}O \qquad k_{3}, k_{.3}$$

$$12 \qquad M^{-16}O \cdots C^{16}O \qquad \bigoplus \qquad M^{-16}O \cdots C^{16}O \qquad k_{4}$$

Figure 5.23. Proposed sequence of elementary steps for the oxidation of  $C^{18}O$  with  $N_2^{16}O$  over MIL-100 in which it is assumed that there is no significant kinetic influence of the replacement of  $C^{16}O$  with  $C^{18}O$ .

oxygen exchange of CO, and reaction of CO to form  $CO_2$  (k<sub>4</sub>) with oxidized surface intermediates as indicated in Figure 5.23. In this evaluation we neglect the influence of kinetic isotope effects associated with the replacement of  $C^{16}O$  with  $C^{18}O$  (as evaluated in Section D.2.11, Appendix D). Therefore, we can consider that CO sorption steps (Figure 5.23, Steps 3, 8, 9 and 11), oxygen exchange steps (Figure 5.23, Step 6), and  $CO_2$  formation steps (Figure 5.23, Steps 4, 7, 10, and 12) are controlled by the same set of rate constants,  $k_3/k_{-3}$ ,  $k_6 \approx k_{-6}$ , and  $k_4$ , respectively, regardless of the O-isotope involved. By applying the quasi-equilibrium assumption to N<sub>2</sub>O sorption steps and the pseudo-steady state hypothesis to all other intermediates where required, a unique relationship can be derived for determining the formation rate of each species (N<sub>2</sub>, total CO<sub>2</sub>,  $C^{18}O^{16}O$ ,  $C^{18}O_2$ ,  $C^{16}O_2$ , and net  $C^{16}O$ ) and the concentration of each relevant surface intermediate ([M], [M···N<sub>2</sub><sup>16</sup>O],  $[M^{-16}O], [M^{-18}O], [M^{-16}O\cdots C^{18}O], [M^{-18}O\cdots C^{16}O], [M^{-18}O\cdots C^{18}O], and [M^{-18}O\cdots C^{18}O]$ <sup>16</sup>O····C<sup>16</sup>O]) in terms of the rate constants K<sub>1</sub>, k<sub>2</sub>, (or K<sub>1</sub>k<sub>2</sub>), k<sub>3</sub>, k<sub>-3</sub>, k<sub>4</sub>, and k<sub>6</sub>. Full details of the derivations and descriptions for all the equations evaluated to analytically solve the product formation rates and surface concentrations is provided in Section D.2.12 of Appendix D.

The value of the kinetic parameters estimated from the reaction data of  $C^{18}O$  and  $N_2^{16}O$  over MIL-100(Fe) and MIL-100(Cr) are provided in Table 5.11. The values of k' and k'' calculated from the rate constants obtained are consistent with the values estimated from steady-state reaction measurements (Table 5.3 and Table 5.10), moreover, the determined values can accurately describe the reaction kinetics for both materials over all conditions tested (Figure D28). The estimated concentrations of adsorbed N<sub>2</sub>O (M···N<sub>2</sub>O) and

adsorbed CO (M-O···CO) intermediates calculated from the rate constants in Table 5.11 are also predicted to be small (less than 0.05 of the surface fraction at the lowest CO:N<sub>2</sub>O molar ratios evaluated), as shown in Figure 5.24. This result supports simplifications made in the simplified kinetic rate expression (Equation 5.2) that neglects the concentration of these intermediates.

Parameter	MIL-100(Fe)	MIL-100(Cr)
$K_1$ / kPa <sup>-1</sup>	2.01 x 10 <sup>-4</sup>	1.62 x 10 <sup>-2</sup>
$k_2 / s^{-1}$	5.48 x 10 <sup>-1</sup>	2.14 x 10 <sup>-2</sup>
$k_2 K_1 / (k Pa \cdot s)^{-1}$	1.10 x 10 <sup>-4</sup>	3.46 x 10 <sup>-4</sup>
$\overrightarrow{k_3}$ / (kPa·s) <sup>-1</sup>	1.29 x 10 <sup>-2</sup>	8.66 x 10 <sup>-5</sup>
$\overline{k_3}$ / s <sup>-1</sup>	4.94 x 10 <sup>-2</sup>	2.81 x 10 <sup>-2</sup>
$k_4$ / s <sup>-1</sup>	8.87 x 10 <sup>-2</sup>	1.46 x 10 <sup>-2</sup>
$k_{6}$ / s <sup>-1</sup>	6.37 x 10 <sup>-2</sup>	1.78 x 10 <sup>-2</sup>
k'	1.10 x 10 <sup>-4</sup>	3.56 x 10 <sup>-4</sup>
<i>k''</i>	8.38 x 10 <sup>-3</sup>	2.96 x 10 <sup>-5</sup>

**Table 5.11.** Estimated values for the parameters describing CO oxidation and oxygen exchange<br/>reaction from experiments with  $C^{18}O$  (conditions over MIL-100(Fe): 2.9 – 51.6 kPa<br/>N<sub>2</sub>O, 2.5 – 3.1 kPa CO, conditions over MIL-100(Cr): 1.5 – 2.9 kPa N<sub>2</sub>O, 2.5 – 30.7 kPa CO).

Three main features can be observed from the rate constants described in Table 5.11, (1) the estimated magnitudes of  $K_1$  and  $k_2$  are significantly different for iron and chromium, (2) the value of  $k_3$  for chromium is over three orders of magnitude over than that for iron, and (3) the value of  $k_4$  and  $k_6$  are approximately 6 and 3 times greater for iron versus chromium. The later of these features, specifically the values of  $k_4$  and  $k_6$ , are related to the reaction of CO with the oxidized intermediate to form  $CO_2$  (M-O···CO  $\rightarrow$  M···CO<sub>2</sub>) or for oxygen exchange (M-<sup>n</sup>O + C<sup>m</sup>O  $\leftrightarrow$  M-<sup>m</sup>O + C<sup>n</sup>O); moreover, these rate constants may inherently reflect the relative strength of the M-O bond. Results providing higher values of  $k_4$  and  $k_6$  for MIL-100(Fe) over MIL-100(Cr) is consistent with a weaker M-O bond in the former, and is consistent with DFT-predicted trends in M-O reactivity and stability with metal d-electron density,<sup>74,114</sup> as discussed in Section 5.3.9.



■ [M] ■ [M-O] ■ [M-O··CO] ■ [M··N<sub>2</sub>O]

**Figure 5.24.** Fraction of each surface intermediate predicted from rate constants derived from  $C^{18}O$  oxidation data (Table 5.11) for MIL-100(Fe) (left) and MIL-100(Cr) (right) at three different CO to N<sub>2</sub>O molar ratios. T = 473 K.

The significantly small value of  $k_3$  (describing the adsorption of CO to the M-O intermediate) for MIL-100(Cr) suggests that the steady-state concentration of Cr-O intermediates is almost entirely reliant on the rate at which CO adsorbs to the oxidized active site. On the contrary, the estimated value of  $k_3$  for MIL-100(Fe) is over three orders of magnitude larger than that for MIL-100(Cr), providing one of the most significant differences between the two materials (Table 5.11). Depending on the nature of the M-O intermediate formed, specifically, whether it is of more oxo- (M<sup>4+</sup>=O) or oxyl- (M<sup>3+</sup>-O<sup>-</sup>) character, the adsorption of CO may be significantly influenced. Experiments to evaluate

the nature of the Cr-O intermediates formed in MIL-100(Cr) using in-situ XAFS is ongoing and may shed light on this observation.

Another main difference observed between the rate constants estimated for MIL-100(Cr) and MIL-100(Fe) (Table 5.11) is the relative magnitude of  $K_1$  and  $k_2$ , related to the sorption (1) and decomposition (2) of  $N_2O$ . For both materials, the concentration of adsorbed N<sub>2</sub>O is predicted to be represent a very minor fraction of the total surface species under steady state reaction conditions (Figure 5.24); therefore, it may be difficult to accurately assess the relative magnitude of K1 and k2, individually. In the case of MIL-100(Fe), increasing  $K_1$  by one order of magnitude (while reducing  $k_2$  to maintain the same value of k') provides estimated rates which still closely describe the experimentally measured values (Figure D28) with slightly increased deviation at higher oxidation rates (*i.e.* higher N<sub>2</sub>O partial pressures). Increasing  $K_1$  by another order of magnitude, to 2.01 x  $10^{-2}$  kPa<sup>-1</sup>, however, results in significant underestimation of the oxidation rate at high N<sub>2</sub>O partial pressures due to significant coverages of the reactant (Figure D28). Moreover, although variation in the magnitude of  $K_1$  and  $k_2$  can still provide accurate estimations of the steady-state oxidation rate over the range of conditions, values of  $K_1$  which predict significant concentrations of adsorbed N<sub>2</sub>O at 473 K cannot describe the kinetic data. As discussed in Section 5.3.4., it is difficult to asses the extent to which the adsorption and decomposition of N<sub>2</sub>O are coupled, as if dissociation is significantly faster than the desorption of N<sub>2</sub>O, the adsorbed N<sub>2</sub>O may not be considered in quasi-equilibrium with the gaseous reactant. Furthermore, we simply consider the magnitude of  $k_2K_1$ , and not the individual values of the two rate constants, to describe differences between MIL-100(Cr)

and MIL-100(Fe). Specifically,  $k_2K_1$  is approximately three times greater for MIL-100(Cr) over MIL-100(Cr), an observation that supports reduced N<sub>2</sub>O activation barriers over Cr<sup>2+</sup> active sites in comparison to Fe<sup>2+</sup> sites within M<sub>3</sub>O nodes as estimated from previous DFT calculations completed by Barona and Snurr.<sup>74</sup> Despite the ambiguity in the individual rate constants for N<sub>2</sub>O sorption and decomposition, the results and methodology presented provide an unprecedented level of insight into the role of metal identity in metal-oxo stability and reactivity, and how that relates to results of theoretical investigations, to further understand structure-property relationships which effect the redox properties of MOF catalysts, more broadly.

#### **5.4.** Conclusions

Experimental interrogation of the elementary reaction steps facilitating the oxidation of light alkanes with N<sub>2</sub>O in MOFs featuring isolated divalent metal active centers has so far been precluded by the stoichiometric nature of the partial oxidation reaction pathways.<sup>73,106,109,236,237</sup> In this work, CO was applied as a reductant to attain clarity into the reaction steps that mediate redox turnovers with N<sub>2</sub>O over MIL-100 catalysts. Steadystate kinetic measurements evidence for iron MIL-100 that reaction steps involving the sorption and decomposition of N<sub>2</sub>O are rate-determining, with NO in-situ titrations evidencing turnover rates are effectuated by the uniform involvement of every available  $Fe^{2+}$  active site. The mechanism for the reaction could be interpreted as proceeding through a sequential (redox) oxidation series of elementary reaction steps based on results of isotopic, steady-state, and transient kinetic measurements. At increasing N<sub>2</sub>O to CO molar ratios ( $\geq$  20) at 473 K, it is determined that decreased sensitivity of the oxidation rate to N<sub>2</sub>O pressure (and increased sensitivity to CO pressure) can be attributed to significant fractional surface coverages (> 0.2) of oxidized, Fe-O, intermediates at steady state. Predicted coverages of Fe-O intermediates correlated linearly with isotopic exchange rates between surface <sup>16</sup>O and gaseous <sup>18</sup>O<sub>2</sub> co-fed during the reaction. In-situ iron K-edge XAFS measurements supported that the Fe-O intermediates sensed under steady-state reaction conditions are more accurately described by an iron-oxyl (Fe<sup>3+</sup>-O<sup>-</sup>), a result which is consistent with the relative instability of these intermediates over extended timescales in the absence of reductant flow. Extended evaluation of the chromium variant of MIL-100 indicated a significant role of metal identity in altering the relevance of elementary reaction steps within the oxidation and reduction half-cycles. Specifically, MIL-100(Cr) displayed a heightened dependence of oxidation rates on CO partial pressures at the same conditions tested for MIL-100(Fe) due to the increased coverages of Cr-O intermediates present under steady-state reaction. The results of this study provide novel insight into N<sub>2</sub>O-mediated oxidation reaction mechanisms over divalent active sites within MOFs and the role of metal identity in tuning the kinetic relevance of the associated reaction steps using the welldefined trimetal nodes in MIL-100 as a valuable model structure. It can be envisioned that the observations reported could aid in guiding the rational design and identification of structure-property relationships in redox catalysts broadly within the area of heterogeneous catalysis.

### 6. An Investigation into Second Sphere Coordination Effects of Oxo-Bridged Trimer Nodes in a Metal-Organic Framework

The pursuit of higher proficiency catalysts for implementation in industrial processes is reliant on developing novel materials that feature high productivity and selectivity towards a desired chemical product. Not only does homogeneity in active site structure and atomic positioning play a role in promoting higher efficiency catalysts but can aid in understanding their performance from a molecular level and in drawing out structureproperty relationships for improved material development. Metal-organic frameworks embody this standard by combining active metal moieties with structural organic compounds to form periodic, well-defined crystal structures with highly porous environments. Specifically, the framework MIL-100 embodies this concept, as it features an active site pool which contributes near entirely and uniformly as redox centers in the oxidation of CH<sub>4</sub> and CO with N<sub>2</sub>O. In this report, it is demonstrated that the high degree of homogeneity in this material allows for elucidating second sphere coordination effects, associated with the binding of electron-donating ligands to the metal nodes, which imparts consequences on the adsorptive and catalytic properties of the catalyst during CO oxidation.

#### **6.1. Introduction**

In the preceding chapter, the mechanism of CO oxidation by N<sub>2</sub>O over divalent active centers within iron and chromium variants of MIL-100 was extensively evaluated through steady-state, transient, and isotopic kinetic measurements. It was demonstrated that under the experimental conditions tested, the reaction over both catalysts proceeds sequentially through (i) N<sub>2</sub>O decomposition (M + N<sub>2</sub>O<sub>(g)</sub>  $\rightarrow$  M-O + N<sub>2(g)</sub>) and (ii) CO oxidation (CO<sub>(g)</sub> + M-O  $\rightarrow$  M + CO<sub>2(g)</sub>) with effectively irreversible product formation steps, as given by the reaction scheme in Figure 6.1. Moreover, the kinetic relevance of elementary steps within the oxidation and reduction portion of the catalytic cycle was significantly influenced by the identity of the active metal. In this chapter, we investigate the extent to which secondary coordination sphere effects (specifically ligation to the trimer nodes) influences the catalytic properties of a given active center, taking advantage of the uniform nature of the material to interpret such effects.

Figure 6.1. Sequential (or redox) oxidation mechanism proposed for the reaction of N<sub>2</sub>O and CO over MIL-100(Fe).

#### 6.2. Materials and Methods

#### 6.2.1. MIL-100 Synthesis and Characterization

MIL-100(Fe) and MIL-100(Cr) were synthesized according to previously published procedures.<sup>109,236</sup> The porosity, crystallinity, and composition of the samples were confirmed through N<sub>2</sub> physisorption, X-ray diffraction, and thermogravimetric analysis.

#### **6.2.2.** Oxidation Reaction Experiments

Reaction experiments with CO and N<sub>2</sub>O were completed using the procedures described previously (Section 5.2.3, Chapter 5). Briefly, catalyst samples were thermally activated at elevated temperatures (423 - 523 K) for 12 hours under either inert flow (50 cm<sup>3</sup> min<sup>-1</sup> He, Matheson, Ultra High Purity) or vacuum (P < 0.01 kPa, Pfeiffer Pascal 2005 SD rotary vane vacuum pump). Gas-phase reactant and product concentrations were

estimated using a gas chromatograph (Agilent 7890 B) with an HP-PLOT-Q capillary column (30 m x 320  $\mu$ m x 0.2  $\mu$ m) and thermal conductivity detector. Reaction feeds consisting of N<sub>2</sub>O (Matheson, Research Purity), CO (Matheson, Ultra High Purity), and Ar (Matheson, Ultra High Purity) were balanced with He to produce the desired reactant partial pressures and total flow rate (typically 65 cm<sup>3</sup> min<sup>-1</sup>). During transient reaction experiments, product and reactant concentrations were estimated using an online mass spectrometer (MKS Cirrus 2).

#### 6.2.3. In-Situ Active Site Titrations

In-situ titrations with NO were conducted using two-components gas mixtures of NO, either 1000 ppm NO/N<sub>2</sub> or 10% NO/N<sub>2</sub> (Matheson, Research Grade). Titration experiments with H<sub>2</sub>O (deionized, 18.3 M $\Omega$ ) were completed using a syringe pump (KD Scientific, Model 100), with gas lines maintained at 383 K to prevent the condensation. The quantity of NO and H<sub>2</sub>O adsorbed by the catalyst sample was determined by comparing the breakthrough curve for the adsorbate relative to the internal standard (Ar or N<sub>2</sub>), with concentrations at the reactor outlet analyzed using an online mass spectrometer (MKS Cirrus 2).

#### **6.2.4. Infrared Spectroscopy Measurements**

Infrared spectroscopy measurements conducted in transmission mode were completed with a Nicolet iS50 FT-IR Spectrometer (Thermo Scientific) equipped with a Harrick Dewar Transmission/Reflection accessory featuring ZnSe windows ( $25 \times 2$ ,  $32 \times 3$  mm). Self-supporting wafers of MIL-100 samples (15-20 mg) mixed with KBr powders were prepared and thermally treated under Ar flow ( $56 \text{ cm}^3 \text{ min}^{-1}$ , Matheson, Ultra High Purity).

Spectra of the empty IR cell under Ar low was used as a background reference or during NO adsorption experiments, spectra of the thermally-activated sample prior to the introduction of NO was used as the background at the analysis temperature. For a given set of experimental data, all spectra for the analysis were collected using the same catalyst wafer without any further normalization. Origin 8.5 software was utilized for baseline corrections and integrating peak areas.

#### 6.2.5. Coordinated Ligand Exchange and Quantification

In order to produce MIL-100(Fe) catalyst samples with specified quantities of coordinated alcohol (methanol, ethanol, and isopropanol) ligands, the following procedure was employed. First, MIL-100(Fe) was thermally activated at 523 K for 12 hours under He flow to remove a majority of the coordinated water and hydroxide species. The sample was then exposed to 0.2 kPa of the desired alcohol in He flow at 373 K in order to create a catalyst surface containing predominantly only coordinated alcohol and alkoxide species. Next, the samples were purged overnight at temperatures between 423 K to allow for sufficient removal of gaseous alcohol species during which a fraction of the coordinated ligands also desorb from the surface. After purging at 423 K, the catalyst sample was evaluated for the oxidation of CO with N2O and the steady-state rate was determined. After reaction, the quantity of  $Fe^{2+}$  open-metal sites available was determined by in-situ titration. Following this, D<sub>2</sub>O adsorption experiments were conducted to quantify the density of coordinated alcohol ligands. As evaluated in our previous work (Section C2.5, Appendix C).<sup>236</sup> under standard conditions, the introduction of D<sub>2</sub>O vapor over MIL-100(Fe) reveals the evolution of both H<sub>2</sub>O and HDO from the catalyst surface, related to the replacement

of coordinated H<sub>2</sub>O with D<sub>2</sub>O (Fe<sup>3+</sup>...H<sub>2</sub>O + D<sub>2</sub>O<sub>(g)</sub>  $\leftrightarrow$  Fe<sup>3+</sup>...D<sub>2</sub>O + H<sub>2</sub>O<sub>(g)</sub>) and reaction between D<sub>2</sub>O with hydroxides (Fe<sup>3+</sup>...OH<sup>+</sup> + D<sub>2</sub>O<sub>(g)</sub>  $\leftrightarrow$  Fe<sup>3+</sup>...OD<sup>-</sup> + HDO<sub>(g)</sub>), respectively. As shown previously, the cumulative moles of H<sub>2</sub>O and HDO formed can be used to accurately estimate the density of coordinated water (Fe<sup>3+</sup>...H<sub>2</sub>O) and hydroxides (Fe<sup>3+</sup>...OH<sup>-</sup>) as well as the corresponding Fe<sup>3+</sup> and Fe<sup>2+</sup> open-metal sites. Here, an identical methodology is employed to quantify the density of coordinated alcohols, and subsequently determine the alcohol to Fe<sub>3</sub>O molar ratio at each condition (Section E2.1, Appendix E) as the use of D<sub>2</sub>O allows for differentiating between coordinated alcohols and alkoxides. Due to the lack of calibration data available for the deuterated alcohols (specifically for C<sub>2</sub>H<sub>5</sub>OD and (CH<sub>3</sub>)<sub>2</sub>CHOD) the Fe<sup>2+</sup> open-metal site densities were estimated only form the NO titration data, and not from the quantity of deuterated alcohol evolved during D<sub>2</sub>O adsorption experiments.

#### **6.3. Results and Discussion**

#### 6.3.1. Effect on Thermal Treatment on MIL-100(Fe) Turnover Rates

In the work described in Chapter 5, it has been evidenced that turnover rates (mol (mol  $Fe^{2+})^{-1} s^{-1}$ ) measured in the oxidation of CO with N<sub>2</sub>O over MIL-100(Fe) result from the uniform contribution of every  $Fe^{2+}$  active center in fully dehydrated catalyst sample treated at 523 K prior to reaction. Specifically, a linear relationship was determined between the equilibrium adsorption coverage of NO to  $Fe^{2+}$  active sites and the relative oxidation rate at each condition (Chapter 5, Figure 5.2b), indicative of every site titrated contributing equivalently to the overall oxidation rate. Moreover, it could be demonstrated in the oxidation of CH<sub>4</sub> with N<sub>2</sub>O, cumulative yields of CH<sub>3</sub>OH obtained over MIL-100(Fe),

under a given set of reaction conditions, corresponded directly to the Fe<sup>2+</sup> open-metal site density when varied through the extent of thermal treatment (423 - 473 K, under He flow).<sup>109</sup> Results of these experiments have suggested that every available Fe<sup>2+</sup> open-metal site in MIL-100(Fe) participates in the oxidation of CH<sub>4</sub> with N<sub>2</sub>O, and under steady-state oxidation of CO, every Fe<sup>2+</sup> open-metal site in the nearly fully-dehydrated material contributes equivalently to the measured turnover rate.



Figure 6.2. (a)  $Fe^{2+}$  open-metal site density and the  $CO_2$  turnover rate as a function of the activation temperature. (b) Apparent activation energy and the corresponding molar ratio of water to Fe<sub>3</sub>O trimer node at each activation temperature (393 – 423 K, 14.6 kPa N<sub>2</sub>O, 1.5 kPa CO).

To further evaluate the uniform nature of active centers in MIL-100(Fe) probed by the oxidation of CO, the  $Fe^{2+}$  open-metal site density was varied through the extent of thermal treatment (as shown in Figure 6.2a). Notably the oxidation rate per vacant  $Fe^{2+}$  open-metal site was not constant across the five conditions tested and increased systematically with increasing activation temperature (Figure 6.2a) (reaction conditions: 423 K, 14.6 kPa N<sub>2</sub>O, 1.5 kPa CO). At the two extremes tested, the turnover rate measured over MIL-100(Fe)

activated at 523 K was nearly two times greater than the turnover rate measured over the sample activated at 423 K for a reaction temperature of 423 K, with both materials exhibiting a first-order dependence on the partial pressure of N<sub>2</sub>O under the conditions tested (Figure E2). Moreover, experiments over the range of 393 - 423 K provide that turnover rates become decreasingly sensitive to reaction temperature with increasing extent of thermal activation, as indicated by the extracted apparent activation enthalpies (Figure 6.2b).

Considering the reaction mechanism for CO, which we have delved in detail in previous work (see Chapter 5), the decomposition of N<sub>2</sub>O is assumed as the ratedetermining elementary reaction step, providing reaction orders that are approximately first-order in N<sub>2</sub>O and zero-order in CO, CO<sub>2</sub>, and N<sub>2</sub> partial pressure under conditions tested at low N<sub>2</sub>O/CO molar ratios (approximately  $\leq$  20), Figure 5.3, Chapter 5. This provides a simple rate expression for the kinetics of CO oxidation with N<sub>2</sub>O over MIL-100(Fe) as follows

$$\frac{r}{[Fe^{2+}]} = k_2 K_1 [N_2 O] \tag{6.1}$$

where  $k_2$  is the first order rate constant for N<sub>2</sub>O decomposition (Fe···N<sub>2</sub>O  $\rightarrow$  Fe-O + N<sub>2(g)</sub>) and  $K_1$  is the equilibrium adsorption constant for N<sub>2</sub>O to the Fe<sup>2+</sup> open-metal sites. Under kinetic regimes where expression 6.1 is valid, the apparent activation energy measured should represent the free energy difference between the initial state (Fe + N<sub>2</sub>O<sub>(g)</sub>) and the transition-state for N<sub>2</sub>O decomposition (Figure 6.3). Here, we have assumed a value of -30 kJ mol<sup>-1</sup> for the adsorption energy of N<sub>2</sub>O, calculated from DFT simulations for MIL-100(Fe) by Vitillo *et al*,<sup>72</sup> for qualitative purposes in the energy diagram. Moreover, results in Figure 6.2b indicate that the extent of thermal activation imparts a measurable influence on the stability of the kinetically-relevant transition state with respect to the bare catalyst.



**Figure 6.3.** Energy diagram for the proposed CO and N<sub>2</sub>O reaction mechanism over MIL-100(Fe), assuming that N<sub>2</sub>O decomposition is rate determining. The heat of adsorption for N<sub>2</sub>O was provided from DFT-calculations completed in ref.<sup>72</sup>

Unlike in-situ Fe<sup>2+</sup>-selective titration experiments conducted with NO previously (Chapter 5, Figure 5.2), variations of the Fe<sup>2+</sup> open-metal site density through choice of thermal treatment temperature does not solely alter this parameter. Specifically densities of water molecules ligated to, primarily considered "inactive," Fe<sup>3+</sup> open-metal sites are also altered by the extent of thermal treatment. Further we consider for a given trimeric iron node, there can be an average of 0, 1, or 2 water molecules associated with a still vacant Fe<sup>2+</sup> active center (Figure 6.4). Here we consider the water to node ratio (mol H<sub>2</sub>O (mol Fe<sub>3</sub>O)<sup>-1</sup>) to represent the average number of Fe<sup>3+</sup> open-metal sites which are coordinated to water, where a water to node ratio of 2 would represent the scenario in which every Fe<sup>3+</sup> center is ligated to water. As shown in Figure 6.2b, there is a significant variation in the water to node ratio, from approximately 0.6 – 0.03, through modulating the thermal activation temperature between 423 and 523 K.



**Figure 6.4.** Three different trimer node configurations involving zero, one, or two coordinated water molecules which can be associated with a vacant, active Fe<sup>2+</sup> open-metal site.

## 6.3.2. Discussion of Coordination Effects in Trinuclear μ<sub>3</sub>-oxo Bridged Complexes and Relevance to N<sub>2</sub>O Activation

Trinuclear µ3-oxo metallic complexes with the general structure of  $[M_3O(O_2CR)_6(L_3)]^{n+}$ , akin to the metal nodes in MIL-100, have been the focus of intensive study for many decades<sup>288–290</sup> due to their rich magnetic<sup>291–294</sup> and electronic properties.<sup>295–</sup> <sup>299</sup> Analogous trinuclear oxo species in several complexes have been synthesized with a variety of transition metal compositions,<sup>289,290,295,300,301</sup> with several having been demonstrated to catalyze a range of epoxidation, oxidation, and hydrogenation chemistries.<sup>295,302–304</sup> As it relates to this work, the influence of terminal ligands (L), coordinated to the M<sub>3</sub>O center has been considered with respect to electronic, magnetic, and adsorption properties.

It has been extensively observed that the metal ions within the trinuclear oxo-bridged unit are connected, specifically, as the central oxide ion provides a superexchange pathway for magnetic coupling between the metal ions.<sup>289,291</sup> In the case of rhodium, Nikolaou and colleagues described the [Ru<sub>3</sub>O]<sup>+</sup> core as a single metal center, due to the strong electronic and magnetic interactions between the individual metal ions. Yaghi and coworkers

demonstrated with MOF-235 and MOF-236, featuring  $Fe_3O(CO_2)_2$  clusters, that such magnetic coupling interactions between the metal ions can be preserved within the periodic MOF structures when compared to their molecular counterparts.<sup>305</sup>

In a particular evaluation of trinuclear iron acetate  $[Fe_3O(OAc)_6(Py)_n]^+$  completed by Niedner-Schatteburg and colleagues, it was demonstrated through a combination of Infra Red-Multiple Photon Dissociation (IR-MPD) and Collision Induced Dissociation (CID) experiments, supported by DFT simulations, that the coordination of axial pyridine ligands (either 0, 1, or 2) to the Fe<sub>3</sub>O core influences both the geometric and magnetic properties of the complex (Figure 6.5).<sup>294</sup> Specifically, coordination of pyridine distorts the symmetry of the node and leads to elongations in both Fe-Fe and Fe-O<sub>central</sub> bond distances, the later of which critically influences the magnetic coupling constant between two iron atoms, with longer distances weakening the antiferromagnetic coupling. The effects of the geometric and magnetic coupling alterations manifested in pyridine binding energies that decreased significantly (from approximately 134 to 82 kJ mol<sup>-1</sup>) with the addition of each ligand (n = 1, 2, or 3) to the iron core.



**Figure 6.5.** DFT predicted atomic distances and mean Fe-O distances  $(\bar{d}_{FeO})$  in iron(III) acetate  $[Fe_3O(OAc)_6(Py)_n]^+$  (n = 0, 1, 2, 3), reproduced from ref <sup>294</sup>.

Considering the near identical structure of the carboxo-bridged, oxo-centered trinuclear metal centers in MIL-100, it is reasonable to assume that such secondary coordination sphere effects, specifically associated with the increasing ligation of water to a given  $M_3O$  node (Figure 6.4) may influence the properties of an uncoordinated metal site within the same node. Specifically, if the addition of water to the trimer node results in changes in the geometry and electronic configuration, as observed with pyridine in iron acetate,<sup>294</sup> it is possible that such effects may influence the adsorption or redox properties of the uncoordinated  $M^{2+}$  active sites.

It has been commonly reported in kinetic studies of ligand substitution over trinuclear metal complexes  $[M_3O(O_2CR)_6(L_3)]^{n+}$ , that the lability of the terminal ligand (L) is strongly influenced by the bond between the metal and the central oxide ion.<sup>306–308</sup> The influence of trans axial ligands has also been commonly reported in the analysis of metal(IV)-oxo complexes. As reported by Münck, Nam, Que, and coworkers, the basicity of the trans ligand (X) in oxoiron(IV) complexes [Fe<sup>IV</sup>(O)(TMC)(X)] (TMC = tetramethylcyclam, X = OH<sup>-</sup>, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>, N<sub>3</sub><sup>-</sup>, NCS<sup>-</sup>, NCO<sup>-</sup>, and CN<sup>-</sup>) influences the Fe<sup>IV</sup>=O bond lengths, as supported by a combination of DFT simulations, X-ray absorption, Raman, and Mössbauer spectroscopic data.<sup>309</sup> Explicitly, results of this work suggested that the energy of the iron molecular orbitals (d<sub>xz</sub>/d<sub>yz</sub> and d<sub>z2</sub>) directly involved in the Fe(IV)=O bond were perturbed by the extent of  $\sigma$ -donation from the axial ligand (X), with increasing electron donation destabilizing the molecular orbitals and weakening the Fe(IV)=O bond. Related to the application of such metal-oxo complexes in oxidation chemistries, many studies, both experimental and theoretical, have reported the influence of trans axial ligands on the

reactivity of the oxygen atom.<sup>310–314</sup> Specific to the structural active sites in MIL-100-type MOF frameworks, it was described by Vitillo *et al* from DFT calculations that the Fe(IV)=O bond, predicted to form through N<sub>2</sub>O decomposition, is reportedly longer (~1.61-1.62 Å) than that which has been characterized in the extensively evaluated Fe-BEA zeolite, with a Fe(IV)=O bond length of 1.59 Å,<sup>208</sup> due to the absence of the trans axial oxo ligand in the latter.<sup>72</sup> Notably, the Fe(IV)=O species formed in Fe-BEA can also be maintained over extended timescales in the absence of reactant flow,<sup>208,311</sup> unlike the oxidized intermediates formed in MIL-100(Fe) which decompose or decay rapidly as described in Chapter 5, Section 5.3.5. Moreover, it is evident that trans axial ligand effects, potentially induced by changes in the triion node by the coordination of H<sub>2</sub>O, may significantly impact kinetic barriers related to N<sub>2</sub>O reduction and Fe-O formation.

From the results of Niedner-Schatteburg and coworkers in their evaluation of iron acetate, it was demonstrated that with each additional pyridine molecule adsorbed to the complex, a weakening of the antiferromagnetic coupling between the iron ions (evaluated by the magnetic coupling constant, *J*) was calculated due to the increasing Fe-Fe and Fe-O<sub>central</sub> bond distances.<sup>294</sup> The influence of antiferromagnetic coupling between the iron atoms was also considered with respect to light alkane oxidation with N<sub>2</sub>O over MIL-100(Fe) by Gagliardi, Bhan, and colleagues.<sup>73</sup> Specifically, results of DFT simulations described that antiferromagnetic configurations of the iron centers (2S + 1 = 5) were energetically more stable and provided lower calculated activation enthalpy barriers for N<sub>2</sub>O decomposition ( $\Delta H_{app} = 95 \text{ kJ mol}^{-1}$ ) in comparison to the ferromagnetic configuration (2S + 1 = 15), with  $\Delta H_{app} = 110 \text{ kJ mol}^{-1}$ . Furthermore, it is evident that the strength of

antiferromagnetic coupling between the iron ions in MIL-100 may have measurable influences on experimentally measured turnover rates and apparent energy barriers for  $N_2O$ -mediated oxidation chemistries. In the following sections we further investigate through a combination of spectroscopic and in-situ titration data the negative influence of secondary coordination sphere effects, in this case: ligation to the  $M_3O$  node, on the adsorption and catalytic properties of MIL-100 in the context of CO oxidation with  $N_2O$ .

## 6.3.3. Infrared Spectroscopic Analysis of the Influence of Degree of Hydration on NO-Adsorption Properties in MIL-100(Fe)

As demonstrated in Section 6.3.1, it has been observed that the CO oxidation turnover rate measured over MIL-100(Fe) is not independent of the overall extent of dehydration of the catalyst. Here we further probe the extent to which the hydration state of the material influences its characteristic adsorption and catalytic properties. NO serves as an extremely valuable probe of divalent iron centers in MIL-100(Fe) as it binds exclusively to this site at relevant reaction temperatures (423 – 488 K) and, in general, the stretching frequency of the N-O bond is quite sensitive to the extent of  $\pi^*$ -backbonding interactions with the binding metal ion. Specifically, backbonding into the vacant  $\pi^*$  orbitals of the NO ligand can result in weakening of the N-O bond and subsequently a red-shift in v(NO) probed through infrared spectroscopy measurements.<sup>193,315–317</sup>

As shown in Figure 6.6a, exposure of MIL-100(Fe) to NO (0.5 kPa) at 423 K results in for the formation of a v(NO) band, centered near 1808 cm<sup>-1</sup>, which has been assigned to  $Fe^{2+}$ -mononitrosyl adducts based on previous literature assignments in MIL-100(Fe).<sup>60,73,183</sup> Notably, as demonstrated in our previous analysis for MIL-100(Fe) in the oxidation of methane, every Fe<sup>2+</sup> open-metal site is saturated under this condition (0.5 kPa NO, 423 K), regardless of the thermal treatment condition.<sup>109</sup> Close examination of the Fe<sup>2+</sup>-nitrosyl at each activation temperature reveals the band center shifts progressively to lower wavenumber with increasing temperature used for thermal treatment (Figure 6.6a). Figure 6.6b provides for each activation temperature, the wavenumber of the v(NO-Fe<sup>2+</sup>) IR band center as well as the corresponding turnover rate measured at 423 K (14.6 kPa N<sub>2</sub>O, 1.5 kPa CO, 473 K), which follows the inverse trend. It has been commonly expressed that increased backdonation for the iron center, or larger filling of the  $\pi^*$  orbitals of the NO ligand, leads to lower v(N-O) frequencies representing the weakening of the NO bond. <sup>193,315–317</sup> Further, it is apparent that increased hydration of MIL-100(Fe) not only reduces its intrinsic reactivity in the oxidation of CO by N<sub>2</sub>O but also results in weaker binding of NO at 423 K.



Figure 6.6. (a) IR spectra of NO adsorption (0.5 kPa) at 423 K over MIL-100(Fe) thermally activated under He flow. (b) For each activation temperature, the corresponding peak center of the Fe<sup>2+</sup>-nitrosyl band and the CO turnover rate (14.6 kPa N<sub>2</sub>O, 1.5 kPa CO, 423 K).
To further evidence the influence of coordinated water to  $Fe^{3+}$  centers on the average NO binding properties of the Fe<sup>2+</sup> open-metal sites, additional NO adsorption experiments were conducted at higher water coverages. As shown in Figure 6.7a, the center of the IR band corresponding to  $Fe^{2+}$ -nitrosyls in MIL-100(Fe) appears at approximately 1808 cm<sup>-1</sup>. At 423 K under NO flow, 2 µL aliquots of H<sub>2</sub>O were subsequently injected into the gas stream, resulting in a systematic blue shift in the v(NO) band with each additional injection of water (Figure 6.7a). The relative quantity of  $H_2O$  adsorbed to  $Fe^{3+}$  open-metal sites can be estimated from the v(OH) band, centered at approximately  $3672 \text{ cm}^{-1}$ , which has been previously assigned to the asymmetric stretching vibrations of coordinated water molecules  $(H_2O-Fe^{3+})$  in MIL-100(Fe).<sup>60,109,132,154</sup> As indicted in the OH-stretching region of the IR spectra, Figure 6.7b, each injection of water results in an increase in the area of the v(OH)band corresponding to  $Fe^{3+}-H_2O$  adducts. Notably, the introduction of water, although resulting in a measurable shift in the frequency of the  $v(NO-Fe^{2+})$  IR band, does not influence its area (Figure E3b, Appendix E), indicating that under NO flow (0.5 kPa, 423 K) the introduction of water does not significantly alter the NO coverage. This is also supported by only minor increases in the v(OH) region near 3581 cm<sup>-1</sup>, the location previously assigned to hydroxides ( $Fe^{3+}-OH^{-}$ ) formed by the dissociation over H<sub>2</sub>O on  $Fe^{2+}$ open-metal sites.<sup>109</sup> Figure 6.7c indicates the relative shift in the Fe<sup>2+</sup>-nitrosyl band, with respect to the peak position at 1808 cm<sup>-1</sup> prior to the introduction of H<sub>2</sub>O, providing blue shifts of approximately 15 cm<sup>-1</sup> can be measured near complete H<sub>2</sub>O saturation. Moreover, the shift in the v(NO) band correlates well with the growth of the v(OH) band corresponding to coordinated water molecules ( $H_2O-Fe^{3+}$ ) across the four conditions.

Results of this analysis provide further evidence of water coverages having significant influences on the adsorption of NO by  $Fe^{2+}$  open-metal sites which are not directly involved in the adsorption of H<sub>2</sub>O, but in connection to sites (Fe<sup>3+</sup> open-metal sites) which are.



**Figure 6.7.** (a) v(NO) and (b) v(OH) portions of the IR spectrum under NO flow (0.5 kPa) and upon introduction of 2  $\mu$ L injections of H<sub>2</sub>O (~ 1 mol H<sub>2</sub>O (mol Fe)<sup>-1</sup>) at 423 K. (c) Determined blue shift in the v(Fe<sup>2+</sup>-NO) IR band from the starting position and v(H<sub>2</sub>O-Fe<sup>3+</sup>) area.

#### 6.3.4. Reversibility of NO Adsorption during CO Oxidation over MIL-100(Fe)

It has been demonstrated previously that NO adsorbs to every Fe<sup>2+</sup> open-metal site at 0.5 kPa NO and 423 K under reaction conditions (Figure 5.1a, Chapter 5), where for the fully-dehydrated catalyst sample, adsorption is nearly completely irreversible. Here we further investigate the extent to which the adsorption of NO is altered by the overall degree of hydration of the catalyst through in-situ titrations during the oxidation of CO by N<sub>2</sub>O over catalyst samples thermally treated at various conditions between 423 and 523 K. Figure 6.8 shows for MIL-100(Fe), the fractional oxidation turnover rate [(rate following NO titration,  $r_{NO=x}$ )·(rate prior to NO titration,  $r_{NO=0}$ )<sup>-1</sup>] following titration with NO (0.5 kPa) under reaction conditions (423 K, 14.6 kPa N<sub>2</sub>O, 1.5 kPa) for five thermal treatment conditions.



**Figure 6.8.** Following titration with NO (0.5 kPa) under reaction conditions (423 K, 14.6 kPa N<sub>2</sub>O, 1.5 kPa CO), the fractional recovery of the oxidation rate upon purging NO from the reaction system.

The x-axis in Figure 6.8 represents the amount of time under which the NO gas steam has been shut-off and purged with the reactant flow following complete saturation with NO. Consistent with previous analyses, there is minor recovery (~ 3%) of the turnover rate for the catalyst sample thermally treated at 523 K upon purging NO. Both samples activated at 473 and 498 K also show very minimal recovery, approximately 5% and 4%, respectively, of the initial turnover rate when gaseous NO is purged from the system. Notably, increased fractions of the turnover rate can be recovered over the catalyst samples pretreated at lower temperatures of 448 and 423 K, with oxidation rates measured after purging NO representing approximately 18% and 23% of the initial rate, respectively. This result provides further evidence of the binding strength of NO being altered by the presence of coordinated water molecules and is consistent with results of IR spectroscopy analyses indicating that more hydrated samples having, on average, weaker NO binding sites than those in the fully hydrated sample, as evaluated in Section 6.3.3.



**Figure 6.9.** Fraction of Fe<sup>2+</sup> open-metal sites which bind NO reversibly versus irreversibly at 423 K, as determined by NO breakthrough adsorption and temperature-programmed desorption measurements. (Titrated under reaction conditions with 0.5 kPa and 423 K).

It is apparent from the results of the analysis in Figure 6.8 that there can exist  $Fe^{2+}$  open-metal sites in MIL-100(Fe) that bind NO reversibly or irreversibly under reaction conditions, and that the relative fraction of reversible binding sites increases with decreasing extent of thermal dehydration. The total quantity of NO adsorbed at each activation temperature can be easily estimated from the breakthrough adsorption curve for NO, as described in our previous analysis of MIL-100(Fe) for the oxidation of CH<sub>4</sub> (Figure C4, Appendix C).<sup>109</sup> Following purging of NO, the quantity of NO which is irreversibly adsorbed can be measured from temperature-programmed desorption (TPD) following reaction. As provided in Figure E4 of Appendix E, NO irreversibly adsorbed at 423 K can be completely desorbed at temperatures less than 493 K. The temperature ranges for NO to desorption from the Fe<sup>2+</sup> open-metal sites in MIL-100(Fe) (423 – 488 K) is comparable to results obtained over Fe<sup>2+</sup> sites within ZSM-5 zeolites, in which nitrosyls required

temperature ranges of 400 – 650 K to desorb.<sup>318</sup> Furthermore, the total quantity of NO reversibly adsorbed can be estimated from the measured total quantity of NO adsorbed and amount which is irreversibly adsorbed (from NO-TPD), the results of which are summarized in Figure 6.9. As indicated,  $Fe^{2+}$  open-metal sites which bind NO reversibly at 423 K represent a decreasing fraction of the total  $Fe^{2+}$  site density with increasing thermal pretreatment temperature and, consequently, decreasing coordinated water densities.

# 6.3.5. Estimating Density and Contributions of Fe<sup>2+</sup> Sites in Fe<sub>3</sub>O Nodes with 0, 1, or 2 Water Ligands

Results of in-situ NO titrations during the oxidation of CO with N<sub>2</sub>O over MIL-100(Fe) indicate that distributions of Fe<sup>2+</sup> open-metal sites exist which either bind NO irreversibly or reversibly at 423 K. Based on the quantified value of each type of Fe<sup>2+</sup> open-metal site (reversible or irreversible NO binding site), it is apparent that the sites which bind NO irreversibly contribute more significantly to the overall turnover rate measured in the absence of the titrant (Table 6.1). Moreover, there is strong agreement between the oxidation rate normalized by the density of reversible and irreversible binding sites across the five thermal treatment conditions tested, suggesting an overlap in the ensemble of active sites contributing to the overall oxidation rate measured over MIL-100(Fe) samples thermally activated at different conditions.

It can be considered that MIL-100(Fe) thermally treated at 523 K represents both the maximum fraction of active sites which bind NO irreversibly as well as the lowest density of coordinated water species (mol H<sub>2</sub>O (mol Fe<sub>3</sub>O)<sup>-1</sup>  $\approx$  0.03). Furthermore, Fe<sub>3</sub>O nodes

Activation	Activation Oxidation Rate / x10 <sup>-4</sup> mol (mol s		
Temperature / K	(Reversible Binding Sites)	(Irreversible Binding Sites)	
423	0.55	1.96	
448	0.68	1.91	
473	0.59	1.82	
498	0.74	1.70	
523	0.65	1.72	
	$\mu=0.64\pm0.08$	$\mu = 1.82 \pm 0.11$	

**Table 6.1.** The oxidation rate attributed to  $Fe^{2+}$  sites which bind NO reversibly versus irreversibly<br/>at 423 K for samples activated at various temperatures, determined from the<br/>experiments in Figure 6.8 and Figure 6.9. (Reaction conditions: 423 K, 14.6 kPa N<sub>2</sub>O,<br/>1.5 kPa CO).

which have zero coordinated water ligands represent the majority of the Fe<sub>3</sub>O nodes in this material. At a value of 0.03 mol H<sub>2</sub>O (mol Fe<sub>3</sub>O)<sup>-1</sup>, iron nodes with at least one water ligand may represent only a maximum of 3% of the total nodes. Notably, this value is in close proximity to the percentage of Fe<sup>2+</sup> open-metal sites which bind NO reversibly (8%) at 423 K. Similar arguments can also be made for the MIL-100(Fe) catalyst samples activated between 423 and 498 K, where the fraction of reversible NO adsorption sites is comparable to the water to Fe<sub>3</sub>O node ratio (Table 6.2). Considering these results, it is postulated that at low H<sub>2</sub>O to node ratios, it is statistically more favorable to have distributions of Fe<sub>3</sub>O nodes with either 0 or 1 water molecules (representing two active site species), with iron nodes with 2 water molecules representing very small fractions of the total nodes.

Given that irreversible NO binding sites constitute the largest fraction of  $Fe^{2+}$  sites in the nearly fully dehydrated catalyst sample, we make the assumption that the entire density of  $Fe^{2+}$  open-metal sites within nodes containing 0 coordinated water molecules, termed

Activation Temperature / K	mol H2O (mol Fe3O) <sup>-1</sup>	Fraction of Fe <sup>2+</sup> Sites which Bind NO Reversibly
423	0.59	0.52
448	0.40	0.38
473	0.13	0.15
498	0.07	0.09
523	0.03	0.08

**Table 6.2.** For each activation temperature tested, the  $H_2O$  to  $Fe_3O$  node molar ratio and the fractionof  $Fe^{2+}$  open-metal sites which bind NO reversibly at 423 K.

Site 1 (Fe<sub>3</sub>O – 0 H<sub>2</sub>O) bind NO irreversibly at 423 K. Given the statistical probability of low H<sub>2</sub>O to Fe<sub>3</sub>O node ratios producing predominantly nodes with 0 to 1 ligated water molecules, it is assumed that Fe<sup>2+</sup> open-metals sites within nodes with 1 coordinated water molecule, Site 2 (Fe<sub>3</sub>O – 1 H<sub>2</sub>O), bind NO reversibly at 523 K. This assumption is supported by the close correspondence between the fraction of Fe<sup>2+</sup> open-metal sites which bind NO reversibly and the H<sub>2</sub>O to Fe<sub>3</sub>O node ratio, at the low water coverages evaluated thus far (Table 6.2). Moreover, it has been observed from infrared spectroscopic characterization of the adsorption of NO to Fe<sup>2+</sup> open-metal sites in MIL-100(Fe) that frequency of the v(NO) band corresponding to the Fe<sup>2+</sup>-nitrosyls increases systematically with increasing water coverage, evidencing on average weaker binding of NO. Therefore, it can be expected that Fe<sup>2+</sup> open-metal sites within iron nodes with 2 coordinated water molecules, or Site 3 (Fe<sub>3</sub>O – 2 H<sub>2</sub>O), may bind NO even more weakly than Site 2.

Under finite coverages of water, the overall oxidation rate per  $Fe^{2+}$  site will represent the average ensemble of the contributions from Site 1, Site 2, and Site 3 given by the following equation

$$\frac{r_{CO_2}}{Fe^{2+}} = x_1 \left(\frac{r_{CO_2}}{Fe^{2+}}\right)_{Site \ 1} + x_2 \left(\frac{r_{CO_2}}{Fe^{2+}}\right)_{Site \ 2} + x_3 \left(\frac{r_{CO_2}}{Fe^{2+}}\right)_{Site \ 3}$$
(6.2)

where  $x_1, x_2$ , and  $x_3$  represent the relative density of each type of Fe<sup>2+</sup> active site. For MIL-100(Fe) samples activated under various conditions, we know the total H<sub>2</sub>O to Fe<sub>3</sub>O node molar ratio, which will control the maximum densities of Site 2 and Site 3 present at each condition. Furthermore assuming that  $x_1$  is solely represented by the fraction of Fe<sup>2+</sup> openmetal sites which bind NO irreversibly at 423 K, the density Site 2 and Site 3 can be estimated from the following equations

$$1 = x_1 + x_2 + x_3 \tag{6.3}$$

and 
$$\frac{(mol H_2 O)}{(mol Fe_3)} = x_2 + 2x_3.$$
 (6.4)

Evaluation of the MIL-100(Cr) samples thermally activated between 423 and 523 K under these assumptions provides an analytic density of Site 1, Site 2, and Site 3 at each condition (Figure 6.10a). Notably, the distribution of sites under these various activation conditions, *i.e.* specific water to node molar ratios, reflect well the predicted binomial distribution of the three sites (Figure 6.10b). This result reflects that there may be little thermodynamic preference for the formation of Site 2 over Site 3, or vice versa, with increasing water coverages. This observation is consistent with results of Vitillo and Gagliardi providing the DFT-calculated adsorption enthalpies of adding water to a triiron node in MIL-100(Fe) to decrease marginally with the subsequent addition of 1, 2, or 3 water molecules to the node, providing values of -74, -72, and -65 kJ mol<sup>-1</sup>, respectively.<sup>319</sup>

Kinetic measurements conducted at elevated water to node molar ratios were completed by co-feeding water during the reaction of CO and N<sub>2</sub>O. The total quantity of water adsorbed by the fully activated catalyst (treated at 523 K) at a given partial pressure could



Figure 6.10. (a) Estimated fractions of Site 1, Site 2, and Site 3 for MIL-100(Fe) treated at five activation temperatures between 423 – 523 K. (b) Comparison of the site fractions from (a) to the site fractions estimated from a binomial distribution.

be determined by measuring the breakthrough adsorption curve during introduction of the titrant (Figure E5a, Appendix E). This value, however, does not discern between water adsorbed to  $Fe^{3+}$  or  $Fe^{2+}$  open-metal sites, furthermore, NO titration was completed at the end of each experiment to quantify the residual  $Fe^{2+}$  open-metal site density (Figure E5c, Appendix E), subsequently allowing for estimation of the coordinated water ( $Fe^{3+}\cdots H_2O$ ) density and the water to Fe<sub>3</sub>O node molar ratio. Results for various partial pressures of water evaluated are provided in Table 6.3, as determined by the following expressions:

$$\frac{mol H_2 O \ adsorbed \ to \ Fe^{2+}}{mol \ Fe} = \frac{0.30 \ mol}{mol \ Fe} - \frac{mol \ NO \ adsorbed}{mol \ Fe},\tag{6.5}$$

$$\frac{mol H_2 O \ adsorbed \ to \ Fe^{3+}}{mol \ Fe} = \left(\frac{mol \ H_2 O \ adsorbed \ to \ tal}{mol \ Fe}\right) - \left(\frac{mol \ H_2 O \ adsorbed \ to \ Fe^{2+}}{mol \ Fe}\right), \quad (6.6)$$

and 
$$\frac{mol H_2 O}{mol Fe_3 O} = \frac{3 mol Fe}{mol Fe_3 O} \left( \frac{mol H_2 O \text{ adsorbed to } Fe^{3+}}{mol Fe} + \frac{0.01 mol H_2 O}{mol Fe} \right)$$
(6.7)

where the value of 0.30 mol (mol Fe)<sup>-1</sup> in equation 6.5 corresponds to the initial density of  $Fe^{2+}$  open-metal sites (theoretical maximum is 1/3 mol (mol Fe)<sup>-1</sup>). The value of 0.01 mol

 $H_2O$  (mol Fe)<sup>-1</sup> in equation 6.7 represents the amount of water present already coordinated to Fe<sup>3+</sup> open-metal sites in the absence of  $H_2O$  co-feed, where for the material activated at 523 K, the Fe<sup>3+</sup> open-metal site density is approximately 0.65 mol (mol Fe)<sup>-1</sup> (theoretical maximum is 2/3 mol (mol Fe)<sup>-1</sup>).

**Table 6.3.** Under various partial pressures of water co-fed during the oxidation of CO with N<sub>2</sub>O, the corresponding total quantity of H<sub>2</sub>O adsorbed and NO adsorbed to Fe<sup>2+</sup> (measured after reaction), Reaction conditions: 423 K, 14.6 kPa N<sub>2</sub>O, 1.5 kPa CO.

Water Partial Pressure / kPa	Total H <sub>2</sub> O Adsorbed / mol (mol Fe) <sup>-1</sup>	NO Adsorbed / mol (mol Fe) <sup>-1</sup>	H <sub>2</sub> O Adsorbed to Fe <sup>3+</sup> OMS/ mol (mol Fe) <sup>-1</sup>	mol H <sub>2</sub> O (mol Fe <sub>3</sub> O) <sup>-1</sup>
0.15	0.42	0.21	0.33	1.02
0.35	0.60	0.10	0.40	1.26
0.54	0.75	0.06	0.51	1.56
0.78	0.92	0.02	0.64	1.95

Figure 6.11 indicates the oxidation rate per total Fe<sup>2+</sup> open-metal sites measured as a function of the water to Fe<sub>3</sub>O node molar ratio, which has been modulated either through the extent of thermal activation or under water co-feed, demonstrating the average turnover rate decreases systematically with water coverage. Under H<sub>2</sub>O co-feed, the same rigorous evaluations of NO reversible/irreversible adsorption at 523 K cannot be applied as H<sub>2</sub>O co-feed promotes the desorption of NO after purging NO from the gas stream. Furthermore, as distributions of Site 1, 2, and 3, corresponding to 0, 1, or 2 water molecules per node, could be well described by the binomial distribution at low mol H<sub>2</sub>O (mol Fe<sub>3</sub>O)<sup>-1</sup> ratios ( $\leq$  0.59), as shown in Figure 6.10b, we make the assumption that this distribution holds true at high mol H<sub>2</sub>O (mol Fe<sub>3</sub>O)<sup>-1</sup> ratios (0.59 < x  $\leq$  2). Moreover, the fractional density of Site 1, 2, and 3 can be estimated using the combination of equations 6.3, 6.4, and the following



Figure 6.11. Turnover rate as a function of the water to Fe<sub>3</sub>O molar ratio, varied through thermal treatment or by  $H_2O$  co-feed (14.6 kPa N<sub>2</sub>O, 1.5 kPa CO, 423 K). The dashed line represents the estimated rate from the regressed turnover rates for Site 1, 2, and 3 (Table 6.4).

Assuming the density of iron nodes with either 0, 1, or 2 water molecules follows the binomial distribution across all water to node ratios, the turnover rate for each site can be determined by solving for the predicted oxidation rate, by equation 6.2, that minimizes the weighted ( $w_i$  = inverse of the measured overall oxidation rate) sum of squared residuals (SSR) between the measured and estimated overall formation rates, given by the following

$$\sum_{i} w_{i} * (r_{i,measured} - r_{i,estimated})^{2}.$$
(6.9)

Here, it is estimated that the turnover rate for a given  $Fe^{2+}$  open-metal site decreases by approximately 77% and 97% with the addition of 1 and 2 water molecules to the Fe<sub>3</sub>O node, respectively. Moreover, results of this analysis provide a quantitative measure of the drastic influence of increasing H<sub>2</sub>O ligation on the turnover rate for an Fe<sup>2+</sup> site within a given tri-iron node, a result which can be rationalized by destabilization of the kineticallyrelevant transition state for N<sub>2</sub>O decomposition, as present in Section 6.3.1.

Site Identity	Turnover Rate / x10 <sup>-4</sup> mol (mol Fe <sup>2+</sup> ) <sup>-1</sup> s <sup>-1</sup>
Site 1 (Fe <sub>3</sub> O-0H <sub>2</sub> O)	$1.816\pm0.190$
Site 2 (Fe <sub>3</sub> O-1H <sub>2</sub> O)	$0.409\pm0.043$
Site 3 (Fe <sub>3</sub> O-2H <sub>2</sub> O)	$0.060\pm0.006$

**Table 6.4.** Turnover rate estimated for  $Fe^{2+}$  open-metal sites within  $Fe_3O$  nodes with 0, 1, or 2 watermolecules, estimated from the data in Figure 6.11.

#### 6.3.6. Site Non-Uniformity Evidenced at Sub-NO Saturation Conditions

As applied in the previous sections, the enhanced interaction of NO with  $Fe^{2+}$  openmetal sites allows for attaining accurate quantification of site densities under a range of experimental conditions and an unprecedented level of clarity into the distributions of  $Fe^{2+}$ site properties that are influenced by the local coordination of water to neighboring  $Fe^{3+}$ open-metal sites within the same triiron node. In the previous evaluation of MIL-100(Fe) for the oxidation of CO with N<sub>2</sub>O (Chapter 5), it could be observed at sub-saturation pressures of NO (0.003 – 0.02 kPa NO) at 488 K that the oxidation rate decreased linearly with the fraction of  $Fe^{2+}$  sites titrated in the fully-dehydrated catalyst sample (activated and 523 K), supporting a uniform contribution of active centers to the overall oxidation rate (reproduced in Figure 6.12a). Here, we demonstrate that under finite water coverages, nonlinear reductions in the oxidation rate with NO coverage can be observed.

To induce a significant concentration of coordinated water molecules in MIL-100(Fe) at 488 K, H<sub>2</sub>O was co-fed during CO oxidation with N<sub>2</sub>O. As provided in Table 6.5, at a water partial pressure of 0.35 kPa, iron open-metal sites are not completely saturated by water, providing a residual  $Fe^{2+}$  open-metal site density of 0.23 mol (mol Fe)<sup>-1</sup> and a water to Fe<sub>3</sub>O molar ratio of 1.08. Under this condition, as shown in Figure 6.12, the overall



**Figure 6.12.** Fractional rate as a function of the fraction of Fe<sup>2+</sup> open-metal sites titrated (0.003 – 0.2 kPa NO, reaction conditions: 14.5 kPa N<sub>2</sub>O, 1.5 kPa CO, 488 K) over MIL-100(Fe) (a) activated at 523 K and (b) under H<sub>2</sub>O co-feed (0.35 kPa).

**Table 6.5.** Under water co-feed, the quantity of water adsorbed, the remaining density of Fe<sup>2+</sup> openmetal sites (determined by NO titration), and the corresponding H<sub>2</sub>O to Fe<sub>3</sub>O node molar ratio (0.35 kPa H<sub>2</sub>O co-fed during reaction at 215 °C, 2.9 kPa N<sub>2</sub>O, 1.5 kPa CO).

mol H2O adsorbed	Fe <sup>2+</sup> Site Density /	mol H2O
(total mol Fe) <sup>-1</sup>	mol (total mol Fe) <sup>-1</sup>	(mol Fe3O) <sup>-1</sup>
0.42	0.23	1.08

oxidation rate can be completely reduced by NO titration up to 0.2 kPa. Notably, however, the oxidation rate decays non-linearly with the equilibrium coverage of NO, specifically, the sites which bind NO at the lowest partial pressures contribute more significantly to the overall oxidation rate than those titrated at higher partial pressures. Indication of the non-uniform contribution of  $Fe^{2+}$  open-metal sites under this condition is consistent with the prediction of an ensemble of nodes containing either 0, 1, or 2 water molecules at this water to node ratio (Figure 6.10b). The general observation that the  $Fe^{2+}$  open-metal sites titrated at lower partial pressures contribution rate is

also consistent with infrared and in-situ titration experiments conducted with NO as discussed in previous sections (6.3.3 and 6.3.4).

#### 6.3.7. Influence of Ligand Species on Coordination Effects in MIL-100(Fe)

In this section the nature of the coordinated ligand ( $Fe^{3+}-X$ ) on the catalytic properties of an Fe<sup>2+</sup> open-metal site within a given Fe<sub>3</sub>O node is considered. Specifically, the effect of replacing coordinated water ligands with alcohols (methanol, ethanol, and isopropanol) of increasing proton affinity is evaluated in the context of CO oxidation. Methodology for the alcohol exchange is described in the experimental section (Section 6.2.5). Briefly, exposure of thermally activated MIL-100(Fe) catalyst samples to the desired alcohol at 423 K, following thermal treatment at low temperature (423 K) overnight, allowed for producing materials with similar densities of coordinated alcohols (0.48 - 0.52 mol R-OH)per mol Fe<sub>3</sub>O, Table E2, Appendix E). As H<sub>2</sub>O-containing MIL-100(Fe) contained a slightly higher density of coordinated water molecules (~ 0.59 mol H<sub>2</sub>O (mol Fe<sub>3</sub>O)<sup>-1</sup>) following thermal treatment at 423 K, a slightly higher activation temperature of 436 K was employed to produce a comparable water to node molar ratio (0.49 mol H<sub>2</sub>O (mol  $Fe_3O$ )<sup>-1</sup>). Results of the analysis are summarized in Figure 6.13, indicating that at similar coordinated H<sub>2</sub>O/alcohol (X-OH) to iron node ratios (0.48 - 0.52), the CO oxidation turnover rate decreases systematically with increasing proton affinity or the coordinated ligand. This result suggests that the negative effects imparted on a given Fe<sup>2+</sup> open-metal site for the oxidation of CO by N<sub>2</sub>O is influenced by the nature of the ligand coordinated to the  $Fe^{3+}$  sites within the same triiron node.



**Figure 6.13.** Effect of oxygenate identity, with increasing proton affinity (NIST Database: Hunter & Lias, *J. Phys. Chem. Ref. Data* (1998)), on the CO oxidation turnover rate at similar molar ratios of oxygenate (x-OH) to Fe<sub>3</sub>O nodes. (14.6 kPa N<sub>2</sub>O, 1.5 kPa CO, 423 K).

As the bonding of H<sub>2</sub>O to the Lewis acidic Fe<sup>3+</sup> open-metal sites can be described by a simple Lewis acid-base bonding interaction, electron donation to the Fe<sup>3+</sup> open-metal sites from the ligand can be considered as a primary interaction leading to increased energy barriers for the reaction of N<sub>2</sub>O and CO over MIL-100(Fe). Moreover, increasing the proton affinity of the ligand (by with replacement of water, ethanol, and isopropanol, respectively) leads to further decrease in the oxidation turnover rate. In the case of isopropanol ligands, which had the largest effect on the turnover rate at a given alcohol to Fe<sub>3</sub>O node molar ratio, the apparent activation energy measured is approximately 8 kJ mol<sup>-1</sup> higher than that measured for the partially hydrated MIL-100(Fe) sample and 17 kJ mol<sup>-1</sup> greater than that for the nearly fully dehydrated sample (Table 6.6).

Ligand (x-OH)	mol x-OH (mol Fe <sub>3</sub> O) <sup>-1</sup>	E <sub>app</sub> / kJ mol <sup>-1</sup>
No ligand	N/A	$69.1 \pm 0.5$
Water	0.49	$77.8 \pm 1.0$
Isopropanol	0.51	$86.2\pm1.7$

**Table 6.6.** Apparent activation energy for fully dehydrated MIL-100(Fe) (treated at 523 K for 12 h under He flow, prior to reaction) and under conditions of partial ligation with water or isopropanol (reaction conditions: 14.6 kPa N<sub>2</sub>O, 1.5 kPa CO, 393 – 473 K).

As discussed in Section 6.3.1, the apparent activation energy measured under the conditions tested should approximate the energy difference between the initial catalyst state (Fe<sub>3</sub>O - n x-OH) and the transition state for the kinetically-relevant N<sub>2</sub>O decomposition reaction step (Figure 6.3). Moreover, it can be observed that the coordination of the increasing basic ligands leads to further destabilization of the transition state with respect to the initial state of the catalyst. It is noted that we do not have further insight into how such secondary coordination sphere effect the adsorption energy of N<sub>2</sub>O or how this may impact the intrinsic activation energy barrier for this elementary reaction step.

## 6.3.8. The Case of MIL-100(Cr): Coordination Effects on the Kinetic-Relevance of Oxidation and Reduction Elementary Reaction Steps

Thus far it has been demonstrated that coordination effects associated with the ligation of water (or other alcohol molecules) imparts significant influences on the oxidation turnover rate measured over an  $Fe^{2+}$  within a given tri-iron node within MIL-100(Fe). Previously in the oxidation of CO with N<sub>2</sub>O over the chromium-variant of MIL-100(Cr), it was observed that the identity of the active metal has significant influence on the ratecontrolling nature of different elementary reaction steps within the oxidation mechanism (Section 5.3.9, Chapter 5). Specially, for MIL-100(Cr) it was observed that steady-state 168 surface fractions of oxidized Cr intermediates (Cr-O) may represent nearly the entirety of the  $Cr^{2+}$  site density, the concentration of which, also depending strongly on the reaction temperature and N<sub>2</sub>O to CO molar ratio (Figure 5.18, Chapter 5), being described by the following simplified rate expression

$$r = \frac{k_2 K_1 [N_2 O]}{1 + \frac{k_2 K_1 [N_2 O]}{\overline{k_3} [CO] \left(1 - \frac{\overline{k_3}}{\overline{k_3} + k_4}\right)}} = \frac{k' [N_2 O]}{1 + \frac{k' [N_2 O]}{k'' [CO]}}$$
(6.10)

where the term in the denominator is related to the surface coverage of Cr-O intermediates in correspondence with the mechanism in Figure 6.1. Here we further investigate the extent to which secondary-coordination sphere effects of increasing hydration of the  $Cr_3O$  nodes influences the kinetics of CO oxidation over MIL-100(Cr).

Analysis of MIL-100(Cr) thermally activated with increasing extents of dehydration provides both increasing Fe<sup>2+</sup> open-metal site densities and decreasing water to Cr<sub>3</sub>O node molar ratios (Figure 6.14). Similarly to results obtained over MIL-100(Fe) (Figure 6.2a), the oxidation turnover rate (mol (mol Cr<sup>2+</sup>)<sup>-1</sup> s<sup>-1</sup>) measured over MIL-100(Cr) increases systematically with the extent of dehydration (Figure 6.14). In this case, thermal activation at 523 K in vacuum has a significant influence on the capability to evacuate the strongly coordinated water species from MIL-100(Cr), resulting in a substantial increase in the turnover rate measured for this sample in comparison to those activated with increasing temperature under He flow.



**Figure 6.14.** CO turnover rate and the molar ratio of water to Cr<sub>3</sub>O trimer node as a function of the activation temperature (reaction conditions: 448 K, 51.4 kPa N<sub>2</sub>O, 30.9 kPa CO). Samples activated at the indicated temperature under He flow or in vacuum (indicated by \*).

The effect of the overall degree of hydration on the reaction orders for N<sub>2</sub>O and CO over MIL-100(Cr) was further considered. As provided in Figure 6.15, a decreasing dependence of the oxidation rate on the partial pressure of N<sub>2</sub>O can be observed with increasing extent of thermal activation (Figure 6.15). Based on the proposed reaction mechanism and rate expression (Eq. 6.10), the relative rate dependence on the CO and N<sub>2</sub>O partial pressures can be primarily described by steady-state concentrations of oxidized and vacant  $Cr^{2+}$  sites, respectively. In other words, higher CO reaction orders were measured at higher Cr-O concentrations, while higher N<sub>2</sub>O reaction orders were measured at higher vacant  $Cr^{2+}$  site concentrations. Moreover, results presented here suggest that the increasing hydration of the Cr<sub>3</sub>O nodes results in increasing fractions of vacant sites, relative to oxidized intermediates (Cr-O), at a given reaction condition.



**Figure 6.15.** CO oxidation rate dependence on the N<sub>2</sub>O partial pressure over MIL-100(Cr) pretreated at various conditions (14.3 – 51.4 kPa N<sub>2</sub>O, 30.9 kPa CO, 448 K).

**Table 6.7.** N<sub>2</sub>O reaction orders determined for MIL-100(Cr) pretreated at various conditions, tested at 14.3 – 51.4 kPa N<sub>2</sub>O, 30.9 kPa CO, and 448 K.

Activation Condition	N <sub>2</sub> O Reaction Order
448 K, He	0.55
498 K, He	0.30
523 K, He	0.22
523 K, vacuum	0.15

Further evaluation of the catalyst at the two extremes of activation conditions tested (448 K in He and 523 K in vacuum) was conducted to determine the specific influence of the degree of hydration on the individual lumped rate constants, k' and k". As indicated by the parity plots in Figure 6.16, kinetics over MIL-100(Cr) can be described the simplified rate expression (Eq. 6.10) for both thermal activation conditions at a reaction temperature of 448 K. The corresponding lumped kinetic parameters estimated are provided in Table

6.8. Notably, the constant k', associated with the sorption (K<sub>1</sub>) and decomposition of N<sub>2</sub>O (k<sub>2</sub>), is over five times higher for the sample activated at 523 K (vacuum) in comparison to activation at 448 K (He flow). A smaller influence of degree of hydration is observed on the constant k", which is related to the sorption of CO to the Cr-O intermediates (k<sub>3</sub>/k<sub>-3</sub>) and reaction to form CO<sub>2</sub> (k<sub>4</sub>). Specifically, in this case k" was approximately 1.9 times higher for the sample activated at 523 K in comparison to the sample activated at 448 K.



**Figure 6.16.** Comparison of the estimated (from equation 6.10) and measured turnover rate at 448 K over MIL-100(Cr) pretreated at 448 K under He flow (left) and at 523 K under vacuum (right). Conditions: 2.9 – 51.4 kPa N<sub>2</sub>O, 3.5 – 32.2 kPa CO.

Comparison to MIL-100(Fe) at a similar water to Fe<sub>3</sub>O node molar ratio, the oxidation turnover rate of the nearly fully-dehydrated sample (523 K activation, He) was approximately 1.9 times greater than the sample with a water to Fe<sub>3</sub>O molar ratio of 0.59 (423 K activation, He), as provided in Figure 6.2a at a reaction temperature of 423 K. Under the conditions tested for MIL-100(Fe), the overall measured rate could be described solely as  $r \approx k_2 K_2 [N_2O]$ , furthermore coordination effects on the reduction portion of the redox cycle could were not probed. Moreover, the magnitude of k' measured over MIL-100(Cr) is significantly more affected by the degree of hydration at low  $H_2O$  to node molar ratios (~ 0.61), as indicated in Table 6.8, in comparison to MIL-100(Fe) at similar reaction temperatures (423 – 448 K). It can also be identified that secondary coordination sphere effects may also influence elementary reaction steps associated with CO sorption and reaction with the Cr-O intermediates.

**Table 6.8.** Lumped kinetic parameters for MIL-100(Cr) estimated from fitting steady-state reaction data to the simplified rate expression (equation 6.10) for samples pretreated under various conditions. (Reaction at 175 °C, 2.9 – 8.7 N<sub>2</sub>O, 3.5 – 32.2 CO).

Parameter	Equivalence	Activation Condition	Value	mol H <sub>2</sub> O (mol Cr <sub>3</sub> O) <sup>-1</sup>
1-1		448 K, He	2.62 x 10 <sup>-5</sup> (kPa·s) <sup>-1</sup>	0.61
R	$\kappa_2 \kappa_1$	523 K, vacuum	1.40 x 10 <sup>-4</sup> (kPa·s) <sup>-1</sup>	0.14
k'' Ī	$\overrightarrow{k}$ $(1  \overleftarrow{k_3})$	448 K, He	1.04 x 10 <sup>-5</sup> (kPa·s) <sup>-1</sup>	0.61
	$k_3 \left( 1 - \frac{1}{\overline{k_3} + k_4} \right)$	523 K, vacuum	1.98 x 10 <sup>-5</sup> (kPa·s) <sup>-1</sup>	0.14

Lastly, we further demonstrate through transient kinetic analyses that the overall degree of hydration of MIL-100(Cr) significantly influences the kinetic relevance of N<sub>2</sub>O sorption and decomposition elementary reaction steps during CO oxidation. Specifically, hydration of the catalyst sample up to complete saturation with water was modulated by exposing the catalyst to a low molar flow rate of H<sub>2</sub>O ( $3.77 \times 10^{-4} \text{ mol H}_2\text{O} (\text{mol Cr})^{-1} \text{ s}^{-1}$ ) during steadystate oxidation experiments. The transient reduction in the overall oxidation rate as H<sub>2</sub>O propagates and eventually breaks through the catalyst bed was evaluated at reaction conditions differing only by the N<sub>2</sub>O partial pressure employed (2.9 or 9.0 kPa). As shown in Figure E6, Appendix E, changing the N<sub>2</sub>O partial pressure has negligible influence on the time required to H<sub>2</sub>O to be detected at the reactor outlet or the total quantity of H<sub>2</sub>O adsorbed by the sample (~  $0.96 \text{ mol H}_2\text{O} \text{ (mol Cr)}^{-1}$ ), (reaction conditions: 2.9 kPa N<sub>2</sub>O, 31.9 kPa CO, 423 K). Upon introduction of H<sub>2</sub>O at a time equal to 0 minutes, the oxidation rate measured decreases non-linearly as a function of time (Figure 6.17a) and the total quantity of H<sub>2</sub>O adsorbed (Figure 6.17b). Notably, at 9.0 kPa N<sub>2</sub>O the normalized oxidation rate at a given time and quantity of H<sub>2</sub>O adsorbed is greater than that measured at 2.9 kPa. As the rate is normalized by the oxidation rate prior to the introduction of H<sub>2</sub>O, this result indicates that oxidation rates over Cr<sup>2+</sup> sites within regions of the catalyst bed already contacted by H<sub>2</sub>O are more sensitive to N<sub>2</sub>O partial pressure than the Cr<sup>2+</sup> sites in the activated catalyst.



**Figure 6.17.** CO oxidation rate over MIL-100(Cr) (normalized by the oxidation rate in the absence of H<sub>2</sub>O co-feed) (a) with time when H<sub>2</sub>O ( $3.77 \times 10^{-4} \text{ mol (mol Cr)}^{-1} \text{ s}^{-1}$ ) is introduced at t = 0 minutes and (b) as a function of the total quantity of H<sub>2</sub>O adsorbed.

A similar analysis was conducted over MIL-100(Fe) as a reference. At 423 K, the nearly fully-dehydrated MIL-100(Fe) catalyst sample exhibits a first-order dependence on the partial pressure of  $N_2O$  and this dependence is maintained at higher coverages of  $H_2O$ (Figure E2). Moreover, the normalized oxidation rate measured over MIL-100(Fe) during the breakthrough adsorption of  $H_2O$  under oxidation reaction conditions is independent of the partial pressure of  $N_2O$  (Figure E8). This result further emphasizes that kinetics measured over MIL-100(Cr) allow for sensing the kinetic-relevance of the  $N_2O$  sorption and decomposition elementary reaction steps, with respect to the steps in the reduction portion of the catalytic cycle, beyond that which can be evaluated in MIL-100(Fe). Here, the nonlinear reduction in the oxidation rate with the quantity of  $H_2O$  adsorbed also reflects the heterogeneity in site speciation, imparted by increasing hydration with water.

#### **6.4.** Conclusions

Within MIL-100 redox catalysts, for which every potential open-metal site exhibits identical kinetic properties in the fully-dehydrated material, the unequivocal presence of secondary coordination sphere effects can be assessed through rigorous kinetic analyses. Specifically, measurements conducted at steady state indicate that the extent of dehydration of the material influences the catalytic turnover rate per available active site ( $M^{2+}$ ). For MIL-100(Fe), in-situ titration and infrared spectroscopy measurements conducted with NO further emphasize the influence of water coordinated to the Fe<sub>3</sub>O nodes on the strength of adsorption of NO at the reaction temperature (423 K). Specifically, Fe<sup>2+</sup> sites which bind NO irreversibly at 423 K are identified to belong within fully dehydrated iron nodes (Fe<sub>3</sub>O-0 H<sub>2</sub>O), whereas, those which bind NO reversibly feature either 1 or 2 ligated water molecules (Fe<sub>3</sub>O-1H<sub>2</sub>O or Fe<sub>3</sub>O-2H<sub>2</sub>O). This unique feature of NO adsorption reversibility at 423 K allows for directly quantifying the density of each type of active site using in-situ titrations, providing estimations for the turnover rate with increasing water ligation (n = 0, 1, or 2). Results of this analysis are consistent with sub-saturation NO titration experiments

conducted at elevated temperature (488 K) under water co-feed that displays a non-linear reduction in the oxidation rate with the quantity of  $Fe^{2+}$  sites titrated by NO. Exchange of water ligands with alcohol molecules of increasing proton affinity results in further systematic reduction of the turnover rate at a given alcohol coverage, suggesting the degree to which the node is affected by coordination is influenced by the identity of the ligand. Lastly, we demonstrated that the secondary coordination sphere effects observed are not exclusive to MIL-100(Fe), but also observable in the chromium-analogue as well. Specifically, MIL-100(Cr) catalysts showed increased rate dependence on  $N_2O$  partial pressure and reduced turnover rates with increasing water ligation. Results provide that the kinetic relevance of  $N_2O$  activation elementary steps become increasing kinetically relevant in the hydrated Cr<sub>3</sub>O nodes, suggesting that ligation to the node disproportionately influences the oxidation half cycle of the reaction. Furthermore, this study demonstrates for the first time in MIL-100, the capability to tune the adsorption and catalytic properties of the material using ligand coordination to spectator metal ions as a lever – results of which could provide novel avenues for improving the atomic level properties of MOF materials for adsorption and catalysis applications, more broadly.

### 7. Metal-Organic Framework MIL-100 Catalyzed Acetalization: Lewis or Brønsted Acid Catalysis?

MOFs present an opportunity to develop Lewis acid catalysts with uniform, welldefined, tunable, isolated active sites for a range of chemical transformations. A common example of such a transformation is the acetalization of carbonylic compounds with alcohols over MIL-100. Despite numerous reports focused on the acetalization performance of MIL-100 and related MOF materials, the identity of MIL-100 active sites still remains a point of contention. We present herein a range of catalytic, in-situ titration, and spectroscopy data that can all plausibly be interpreted under the assumption of the near-exclusive contribution of Brønsted acid sites towards effecting acetalization turnovers for MIL-100(Cr) and MIL-100(Fe). The principles and methodology used in this study are broadly applicable within the domain of MOF-mediated catalysis, and reinforce the need for a careful evaluation of active site speciation *under* reaction conditions to more fully realize the promise of MOF materials as Lewis acid catalysts. This chapter is adapted from the following peer-reviewed article

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#### 7.1. Introduction

Metal-organic frameworks are a relatively novel class of high-surface area, crystalline, nanoporous materials that have emerged as promising candidates for targeted applications including gas separation,<sup>7,59,170,180,320,321</sup> drug delivery,<sup>11,322,323</sup> and heterogeneous catalysis.<sup>19,108,324,325</sup> A principal advantage that these materials offer is the large diversity of inorganic nodes and organic linkers potentially available for exploration and exploitation.<sup>1,4,326,327</sup> In particular, coordinatively unsaturated metal sites (or open-metal

sites) in MOFs have shown promise as active sites for Lewis acid-catalyzed reactions.<sup>53,55–</sup> <sup>57,328</sup> Compared to their zeolitic counterparts,<sup>222,329</sup> they offer the potential to be more uniform, isolated, well-defined, and tunable in coordination environment for importance to biomass upgrading and oxidation of light alkane reactions.<sup>36,72,73,330</sup> A full realization of the promise that these materials offer as Lewis acid catalysts, however, has for the most part been predicated on the tacit assumption that acid-catalyzed turnovers occur exclusively over coordinatively unsaturated sites, and not elsewhere in the MOF.<sup>66,331,332</sup>

A prototypical example of such a MOF is MIL-100 (MIL = Materials of Institut Lavoisier):<sup>43</sup> a porous trivalent metal carboxylate that has been studied as a candidate not only for Lewis acid-catalyzed reactions like olefin oligomerization,<sup>70,71,333</sup> but also for lowtemperature hydrocarbon oxidation.<sup>72,73,198,334</sup> Key to its potential as a Lewis acid catalyst are its  $\mu_3$ -oxo centred metal trimer nodes having labile water ligands occupying terminal positions, the removal of which allows for the formation of coordinatively unsaturated or open-metal sites.<sup>42,54,68,131,132</sup> Specifically, acetalization of carbonylic compounds represents, arguably, the most commonly studied acid-catalyzed reaction on this class of materials.<sup>34,66,127,335–340</sup> Although the acetalization performance of MIL-100/MIL-101 has been assessed repeatedly, the source of catalytic activity (Lewis versus Brønsted acid catalysis) remains a point of contention, as reflected by the variety of contradictory claims reported in the literature (Table 7.1). For example, some authors have concluded that the turnovers are Lewis acid catalyzed based on *in-situ* titration data with pyridine-<sup>66,335</sup> although it is capable of titrating both Lewis and Brønsted acid sites.<sup>257,341–343</sup> Others have used comparisons of kinetic profiles of MOFs and homogeneous Lewis acid catalysts

endowed with the same metal cation (but not the identical node) to reach similar conclusions.<sup>66,336</sup> Janiak and colleagues, on the other hand, used solution pH measurements to conclude that MIL-101 catalyzes the acetalization of benzaldehyde and methanol as a Brønsted acid catalyst, and suggested that water molecules coordinated to metal atoms act as the source of Brønsted acidity.<sup>338</sup>

**Table 7.1.** Reports for which MIL-100/101 has been evaluated for the acetalization of aldehydes with alcohols, and a summary of the conclusions relating to Lewis/Brønsted acid catalysis.

Catalyst	Substrates	<b>Reaction Conditions</b>	Conclusions	Ref.
Fe(BTC)*	Benzaldehyde and methanol	Benzaldehyde (0.94 mmol), methanol (3 mL), catalyst (50 mg), room temperature	Lewis acid catalysis based on in-situ titrations with pyridine	335
MIL-101(Cr)	Benzaldehyde and methanol	Benzaldehyde (3.34 mmol), methanol (6.7 mL), catalyst (10 mg), 298 – 328 K	Consider the possibility of both mildly acidic Brønsted and Lewis acid sites in the total acid site density	339
Fe(BTC) <sup>*</sup> MIL-100(Fe)	Benzaldehyde/ cinnamaldehyde and methanol	Benzaldehyde (0.3 mL) or cinnamaldehyde (0.25 mL), methanol (5 mL) 9 mg Fe(BTC) or 10 mg MIL 100(Fe) 313 K	Lewis action of the initial reaction rate to homogeneous	336
MIL-101	Benzaldehyde and glycol	Benzaldehyde (70 mmol), glycol (126 mmol), catalyst (0.12 g), and cyclohexane (8 mL, water-carrying agent), 353 K	Comparison of MIL-101 to sulfonic-acid functionalized MIL-101 and concluded the residual catalytic activity on the pure material was a result of the presence of unsaturated Lewis acid centers	337
MIL-100(Fe, Cr) MIL-101(Fe, Cr)	Benzaldehyde and ethanol	Benzaldehyde (10 mmol), ethanol (20 mmol), 1 wt.% of catalyst, 333 K	Higher performance of MIL- 100(Fe, Cr) over MIL-101(Fe, Cr) was attributed to a greater number of "weak-medium" acid sites in MIL-100 determined from NH <sub>3</sub> TPD at 323 – 623 K	127
MIL-101(Cr)	Benzaldehyde and methanol	Benzaldehyde (3.34 mmol), methanol (166 mmol), catalyst (10 mg)	pH measurements suggesting acidity originating from MIL- 101, a consequence of dissociation of the ligated water molecules (Cr-OH <sup>-</sup> /H <sup>+</sup> )	338
MIL-100(Fe)	Benzaldehyde, and glycol	Benzaldehyde (70 mmol), glycol (126 mmol), cyclohexane (10 mL, water- carrying agent), catalyst (0.2 g), 353 K	Lewis acid catalysis by comparison of MIL-100(Fe) with iron nitrate and by pyridine titrations	66,340
MIL-100(Fe)	Benzaldehyde and methanol	Benzaldehyde (0.3 mL), methanol (5 mL), catalyst (0.02 g), room temperature	No conclusion with respect to Lewis or Brønsted acid catalysis	34

More broadly, a range of possible site requirements have been put forth in the context of Lewis acid-catalyzed acetalization by homogenous and heterogeneous catalysts. For example, Clerici *et al.* have proposed that the formation of the key intermediate in the case of chlorotitanium methoxide involves simultaneously activating methanol and the aldehyde in two vacant coordination positions in the complex.<sup>344</sup> Others studies have also pointed to the importance of activating both reactants at the Lewis acid center, such as the one by Venazi and colleagues focusing on cyclohexanone and 1,2-ethanediol condensation over homogenous Ru complexes.<sup>345</sup> Janiak and coworkers used this proposal, in which transition metal catalysts require two vacant coordination positions, as part of the justification for eliminating the possibility that MIL-101(Cr) acts a Lewis acid catalyst.<sup>338</sup> They note that the presence of MIL-101 structural defects (*e.g.* dangling or missing organic linkers) that could potentially lead to two or more free coordination positions at the metal atom, are not observed/reported as prominently for as in the case of defect-rich MOFs such as UiO-66.<sup>346,347</sup> Others, however, including Pescarmona and coworkers suggest that one coordination position is sufficient to catalyze acetalization of acetone with glycol over heterogenous catalysts like Zr-TUD-1, Hf-TUD-1, and Sn-MCM-41.348 Further complicating matters, Bhargava and coworkers proposed a mechanism in which a *combination* of a Lewis acid site (that activates the carbonyl function) and a neighboring Brønsted acid site (that protonates the intermediate formed in the previous step) plays a role in the acetalization of acetone and glycol over Cu-mordenite.<sup>349</sup> Mechanisms involving only Brønsted acid sites have also been presented, like those proposed for SO<sub>3</sub>Hfunctionalized ionic liquids.<sup>350,351</sup> The elimination, therefore, of the possibility of Lewis acid catalysis, solely based on the maximum number of available coordination positions, may not necessarily be valid, and may in fact warrant supporting evidence for the occurrence of Brønsted acid catalysis.

We reemphasize the fact that despite several groups having reported catalytic data over MIL-100 type materials, the nature of active sites catalyzing this chemistry still remains unclear. In this work, we present a range of catalytic and in-situ spectroscopic data, all of which can be plausibly interpreted as being consistent with the near-exclusive contribution of Brønsted acid sites originating from water coordinated to MIL-100 metal atoms, towards liquid-phase acetalization of benzaldehyde with methanol. To this end, in Section 7.3.1, we briefly discuss the catalytic performance of MIL-100(Fe) and MIL-100(Cr). In Section 7.3.2, in-situ titrations with pyridine and 2,6-di-*tert*-butylpyridine (DTBP) are reported that point to the involvement of Brønsted acid sites in the chemistry under consideration. In Section 7.3.3 thermal treatment protocols known to modulate Lewis and Brønsted acid site densities are exploited to probe the source of Brønsted acidity. Section 7.3.4 seeks to address one of the main open questions raised by the data reported in previous sections: why does DTBP, unlike pyridine, titrate only a fraction of the Brønsted acid sites in MIL-100? The approach used in our investigation of active site density and speciation, although focused specifically on MIL-100 catalyzed acetalization, may be applicable much more broadly within the domain of MOF-mediated acid catalysis.

#### 7.2. Materials and Methods

#### 7.2.1. MIL-100(Cr) Synthesis

MIL-100(Cr) was synthesized by adapting the procedure developed by Mao *et al.*<sup>139</sup> 9 g of CrCl<sub>3</sub>·6H<sub>2</sub>O (Sigma Aldrich  $\geq$  98.0%) and 3.55 g of trimesic acid (Alfa Aesar, 98%) were ground by a mortar and pestle at room temperature for 30 minutes. The resulting mixture was transferred to a stainless steel autoclave with a 45 mL PTFE liner and heated at 493 K for 15 hours under rotation. The sample was then washed with 500 mL of deionized water (18.3 MΩ) and 500 mL of ethanol (Decon Laboratories Inc., 200 Proof) subsequently for 3 hours at 343 and 338 K, respectively, in a 500 mL Erlenmeyer flask (Wilmad-LabGlass) fitted with a reflux condenser (Glassco, 200 mm). The solid sample was collected with fresh ethanol and dried at 343 K overnight. A final thermal treatment in a vacuum oven (MTI Corporation, P < 3 x 10<sup>-3</sup> bar) at 423 K for 12 hours was completed to remove excess solvent molecules. Several catalyst batches following the same procedure were combined to produce a large enough quantity of material to be used for all of the analyses in this work.

#### 7.2.2. MIL-100(Fe) Synthesis

MIL-100(Fe) was synthesized according to a procedure developed by Zhang and coworkers.<sup>66</sup> 16.16 g of Fe(NO)<sub>3</sub>·9H<sub>2</sub>O (Alfa Aesar, > 98%), 7.56 g of trimesic acid (Alfa Aesar, 98%), and 24 mL of deionized water (18.3 M $\Omega$ ) were mixed in a round bottom flask (250 mL) at 600 rpm for 12 hours at 368 K. The product was purified by alternating washing with deionized water (18.3 M $\Omega$ ) and ethanol (Decon Laboratories Inc., 200 Proof) in 160 mL quantities at 343 K. This step included a total of 6 steps (3 washes with water

and 3 washes with ethanol) over a period of approximately 20 hours. The sample was collected with fresh ethanol and transfered to an oven at 353 K to remove excess solvent. Lastly, the product was treated at 423 K in a vacuum oven (MTI Corporation,  $P < 3 \times 10^{-3}$  bar) for 10 hours.

#### 7.2.3. MIL-101(Cr) Synthesis

MIL-101(Cr) was synthesized using a previously reported procedure.<sup>352</sup> 2 g of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 0.554 g of terephthalic acid were ground together with a mortar and pestle at room temperature for approximately 15 minutes. The sample was then transferred to a 125 mL PTFE-lined stainless steel autoclave and heated at 493 K for 4 hours. The product was further transferred to a 500 mL Erlenmeyer flask (Wilmad-LabGlass) fitted with a reflux condenser (Glassco, 200 mm) and washed with 500 mL of ethanol (Decon Laboratories Inc., 200 Proof) for 15 hours at 343 K. The resulting solid was then collected, dried to 2 hours at 353 K to remove excess solvent, and then treated at 473 K for 12 hours in a vacuum oven (MTI Corporation,  $P < 3 \times 10^{-3}$  bar).

#### 7.2.4. Cr-oxo Homogeneous Complex Synthesis

A Cr-oxo bridged cluster  $[Cr_3O(O_2CPh)_6(H_2O)_3](NO_3) \cdot nH_2O$  (**Cr-oxo**) was synthesized using a previously reported procedure.<sup>300,333</sup> 8.0 g of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 4.8 g of benzoic acid were mixed in ethanol (Decon Laboratories Inc., 200 Proof) for 3 hours under reflux. The mixture was then cooled to room temperature and stored overnight in a freezer. While cool, the sample was filtered and washed with > 300 mL of ethanol and then dried in a vacuum oven (MTI Corporation, P < 3 x 10<sup>-3</sup> bar) at room temperature for 24 hours.

#### 7.2.5. Material Characterization

Powder X-ray diffraction (XRD) was completed using an Empyrean Malvern Panalytical diffractometer equipped with a Cu K $\alpha$  X-ray source ( $\lambda = 1.54$  Å). A glass sample holder (Rigaku, 0.2 mm indentation) was loaded with approximately 0.02 g of sample prior to analysis. Diffraction patterns were collected in the 2.5 – 20° range with a step size of 0.013° and speed of 23.8 s per step. Nitrogen physisorption experiments were completed on a Micromertics 3Flex Surface Characterization Analyzer. Approximately 0.05 g of sample was evacuated (P ~ 1 x 10<sup>-4</sup> bar) for 15 hours at 423 K using a Micromertics VacPrep degassing system. Thermogravimetric analyses (TGA) were conducted with a Tarsus TG 209 F3 instrument. Experiments were completed in air (40 mL min<sup>-1</sup>, Matheson, zero-grade) at a heating rate of 1 K min<sup>-1</sup>.

#### 7.2.6. Procedure for the Acetalization of Benzaldehyde with Methanol

Batch liquid-phase reaction runs were completed in a three-neck round bottom flask (100 mL) fitted with a reflux condenser. The reaction temperature was controlled at 303 K in a mineral oil bath. 10 mL of methanol, 1 mL N,N-dimethylformamide (DMF) (internal standard), and catalyst 0.1 g were stirred at the reaction temperature at 800 rpm. The reaction was initiated by a 1 mL injection of benzaldehyde into the flask. (For MIL-100(Fe), 50 mL of methanol, 5 mL DMF, and 5 mL of benzaldehyde was used due to higher reactivity of this material). Reaction aliquots were sampled periodically and analyzed by gas chromatography (Agilent 7890B) with an FID detector a capillary column (HP-5, 30 m x 0.32 m x 0.25  $\mu$ m). Thermal catalyst pretreatments were completed in a vacuum oven (MTI Corporation, P < 3 x 10<sup>-3</sup> bar) for 15 hours at temperatures between

373 – 523 K. Following pretreatment, catalyst samples were transfered immediately to the reaction solution.

#### 7.2.7. Infrared Spectroscopy Titration Experiments

Transmission infrared spectroscopy analyses were performed using a Nicolet iS50 FT-IR Spectrometer (Thermo Scientific) with a Harrick Dewar Transmission/Reflection Accessory equipped with ZnSe windows (25 x 2, 32 x 3 mm). Self-supporting wafers (15 – 20 mg) were analyzed treated under inert flow (N<sub>2</sub> or Ar, Matheson Ultra High Purity). Spectra were collected using a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen (77 K) averaging 64 scans at 4 cm<sup>-1</sup> resolution in the 720 - 4000 cm<sup>-1</sup> range. An empty cell reference was collected under inert flow and used as a background reference for all spectra. Indicated IR spectra reported here were baseline-corrected and peak areas determined using Origin 8.5. Liquid injections of pyridine, 2,6-di-*tert*-butylpyridine, methanol, and water were completed in 2 – 10  $\mu$ L quantities through manual injection into an inert flow (N<sub>2</sub> or Ar, Matheson Ultra High Purity). Gas lines were held at a temperature of approximately 373 K and the sample cell was maintained at 373 K for all liquid injections to prevent condensation of vapors.

#### **7.3. Results and Discussion**

#### 7.3.1. Catalytic performance of MIL-100(Cr) and MIL-100(Fe).

MIL-100(Cr) and MIL-100(Fe) were synthesized using previously published literature reports and exhibit crystal structures, porosities, and compositions consistent with these studies (Section F1.1 and F1.2, Appendix F).<sup>66,139</sup> The acetalization of benzaldehyde with methanol (Figure 7.1) was tested as described in Section 7.2.6. MIL-100(Cr) and MIL-

100(Fe) can both effect hundreds of turnovers (calculated by assuming each metal atom to be an active site) without any catalyst pretreatment (Figure 7.2a), with benzaldehyde dimethyl acetal (BDA) being the only observed product. The amount of carbon measured as BDA product approximates (within 10% error) to the amount of carbon converted (Figure 7.2b). Also, MIL-100(Fe) effects a significantly higher number of net turnovers compared to MIL-100(Cr) under the same conditions, consistent with the results of Cho and coworkers in which initial rates of the acetalization of benzaldehyde with ethanol were 1.94 and 1.28 mmol min<sup>-1</sup> g<sup>-1</sup> for MIL-100(Fe) and MIL-100(Cr), respectively.<sup>127</sup>



Figure 7.1. Acetalization of benzaldehyde with methanol to form benzaldehyde dimethyl acetal (BDA) and water.



Figure 7.2. Comparison of the net moles of BDA per mole metal formed as a function of time (a), carbon balances for acetalization batch reaction runs (b), and filtration tests (c) for MIL-100(Fe) and MIL-100(Cr). (5 mL benzaldehyde, 50 mL methanol, 0.01 g catalyst, T = 303 K)

Despite running under conditions of excess methanol (methanol to benzaldehyde molar ratio = 25), thermodynamic effects cannot be eliminated from consideration; specifically, an equilibrium benzaldehyde conversion of approximately 87% was estimated for these conditions (calculations in Appendix F, Section F2.1). We emphasize in this context that the data reported here do not allow for the rigorous measurements of acetalization reaction rates, in part resulting from possible diffusion limitations, and in part owing to a finite approach to equilibrium through most of the activity profile in Figure 7.2c. We present instead, for the most part, the net turnover number- the difference between the cumulative number of turnovers of the forward and reverse reaction occurring up to any time in a batch reaction run, assuming the number of metal atoms corresponds to the number of active sites. Although the number of active sites may only be a fraction of the total metal atoms, the metric used provides no consequence on the conclusions drawn hereafter.

Further, to evaluate the source of catalytic activity in batch experiments, catalysts were filtered from the reaction medium after approximately 15 minutes of reaction, and the activity of the residual solution monitored (Figure 7.2c). Contrary to the observation of significant activity after filtration that can be observed due to contributions from solution phase catalysis, the absence of catalytic activity after filtration can be interpreted as consistent with catalysis proceeding over the metal organic framework.<sup>353–355</sup> After filtration at 15 minutes, the reaction was observed to proceed with residual activity comparable to the background reaction under these conditions, consistent with a majority of measured turnovers occurring over active centers of the MOF, and not in the solution phase owing to leached active species. These results mirror those reported by Zhang and

coworkers, in which the reaction of benzaldehyde with glycol ceased following filtration of MIL-100(Fe), with no detectable amount of iron in the filtrate when analyzed by ICP-AES.<sup>66</sup> Filtration tests suggesting that the catalytic activity originates from active sites on MIL-100, however, do not provide any clues as to the nature (Lewis or Brønsted acid), identity, or density of active sites. To gain insights into active site requirements, we carried out in-situ titrations with organic bases, the results of which are described in the next section.

#### 7.3.2. Can MIL-100 acid sites be titrated in-situ by pyridine and DTBP?

To probe the nature of MIL-100 acid sites contributing to acetalization turnovers, a series of in-situ titrations were carried out in which two titrants, pyridine and 2,6-di-*tert*-butylpyridine (DTBP), were employed. Pyridine has been used extensively as an in-situ titrant for acid sites.<sup>66,129,356-359</sup> Whereas pyridine can bind both Lewis and Brønsted acid sites, DTBP is selective to the latter. Brown and Kanner first discovered DTBP will react with hydrogen chloride but not methyl iodide or boron trifluoride, providing evidence of its ability to react with only protonic acids and not Lewis acids.<sup>360</sup> Since then, several authors have utilized dialkyl pyridines (DTBP or 2,6-dimethylpyridine) to probe Brønsted acidity present in several solid acid catalysts including alumina,<sup>361</sup> molybdenum carbide,<sup>362</sup> tungsten oxide,<sup>257,363,364</sup> and zeolites.<sup>365-367</sup> For example, Iglesia and coworkers demonstrated the insensitivity of alcohol dehydration rates to DTBP concentration when using γ-Al<sub>2</sub>O<sub>3</sub>, a catalyst endowed with solely Lewis acid sites.<sup>257</sup> Moreover, the selectivity of DTBP towards Brønsted acid sites has been evidenced by higher uptakes of pyridine, compared to DTBP, to achieve an identical decrease in reaction rates for the dehydration
of 2-butanol over WO<sub>x</sub>/ZrO<sub>2</sub><sup>257</sup> and dimethyl ether synthesis over chemically-dealuminated USY zeolite,<sup>366</sup> providing evidence for the negligible contribution of Lewis acid sites to the catalytic activity in these two reports. In their study of external acid sites in hierarchical zeolites, Góra-Marek *et al.* used IR spectroscopic measurements to observe the interaction of DTBP with acid sites based on its characteristic  $\equiv$ N-H<sup>+</sup> stretching vibration; despite the presence of Lewis acid sites, no spectral features indicative of DTBP coordinated to Lewis acid sites were observed in the 1450 - 1600 cm<sup>-1</sup> range.<sup>368</sup> In our experiments, we use these previous studies as a basis for considering DTBP as a Brønsted acid selective titrant.

The net TON after 15 minutes of reaction decreases monotonically with increasing titrant:metal molar ratio when the titrant is injected into the reactant solution at the zeroth turnover (Figure 7.3), consistent with the titration of progressively larger fractions of active sites with increasing pyridine/DTBP ratios. More specifically, the net TON reduces to that of the background reaction at an initial pyridine to metal molar ratio of 1, suggesting that Lewis and/or Brønsted acid sites are related (in provenance) to the metal atoms. Zhang and coworkers also observed a significant decrease in yield of benzaldehyde glycol acetal over MIL-100(Fe), close to that in the absence of any catalyst, in the presence of stoichiometric quantities of pyridine.<sup>66</sup> Titration with DTBP, a Brønsted acid selective titrant, also leads to a significant reduction in net TON as a function of titrant:metal molar ratio, but crucially, results in a residual untitrated fraction of sites even at ratios as high as 1. Specifically, an approximately 63% reduction in net TON is observed at a titrant to metal molar ratio of 1 for both MIL-100(Fe) and MIL-100(Cr). Considering existing evidence



**Figure 7.3.** Ratio of the net TON for MIL-100 in the presence of pyridine or DTBP to the net TON in the absence of any titrant after 15 minutes of reaction as a function of the titrant to metal molar ratio. Closed and open symbols represent MIL-100(Cr) and MIL-100(Fe), respectively.

supporting the inability of DTBP to titrate Lewis acid sites,<sup>360,361</sup> at least part of the acetalization activity over MIL-100 can be attributed to contributions from Brønsted acid sites, thereby eliminating the possibility of exclusively Lewis acid catalysis, as suggested in some previous literature reports.<sup>66,335,336,340</sup> Not only do the titration data eliminate the possibility of solely Lewis acid catalysis, but point to a significant portion of the catalytic activity being associated with Brønsted acid sites. The titration data, although definitive in terms of the contribution of Brønsted acid sites, also raises the question as to why DTBP, unlike pyridine, titrates only a fraction of the acid sites. Two distinct possibilities exist in this context: 1) both Brønsted and Lewis acid sites contribute significantly to the activity, with DTBP titrating Brønsted acid sites and pyridine titrating both or 2) the acetalization activity originates predominantly or exclusively from Brønsted acid sites, but a portion of

the Brønsted acid sites are accessible only to pyridine, not DTBP, under the reaction conditions used in this study. In the next section we address the possibility of the former, in part by exploring the genesis of Brønsted acidity in MIL-100, and in Section 3.4 we address the relevancy of the question of DTBP accessibility raised in the latter.

#### 7.3.3. What is the source of Brønsted Acidity in MIL-100?

The creation of coordinatively unsaturated metal sites in MIL-100 that can function as Lewis acid sites has been the subject of numerous investigations.<sup>47,70,71,369,370</sup> For example, Vimont and coworkers demonstrated a progressive increase in density of MIL-100(Cr) open-metal sites with increasing thermal treatment temperature, with up to approximately two-thirds of the total metal content being accessible when outgassed at 523 K.<sup>132</sup> Additionally, Yoon *et al.* demonstrated the possibility of accessing both Fe<sup>3+</sup> and Fe<sup>2+</sup> sites in MIL-100(Fe) with the concentration of open-metal sites reaching approximately 3.55 mmol g<sup>-1</sup> (theoretical total iron = 5.02 mmol g<sup>-1</sup>) when activated under vacuum for 12 hours at 523 K, with Fe<sup>2+</sup> sites representing 23% of the sites measured with CO adsorption.<sup>42</sup> Further, others like Zhang and colleagues have related such changes in open-metal site density to catalytic performance, for example ethene oligomerization.<sup>70,71</sup>

The genesis of the Brønsted acidity in MIL-100, on the other hand, unlike that of Lewis acidity, remains less well-ascertained. One suggestion in this respect, however, is that water molecules ligated to metal atoms are a potential source of Brønsted acidity.<sup>132,155,338</sup> This property was first reported by Vimont and coworkers in a series of studies investigating acid sites in MIL-100(Cr).<sup>132,155</sup> CO has been used extensively in characterization the both Lewis and Brønsted acid sites in solid materials due to the

proposed sensitivity of the carbonyl vibrational frequency to the acid strength and metal oxidation state.<sup>197,371–373</sup> Using infrared spectroscopy to investigate the interaction of CO with MIL-100, the authors concluded that the acid strength of coordinated water molecules was close to that of alkali-exchanged faujasite zeolites.<sup>374</sup> Notably, the terminal hydroxides present displayed a weaker interaction with CO, to which the authors indicated an acid strength approaching that of silanol groups.<sup>132,375</sup> In their evaluation of MIL-101(Cr) as a Brønsted acid catalyst for the acetalization of benzaldehyde with methanol, Janiak and coworkers completed pH measurements of the catalyst suspended in methanol and coated on KBr disks.<sup>338</sup> The pH values measured for both techniques ranged from 3.0 - 3.9 for MIL-101(Cr), with the lowest pH values being measured nearest to the catalyst particles, suggestive of the Brønsted acidity arising from the material. Indication of Brønsted acidity in MIL-100 was also demonstrated by pH values of 3.1 and 2.9 measured for MIL-100(Fe) dissolved in water in two separate studies.<sup>376,377</sup> Other sources of Brønsted acidity have also been put forth in the literature, for example, the suggestion by Horcajada and coworkers was that such acidification could be a result of deprotonation of carboxylic acids in the framework of MIL-100(Fe).377 We emphasize here that we do not delve into considerations of acid strength in our study, but merely present evidence consistent with the *participation* of Brønsted acid sites in MOF-mediated acetalization.

Given the increase in Lewis acid site density and the proposed concurrent decrease in Brønsted acid site density upon thermal treatment at progressively higher temperatures, we hypothesize that the exclusive participation of Lewis acid sites in acetalization would result in net TONs that increase with treatment temperature; on the other hand, the exclusive

participation of Brønsted acid sites should result in net TONs that decrease monotonically with treatment temperature (Figure 7.4). Treatment temperatures ranging from room temperature to 523 K were used to vary the density of water coordinated to metal sites, with the hydroxyl region in the infrared spectra confirming this expectation (vide infra). In contrast with trends expected due to a predominant contribution of open-metal Lewis acid sites, a monotonic decrease in net turnovers at any particular batch reaction time was observed as a function of increasing pretreatment temperature, with a near-complete loss of activity (about 10% of that of the untreated sample) observed at a treatment temperature of 523 K (Figure 7.5a). In order to eliminate the possibility of structural degradation resulting from thermal treatment being a cause of the decrease in net turnovers, a rehydration experiment was completed on the catalyst sample treated at 523 K. If the loss in turnovers at higher treatment temperatures is a consequence of structural degradation, not dehydration, the original activity should not be recovered upon exposure to ambient conditions. We expect that during the process of cooling to room temperature for 2 hours following thermal treatment the sample will re-adsorb a significant fraction of water at the hydrophilic open metal sites created during activation, rendering it much closer in degree of hydration to the untreated material that exhibits a H<sub>2</sub>O to Cr molar ratio of 5.5 (TGA data, Figure F1, Appendix F). The rehydrated sample effects a significantly higher number of net turnovers than the material immediately following thermal activation at 523 K (Figure 7.5b), inconsistent with significant (presumably irreversible) structural degradation upon thermal treatment. Rather than pointing to structural degradation as a contributing factor, this test in fact reemphasizes the validity of using the degree of hydration of the

material at the zeroth turnover to interpret the effect of treatment temperature on net TONs

(Figure 7.5a).



**Figure 7.4.** Representation of the thermal activation process in MIL-100 leading to the progressive removal of coordinated water molecules (source of Brønsted acidity) and the creation of open-metal sites (source of Lewis acidity).



**Figure 7.5.** (a) Net moles of BDA formed as a function of time for MIL-100(Cr) activated prior to reaction at the specified temperature for 15 hours under vacuum. (b) Net moles of BDA as a function of time for MIL-100(Cr) before and after pretreatment at 523 K.

Crucially, treatment at 523 K results in an 89% decrease in net TON to a value of 17 mol BDA (mol Cr)<sup>-1</sup>, a value approaching 4.5 mol BDA (mol Cr)<sup>-1</sup> measured for the

background reaction without catalyst. This near-complete elimination of measured turnovers (compared to 150 mol BDA (mol Cr)<sup>-1</sup> measured for the untreated sample) upon dehydration/dehydroxylation at 523 K suggests that a significant fraction of the turnovers over the untreated material *cannot* plausibly be associated with open-metal sites created upon thermal treatment. 523 K represents the treatment temperature at which the largest contribution from Lewis acid sites to the catalytic activity can be expected, meaning that the 40% residual turnovers detected after titration with DTBP (Section 7.3.2) cannot predominantly be associated with Lewis acid sites, but may instead point to active sites that cannot be accessed by DTBP under the experimental conditions used in this study. This result further suggests that there exists a fraction of Brønsted acid sites inaccessible to DTBP, but not pyridine, which are eliminated during thermal treatment protocols that serve to dehydrate the material. Overall, these data hint at the initial degree of hydration (manipulated using thermal treatment protocols) as being a key determinant of catalytic activity, and hence, point to the role of Brønsted acidity, rather than the density of coordinatively unsaturated sites (or Lewis acid sites), in effecting acetalization turnovers. We note that the attribution of active site identity to water coordinated to metal sites, although consistent with the data presented thus far, has not been demonstrated through direct evidence. We now discuss the use of in-situ infrared spectroscopy in the presence and absence of titrants to *directly* relate Brønsted acidity to coordinated water.

Infrared spectra of MIL-100(Cr) treated at 373 K exhibit two bands in close proximity between 3685 - 3645 cm<sup>-1</sup> (Figure 7.6a), previously assigned to asymmetric OH stretching vibrations of water coordinated directly to the Cr<sup>3+</sup> metal sites in MIL-100(Cr).<sup>132</sup> The

sharp band observed at lower wavenumbers (3580 cm<sup>-1</sup>) has been identified as corresponding to terminal hydroxides on the Cr<sup>3+</sup> sites. Upon DTBP introduction in sequential 10 µL injections, there is a systematic shift in the frequency of the OH bands to lower wavenumbers with subsequent doses, indicative of an increase in oxygen-hydrogen bond length upon DTBP adsorption. Additionally, the formation of a new band at approximately 3377 cm<sup>-1</sup> can be noted, the area of which increases monotonically with each additional injection of DTBP (Figure 7.6b). Corma and coworkers, in their investigations using DTBP as a probe molecule for characterizing external Brønsted acid sites in zeolites, found that an v(NH) band at 3370 cm<sup>-1</sup> could be observed upon reaction of DTBP with trifluoracetic acid and upon adsorption of DTBP onto protons in mordenite.<sup>365</sup> They concluded that this peak corresponded to the N-H bond between DTBP and the Brønsted acid site upon protonation of the amine. Gora-Marek et al. also observed a peak corresponding to the 3370 cm<sup>-1</sup> stretching vibration of DTBP following titration of external Brønsted acid sites in a series of zeolite materials, the area of which was unaffected by Lewis acid site density.<sup>368</sup> Based in part on these previous peak assignments, we assign the 3377 cm<sup>-1</sup> peak to the asymmetric N-H stretch originating from DTBP coordinated to Brønsted acidic water molecules on MIL-100 nodes.



Figure 7.6. (a) IR spectra of MIL-100(Cr) following activation at 373 K for 2 hours and then after 4 subsequent 10 μL doses of DTBP at 373 K. (b) Area of the 3377 cm<sup>-1</sup> band corresponding to N-H stretch of coordinated DTBP with increasing amount of DTBP introduced.

As explained earlier, MIL-100 Brønsted acid site density should be a strong function of thermal pretreatment temperature if these acid sites owe their genesis to the coordination of water to metal sites. In an effort to verify this expectation, MIL-100 was evacuated at progressively higher temperatures between 373 and 523 K, and then brought back to 373 K, at which temperature DTBP was dosed into the sample chamber. The area of the OH bands corresponding to coordinated water and hydroxide species progressively diminish with increasing thermal pretreatment temperature (Figure 7.7a), consistent with dehydration/ dehydroxylation processes responsible for the formation of open-metal sites. Crucially, the area of the N-H vibration corresponding to the binding of DTBP to coordinated water shows a concurrent increase as a function of treatment temperature (Figure 7.7b), evincing a relationship between the availability of coordinated water and Brønsted acid site density. A linear correlation between the area of the OH band corresponding to coordinated water molecules and the area of the N-H band (Figure 7.7c) supports the central hypothesis underlying this study- that the origin of Brønsted acid sites responsible for acetalization catalysis is linked to the coordination of water molecules to MIL-100 open-metal sites. Although there is a change in the intensity of OH band at 3580 cm<sup>-1</sup>, corresponding to the terminal hydroxides, upon the introduction of DTBP (Figure 7.6a), it is unclear to what extent they interact with the titrant or contribute to the catalytic performance of MIL-100 for the acetalization reaction. However, the strong correlation between the 3370 cm<sup>-1</sup> N-H vibration and the initial area of the OH band corresponding to coordinated water (Figure 7.7c) suggests their linear dependence in the absence of contributions from hydroxides interacting with DTBP. Further, we will analyze coordinated water molecules only, however, it is possible that the hydroxides may also exhibit Brønsted acidity which contributes to the activity of MIL-100.



Figure 7.7. (a) IR spectra of MIL-100-Cr following pretreatment at the indicated temperature. (b) Area the v(NH) band corresponding to titrated DTBP at 373 K. (c) Correlation between the area of the v(OH) stretch (coordinated water) and the v(NH) stretch of coordinated DTBP.



**Figure 7.8.** Comparison of the net TON obtained following pretreatment at 373, 423, 473, and 523 K as a function of the area of the v(OH) stretch for coordinated water molecules obtained from IR spectroscopy for each treatment temperature.

Moreover, cumulative net turnovers at 15, 30, and 60 minutes correlate positively with the area of the OH vibration associated with coordinated water molecules- a marker of Brønsted acid site density (Figure 7.8). The correlation between net TONs and Brønsted acid site density, achieved through analysis of the O-H band and DTBP N-H vibrations, emphasizes the contribution of coordinated water molecules to acetalization chemistry under the conditions used in this study. We assert that the propensity of these water molecules (presumably polarized through coordination to Cr Lewis acid centers) to catalyze the reaction under consideration is what underlies the increase in activity with degree of hydration discussed earlier in this section. A predominant contribution of Brønsted acid sites towards acetalization, however, still leaves unaddressed the question as to why a significant fraction of them are left untitrated by DTBP- a Brønsted acid site selective titrant- but not pyridine. In the next section, the question of accessibility of MIL- 100 Brønsted acid sites to pyridine and DTBP is taken on in greater detail, with the goal of improving our understanding of what differentiates titrated sites from untitrated ones.

#### 7.3.4. Are the turnovers left untitrated by DTBP also Brønsted acid-catalyzed?

In-situ titration data (Section 7.3.2), combined with the effect of thermal pretreatments (Section 7.3.3), point to a predominant contribution of Brønsted acid sites towards catalyzing acetalization turnovers under the experimental conditions explored in this study. Since the possibility of significant contributions of Lewis acid sites can be eliminated based on the large reduction in net TONs observed upon treatment at temperatures higher than 473 K (Figure 7.5a), we postulate that there must be a characteristic of pyridine that allows it to titrate a larger fraction of MIL-100 Brønsted acid sites than DTBP. A possible factor in this respect is the significantly larger kinetic diameter of DTBP  $(10 \text{ Å})^{362}$  compared to pyridine (5.4 Å).<sup>368</sup> To further gauge the accessibility of the Brønsted acid sites to DTBP in MIL-100, constraints imposed by the framework's topology must first be considered. The structure of MIL-100 contains two types of mesoporous cages with free diameters of 25 and 29 Å, accessible through pentagonal windows of ~ 6 Å diameter and hexagonal windows of ~ 9 Å diameter, respectively.<sup>43,68,334</sup> Note that the larger mesoporous cages have both pentagonal and hexagonal pore windows, the latter of which could provide access to DTBP. It is plausible, therefore, that while pyridine can access both smaller and larger mesoporous cages, DTBP may be able to access only the larger mesoporous cages under the reaction conditions used in this study.

In light of the possibility that DTBP may be able to access MIL-100 Brønsted acid sites only through hexagonal (9 Å) pore windows, we estimated the fraction of sites residing in

small versus large mesoporous cages in MIL-100 using previously published water adsorption isotherms. The bimodal mesoporous structure of MIL-100 is quite evident in its water adsorption isotherm, the two distinct condensation steps of which have been attributed to filling of small and large mesoporous cages at lower and higher relative pressures, respectively.<sup>141,150,157,158,378,379</sup> The sizes of these steps in the adsorption isotherm (Figure F6, Appendix F) translate to open-metal site densities in small and large mesoporous cages of 3.7 and 3.3 mol H<sub>2</sub>O per mol Cr, respectively. The surface areas ratios can then be calculated from the surface area to volume ratios of the cages 25 and 29 Å in diameter (details in Section F2.2, Appendix F). Assuming areal site density to be independent of cage size leads to the suggestion that 42% of sites are located within large mesoporous cages, consistent with that determined from parameters provided on the number of small and large mesoporous cages in the unit cell of MIL-100(Fe) by Papadopoulos and coworkers (Section F2.2).<sup>159</sup>

The mismatch between the fraction of sites titrated by DTBP (63%) and the fraction of sites in large cages (42%) suggests one of two possibilities: 1) DTBP does selectively titrate sites located only within larger cages, but sites in larger cages contribute disproportionately to the activity compared to smaller cages, either due to higher turnover frequencies or lower diffusion limitations or 2) sites titrated by DTBP are not exclusively present in the larger mesoporous cages. Although cage size can be a plausible descriptor of active site accessibility, our study does not present data definitively identifying the location of sites accessible to DTBP, nor does it provide clues as to the relative contributions of the two types of cages to the overall catalytic activity. In the rest of this study, we simply refer to

these sites as accessible and inaccessible sites, without delving into the precise material properties that render only a fraction of the sites accessible to DTBP.

To further probe the role DTBP diffusion constraints play in rendering a fraction of active sites untitrated, we investigate acetalization over materials with topologies that lighten these constraints, while also being endowed with an active site coordination environment identical to MIL-100. The first of these materials, MIL-101, features an identical inorganic node to MIL-100, however its terephthalic linkers delimit pore sizes of 29 and 34 Å accessible through 12 and 14.5 x 16 Å apertures, respectively.<sup>240</sup> We note that both of these window sizes are larger than those in MIL-100, and also larger than the kinetic diameter of DTBP (10 Å). The second material that we consider is a homogeneous complex (Cr-oxo), which in contrast with MIL-100 and MIL-101, is not synthesized in the presence of multidentate ligands; instead, the oxo-bridged trimers are terminated by unidentate benzoate ligands.<sup>300,333</sup> DTBP titrates a progressively greater fraction of acid sites in the order of decreasing diffusion constraints (Figure 7.9), with MIL-100 having the largest and the homogeneous analogue having the smallest fraction of untitrated sites. This observation is consistent with untitrated sites being Brønsted acid sites inaccessible to DTBP, not Lewis acid sites that DTBP is incapable of coordinating to. In addition to this expected effect of topology, invariance in the fraction of untitrated sites with metal identity when comparing MIL-100(Fe) and MIL-100(Cr) titration data (Figure 7.9) lends further credence to the prevalence of size constraints preventing DTBP from titrating all active sites.



**Figure 7.9.** Comparison of the fractional reduction of the net TON as a function of the stoichiometric ratio of titrant introduced for MIL-100(Fe), MIL-100(Cr), MIL-101(Cr), and the homogeneous Cr catalyst (Cr-oxo).

To further investigate the accessibility of MIL-100 Brønsted acid sites to DTBP and pyridine, a series of IR spectroscopy experiments were conducted in which the frequency of the OH vibrations were monitored subsequent to pyridine/DTBP adsorption. Two different sequences of titrant introduction were used, as shown in Figure 7.10. We hypothesize that while the introduction of enough moles of DTBP to saturate the surface would still allow for the further adsorption of pyridine (Figure 7.10, top panel), saturation of the surface first with pyridine would leave no Brønsted acid sites available for DTBP adsorption results in a progressive shift of the OH band towards lower wavenumbers. These red shifts, indicative of an increase in average O-H bond distance upon coordination of DTBP, have been observed previously upon formation of acid-base complexes, and are indicative of the Brønsted acidity of these sites that yield a hydrogen-bonded acid-base complex.<sup>371,380-382</sup>

For example, Maache *et al.* completed CO and pyridine adsorption on mordenites, in which interaction of both adsorbates with hydroxyl groups led to redshifts in the OH band, with the magnitude of the shift interpreted as an indicator of acid strength.<sup>380</sup> Similarly, Vimont and coworkers utilized 2,6-Dimethylpyridine (DMP) in the investigation of Brønsted acid strength over a series of faujasite zeolites.<sup>381</sup> They noted a linear relationship between OH band frequency shifts upon CO adsorption and the position of the DMP N-H band across five zeolites, with strongest Brønsted acid sites providing the largest perturbation in v(OH).



Figure 7.10. Representation of sequential DTBP and pyridine titration experiments.



**Figure 7.11.** IR spectra of MIL-100(Cr) following subsequent 10 µL doses of DTBP and pyridine into an inert flow at 373 K following pretreatment for 2 hours at 373 K.

Interaction of DTBP with water ligands in MIL-100(Cr) can lead to a more complex transformation of the OH stretching region as there will be some decoupling of the OH vibrations of the water molecule; i.e. only one of two hydrogen atoms interact directly with the probe molecule, as discussed previously by Vimont and coworkers in the case of CO adsorption on MIL-100(Cr).<sup>132,155</sup> The authors of this study concluded that the OH vibration corresponding to the free hydrogen atom shifted by a small extent in comparison to the one involved in forming the adsorption complex with carbon monoxide. A similar distinction into two different sets of O-H bonds upon DTBP coordination could explain the complex evolution of the infrared spectra in the OH region. Of the many spectral features within this region, we choose to focus on the shift in the 3653 cm<sup>-1</sup> band, which is the most easily identifiable and pronounced in all experiments. Furthermore, in the absence of direct quantification of the amount of amine adsorbed, which would require accurate estimation of molar extinction coefficients, the progressive redshift of the OH stretch will be considered a qualitative indicator of the fraction of sites titrated by DTBP and/or pyridine. Subsequent injections of DTBP result in a systematic shift in the frequency of the OH band originally at 3653 cm<sup>-1</sup>, and a concurrent growth of the NH band indicative of DTBP coordination to acid sites (Figure 7.11), with the OH frequency reaching a final position of  $3642 \text{ cm}^{-1}$  after four 10 µL injections at 373 K. The injection of pyridine subsequent to the adsorption of DTBP onto all Brønsted acid sites that can be accessed by it (doses 3 and 4) results in a significant redshift of the OH band to 3625 cm<sup>-1</sup>, with only a minor concurrent change in area of the NH band at 3377 cm<sup>-1</sup> (< 30 %), suggesting that a majority of coordinated DTBP is retained in its adsorbed state upon introduction of pyridine. No strong

NH band is observed upon adsorption of pyridine, only a broad increase in absorption in the 2600 – 2200 cm<sup>-1</sup> region of the spectra (Appendix F, Figure F7). Lord and Merrifield reported that the reaction of pyridine with hydrogen chloride results in a structureless band near 2450 cm<sup>-1</sup> corresponding to the N-H bond.<sup>383</sup> Such behavior may be a result of hydrogen bonding between the pyridium cation and the chloride anion, which lengthens the N-H bond and results in its appearance at a much lower frequency.<sup>384</sup> Hydrogen bonding can also occur between pyridinium ion and solid acids featuring hydroxyl groups (e.g. silica), as described by Parry, and is why the ring vibrations of pyridine are often analyzed for interactions with Brønsted acid sites.<sup>343</sup> Substituted amines, including 2,6dimethylpyridine and DTBP, on the other hand, have alkyl groups situated around the nitrogen atom that prevent the complex from forming a stronger coordinative bond with the anion, thereby retaining a shorter N-H bond.<sup>384</sup> Furthermore, as the ring vibrations of pyridinium ions fall in the 1700 - 1400 cm<sup>-1</sup> region,<sup>343</sup> they are not discernable in the spectra of MIL-100(Cr) due to bands corresponding to C-H bonds dominating this region. Hence, shifts in the OH band are used as the sole marker of interactions between pyridine and the Brønsted acid sites.

The significant shift in OH frequency upon pyridine adsorption subsequent to saturation in DTBP (Figure 7.11) supports one of the main themes of this study, which is that a significant fraction of Brønsted acid sites exist which can be titrated by pyridine, but not DTBP. It is important to note that there is an additional OH band at 3534 cm<sup>-1</sup> that appears following the adsorption of pyridine. This band at lower wavenumbers could represent the OH bond containing the hydrogen atom directly involved in the binding of

DTBP, the frequency of which can be much lower than that corresponding to the free hydrogen atom, as discussed above. Regardless of the assignment of this low-frequency OH band, the redshift of OH bands originating from coordinated water supports our assertion that pyridine can access Brønsted acid sites which DTBP cannot.

Completion of the same experiment while reversing the order of titrant introduction (pyridine doses followed by DTBP introduction) provides further evidence of the same. Pyridine adsorption leads to a systematic shift in the OH frequency from 3655 to 3628 cm<sup>-</sup> <sup>1</sup> (Figure 7.12), analogous to the data in Figure 7.11, indicating larger pyridinium surface coverages with each subsequent dose. Unlike the previous case, however, DTBP introduction after pyridine adsorption leads to no discernible change in the IR spectrum, reemphasizing the fact that pyridine can access most if not all acid sites in MIL-100 under these conditions, leaving no Brønsted sites available for DTBP to coordinate to. Consistent with this expectation, no peak corresponding to the NH vibration at 3377 cm<sup>-1</sup> is observed due to the saturation of sites with pyridine preventing DTBP adsorption. In summary, the dependence of the fraction of sites left untitrated by DTBP on framework topology but not metal identity, and shifts in the OH stretching frequency when pyridine is introduced after DTBP adsorption but not vice versa, are both consistent with limited accessibility of DTBP towards a fraction of MIL-100 sites. We reiterate that while these data support the identification of accessibility as the key attribute preventing in-situ titration of all MIL-100 Brønsted sites (Figure 7.3), definitive insights into specific structural features differentiating accessible sites from inaccessible ones are not clearly evident to us at the current stage in our investigation.



**Figure 7.12.** IR spectra of MIL-100(Cr) following subsequent 2 μL doses of pyridine and one 10 μL dose of DTBP into an inert flow at 373 K following pretreatment for 2 hours at 373 K.

#### 7.3.5. Can the presence of excess methanol prevent rehydration of the material?

A key open question this study raises relates to the importance of the degree of hydration preceding the occurrence of turnovers, but not the water content of the reaction solution during liquid phase catalysis, as a determinant of catalytic activity. Given the hundreds of moles of water per mole chromium generated as a byproduct in these runs, it is not exactly clear why water produced during the acetalization runs do not impact rates in such a way as to render insignificant catalytic differences observed as a function of treatment temperature (Figure 7.5). We hypothesize that the presence of excess methanol (CH<sub>3</sub>OH/H<sub>2</sub>O > 100) throughout the catalytic runs is a major factor contributing to the persistence of activity differences well beyond time scales where a mole of water per mole chromium has been produced through acetalization. We posit that activity differences noted as a function of thermal treatment temperature can likely only be sustained if high

methanol:water ratios can prevent water from coordinating to open-metal sites, thereby preventing the creation of Brønsted acid sites under reaction conditions. The propensity of water formed during reaction to bind to an open metal site in the presence of excess methanol was evaluated for MIL-100 thermally treated at 523 K. This condition represents the temperature at which the highest density of open metal sites is expected and was followed by DTBP adsorption to probe Brønsted acid site density. As expected, a significantly lower area of the NH peak was measured for the sample activated at 523 K in comparison to the sample activated at 373 K, resulting from a lower coordinated water to metal ratio (Figure 7.13a,b). Subsequent to DTBP adsorption, a 10  $\mu$ L injection of methanol and water ( $CH_3OH:H_2O$  molar ratio = 100) was introduced into the sample chamber. Methanol and water weakly bound to the sample were then allowed to desorb for 2 hours at 373 K. Crucially, DTBP injections onto this sample treated at 523 K and exposed to water and methanol evince Brønsted acid site densities near-identical to those before exposure to methanol and water, but significantly lower than those measured for the sample treated at 373 K (Figure 7.13a,b).

This invariance of site density upon exposure to methanol and water, in contrast with the recovery of Brønsted acid site densities achieved upon exposure to ambient air containing water vapor in the absence of methanol (Figure 7.5b), points to a lower propensity of methanol-water mixtures towards recreating Brønsted acid sites on MIL-100 nodes compared to pure water. We do not probe further the molecular-level basis for methanol outcompeting water in terms of access to Lewis acid sites; we merely state that it appears plausible, based on this experiment, that coordination of water to metal sites can be severely mitigated by the presence of excess methanol. We also do not seek to elucidate the nature and catalytic contribution, if any, of methanol adsorbed onto metal sites, but instead only seek to present an interpretation of catalytic, in-situ titration, and spectroscopic data consistent with the contribution of Brønsted acid sites owing their genesis to the ligation of water to MIL-100 open-metal sites- an interpretation borne out repeatedly in the trends reported throughout this study.



**Figure 7.13.** (a) IR spectra of MIL-100(Cr) following activation at the temperature indicated and titration by DTBP at 373 K. 523 K\* sample was exposed to a 10  $\mu$ L injection of CH<sub>3</sub>OH and H<sub>2</sub>O (CH<sub>3</sub>OH/H<sub>2</sub>O = 100) and then DTBP. (b) Area of the 3377 cm<sup>-1</sup> band for each condition.

# 7.4. Conclusions

In-situ titration of MIL-100 mediated acetalization of benzaldehyde and methanol with pyridine and DTBP indicates that while pyridine titrates all of the acid sites, DTBP titrates only 63% of the net TON at a batch reaction time of 15 minutes. The near-absence of acetalization turnovers upon thermal treatment at 523 K- the condition corresponding to

the highest open-metal site density in our study- eliminates the possibility of significant contributions from Lewis acid sites. Fractional turnovers untitrated that remain independent of metal identity, but decrease monotonically with lightening diffusion constraints around the oxo-centered trimer node, and the availability of Brønsted acid sites after DTBP injections but not after pyridine injections, all point to accessibility of DTBP as a factor preventing complete titration of active sites under reaction conditions. Linear correlations between not only the coordinated water density and Brønsted acid site density estimated from the DTBP N-H band, but also cumulative net turnovers and coordinated water density, point to ligation of water to open-metal sites in MIL-100 as the source of Brønsted acidity largely responsible for acetalization turnovers measured under the conditions reported here. These observations emphasize the need for exercising caution in claiming Lewis acid catalysis over MIL-100 type materials specifically, and highlight the importance of thoroughly investigating active site speciation under reaction conditions to more fully exploit the potential of MOF materials within and may be even beyond the realm of acid catalysis.

# 8. Concluding Thoughts

## 8.1. Summary

In this dissertation, the formation of redox-active open-metal sites in MOFs has been investigated primarily in the context of light alkane activation. Chapter 1 provided methodology for quantifying open-metal sites in MOF materials using irreversible water adsorption measurements, affording accurate quantification of sites irrespective of oxidation state and metal identity using the framework MIL-100 as an archetype. Chapter 2 delves into the capability of forming reduced divalent open-metal sites within MIL-100 frameworks, characterized through a variety of infrared spectroscopic and volumetric adsorption measurements. In Chapter 3, implications of open-metal sites formed in MIL-100 for the activation of light alkanes is explored, providing the first examples of iron and chromium-based MOFs oxidizing methane with N<sub>2</sub>O at low temperatures and ambient pressures. Chapter 6 utilizes CO as a reductant to further elucidate the kinetic relevance of elementary steps within N<sub>2</sub>O-mediated redox cycles, providing novel clarity into oxidation mechanisms over isolated metal sites within MOFs, more broadly. Chapter 7 investigates an interesting facet associated with MIL-100 oxidation catalysts involving the influence of secondary coordination sphere effects that significantly influence adsorption and catalytic properties of the material. Lastly, Chapter 8 investigates the properties of active sites in MIL-100 MOFs during the liquid-phase acetalization of benzaldehyde, presenting Brønsted-acidic water molecules, polarized by the Lewis acid centers, are primarily responsible for the catalytic turnovers measured under reaction conditions – emphasizing the importance of studying site speciation *under* reaction conditions to fully understand the

promise of MOF materials for acid-catalyzed reactions more broadly. The studies presented here capture the utility of exploring MOFs, specifically those which are endowed with a high level of definition in site structure, for boring out direct structure-function relationships that can not only lead to atomic-level catalyst improvement, but also aid in overcoming scientific challenges that persist in the field of heterogeneous catalyst research.

## 8.2. Recommendations for Future Research

## 8.2.1. Overcoming Limitations for Light Alkane Partial Oxidation

The development of a synthetic catalyst which can efficiently convert light alkanes to partially-oxygenated target species is a prospect that continues to challenge researchers to evaluate and identify novel materials. As described in this report, the potential of metal-organic frameworks to be adapted for applications in light alkane oxidation has been demonstrated experimentally and evaluated comprehensively by theoretical computations. Notably, MOF materials have been identified with desirable features including (1) ability to mimic the structure/function of homogeneous or biological counterparts;<sup>105,106,108</sup> (2) capability to host high densities of well-defined active centers in comparison to analogous synthetic materials;<sup>109</sup> and (3) proficient use a variety of oxidants for catalytic and stoichiometric alkane conversion.<sup>24,105,106,108</sup> The library of structural components available for utilization in MOFs, affords the deliberate targeting of specific functionalities and presents the opportunity to explore an ever increasing number of MOF frameworks for alkane oxidation applications that have yet to be evaluated experimentally.<sup>113,238</sup>

In the pursuit of an industrially-viable process for the partial oxidation of light alkanes, selectivity, productivity, and abundance/cost of the oxidant have all been identified as

important factors to be considered. Additionally, the ability to operate catalytically versus cyclically also significantly impacts the viability of a given system. Of the MOFs evaluated, stoichiometric alkane oxidation has been achieved using O<sub>2</sub> and N<sub>2</sub>O as oxidants, in which product molecule desorption is promoted by reaction with water following reaction.<sup>24,73,109,111,235</sup> This method can provide high selectivity toward partially oxygenated species, as product molecules are released under conditions that prevent undesirable overoxidation, however, can lead to limitations associated with length and productivity per cycle.<sup>385,386</sup> The ability to achieve higher densities of active metal is one way to improve viability of a stoichiometric process, which is one potential advantage offered by MOFs over other synthetic materials evaluated.<sup>387</sup> On the other hand, catalytic systems, although more amendable, will always feature drawbacks associated with the protection of products from overoxidation pathways.<sup>89,388</sup> As demonstrated with MIL-53(Fe,Al) and MIL-47/MOF-48(V) for the oxidation of methane with  $H_2O_2$  and  $K_2S_2O_8$ , <sup>108,235</sup> respectively, catalytic light alkane oxidation with MOFs could be achieved in batch processes. Selective acetic acid formation could be achieved over both vanadium MOFs even at high turnover numbers,<sup>235</sup> and MIL-53(Fe,Al) could yield high partial oxygenate selectivity at low turnovers (< 100) albeit suffering from competing  $H_2O_2$ decomposition pathways.<sup>108,389</sup>

In conclusion, the application of metal-organic frameworks for the partial oxidation of light alkanes is a novel area of research, though one that continues to grow with increasing number of experimental and theoretical evaluations. Efforts to elucidate alkane oxidation pathways, isolate rate-determining reaction steps, and identify global activity descriptors is critical to the advancement of MOF materials for light alkane conversion and will continue to steer the evaluation of new materials, more broadly. Specifically, further understanding of the effect of metal identity, nuclearity, coordination environment, and proximity of active centers to promotional metals or linker-functionalities will be critical to development of new metal-organic frameworks that can surpass current materials in reactivity, productivity, and selectivity. As identified from the current breadth of studies, rigorous elucidation of active site identities and reaction kinetics experimentally, concertedly guided and supported by theoretical evaluations, will be the cornerstone of this effort.

# 8.2.2. Reducing Barriers for Metal-Oxo Formation in N<sub>2</sub>O-Mediated Oxidation Chemistries

As discussed in Chapters 5 and 6 of this dissertation, elementary reaction steps associated with the adsorption and decomposition of N<sub>2</sub>O have significant kinetic relevance during both CH<sub>4</sub> and CO oxidation over iron and chromium-containing MIL-100 MOF frameworks. In general, DFT studies predicting energy barriers in the oxidation of light alkanes by N<sub>2</sub>O over MOF nodes tend to consistently predict that N<sub>2</sub>O decomposition, and metal-oxo site formation, is the most energetically-demanding reaction step, even in comparison to methane C-H activation steps.<sup>72,74,114</sup> Specifically, in their evaluation of MIL-type nodes for the partial oxidation of CH<sub>4</sub>, Barona and Snurr evaluated a large series of mono/multi-metallic cluster compositions ((M<sub>1</sub><sup>3+</sup>)<sub>2</sub>(M<sub>2</sub><sup>2+</sup>)O, M = V, Cr, Mn, Fe, Co, or Ni) and found the corresponding energy barrier for N<sub>2</sub>O activation to be greater than that for C-H activation for 58 of the 66 active sites evaluated.<sup>74</sup>

In Chapter 6, it was demonstrated that increasing ligation of water, or other alcohol molecules, to the M<sup>3+</sup> sites within a given trimetallic node negatively impacts the turnover rate of an  $M^{2+}$  within the same node, regardless of the identity of the metal (Fe or Cr). For MIL-100(Fe), it could be demonstrated that this effect increases the apparent activation energy barrier for the decomposition of N2O, and in chromium MIL-100, this led to increased dependence of the overall oxidation rate on the partial pressure of the oxidant. Although the demonstrated secondary sphere coordination effects negatively affected the performance of the catalyst, the identification of such influences can aid in developing levers for tuning the active site properties in positive dimensions for a given application. For instance, the identification of a ligand, which when coordinated to the trimer node, has the inverse influence. As electron donating ligands with increasing proton affinities lead to systematic reductions in the average turnover rate at a given ligand to node molar ratio, it could be postulated that the coordination of an electron withdrawing ligand may provide a promoting effect on the reactivity of the node toward N<sub>2</sub>O reduction. However, due to the Lewis acidic nature of the trivalent metal centers in MIL-100, the identification of an acidic ligand which remains bound under relevant reaction conditions may be synthetically challenging.

#### 8.2.3. Economical Oxidants for C-H Activation

In the evaluation of mononuclear divalent centers in MOFs for the partial oxidation of light alkanes, N<sub>2</sub>O is the most commonly considered oxidant due the more facile twoelectron oxidation cycle (Fe<sup>2+</sup> + N<sub>2</sub>O  $\leftrightarrow$  Fe<sup>4+</sup>=O + N<sub>2</sub>).<sup>72–74,287</sup> Although quite valuable for evaluating the formation and reactivity of metal-oxo species in MOF supports from a fundamental perspective, the use of N<sub>2</sub>O as a commercial oxidant is costly in comparison to more abundant oxidants such as O<sub>2</sub> or H<sub>2</sub>O. However, N<sub>2</sub>O represents one of the most significant anthropogenic greenhouse gases (7% of the total U.S. greenhouse gas emissions, 2019) with main emission sources including agriculture, fossil fuel combustion, and industrial processes.<sup>390,391</sup> Although the utilization of N<sub>2</sub>O from harmful emission sources could incentivize its use as an industrial oxidant for light alkane conversion, the evaluation of other oxidants could aid in improving the commercial viability of cyclic and catalytic C-H activation routes over MOF catalysts.

A primary feature of methane monooxygenase (MMO) enzymes which makes them of particular interest to scientists is their capability to selectively transform methane to methanol using molecular oxygen.<sup>392,393</sup> Although there have been reports of methane oxidation by O<sub>2</sub> over Cu-oxo species in both zeolites and MOF materials,<sup>24,88,95,111,235,394</sup> primarily only oxidation with H<sub>2</sub>O<sub>2</sub> and N<sub>2</sub>O had been observed for the corresponding Febased catalysts.<sup>108,211,395,396</sup> Recently, however, Andrikopoulos and colleagues demonstrated the capability of binuclear Fe<sup>2+</sup> sites incorporated into ferrierite zeolite to cleave O<sub>2</sub> at room temperature, to form two distinct Fe<sup>4+</sup>=O species, capable of oxidizing CH<sub>4</sub> to CH<sub>3</sub>OH.<sup>397</sup> Importantly for this transformation, the Fe<sup>2+</sup> centers exist as a pair of adjacent sites, separated by a distance of approximately 5 – 5.2 Å, such that a [Fe-O-O-Fe] intermediate can form to yield the final 2[Fe=O] species (Figure 8.1a). Furthermore, it is possible that M-M distances in MIL-100 may also facilitate O<sub>2</sub> dissociation, as adjacent metal sites feature distances as short as approximately 3.8 – 4 Å (Figure 8.1b). Several existing studies have already demonstrated the potential of Fe and Cr MII-100 catalysts for

 $O_2$ -mediated chemistries including the oxidation of cyclohexane,<sup>398</sup> cylcohexene,<sup>399</sup> and  $\alpha$ -/ $\beta$ -pinenes.<sup>400</sup> Additional reports have also indicated the potential for M<sup>2+</sup> sites to form superoxo ( $O_2$ )<sup>-</sup> or peroxo ( $O_2$ )<sup>2-</sup> species upon  $O_2$  adsorption in both Fe and Cr MOFs.<sup>179,180,401,402</sup> Finally, given the tremendous potential for these materials to activate  $O_2$ , future efforts could be geared toward exploring this capability for the oxidation of light alkanes.



**Figure 8.1.** (a) DFT simulated structures of two adjacent Fe sites in ferrierite upon formation of an [Fe-O-O-Fe] intermediate and two [Fe=O] product sites, reproduced from Ref.<sup>397</sup> (b) Schematic of the small pores in MIL-100(Fe) and the relative distance between the metal centers.

### 8.2.4. Evaluation of a Broader Range of Transition Metal MIL-100 MOF Catalysts

In the family of MIL-100 materials, several compositions of metal nodes have been realized including Fe,<sup>68</sup> Cr,<sup>43</sup> V,<sup>173</sup> Sc,<sup>47</sup> Al,<sup>140</sup> In,<sup>247</sup> and Mn.<sup>174</sup> Consequently, several experimental and computational studies have attempted to identify relationships between metal identity and performance in both application of catalysis<sup>47,114,127,247,403,404</sup> and gas adsorption.<sup>173,405,406</sup> Specifically, DFT simulations completed by Rosen *et al.* identified linear relationships between metal group number and the energy barrier for the C-H bond activation of methane.<sup>114</sup> Experimentally, however, the ability to elucidate such trends between metal identity and some activity descriptor has not been demonstrated.

Furthermore, it would be valuable to compare the performance of MIL-100 catalysts with various metal cations for the oxidation of CH<sub>4</sub> and CO. Ideally, turnover-frequencies of CO oxidation and experimentally determined activation energy barriers for the reaction could be used as a basis for comparison of the different metal analogues of MIL-100. As described in Chapter 3 and Chapter 4 of this document, both Cr- and Fe-variants of MIL-100 have been successfully synthesized, in which  $M^{2+}$  active site densities (0.29 – 0.30 mol (mol  $M^{2+})^{-1}$ )<sup>227,236</sup> near the theoretical maximum (0.33 mol (mol  $M^{2+})^{-1}$ ) could be attained upon activation at 523 K in vacuum or under inert flow. Moreover, results of CH<sub>4</sub> and CO oxidation experiments over both catalysts has highlighted the significant role of active metal identity (Fe or Cr) in controlling product selectivity and in the kinetic relevance of oxidation and reduction elementary reaction steps in the redox cycles.

Despite the broad range of transition metal MIL-100 frameworks synthesized, Fe and Cr represent the only two of which significant divalent metal site densities have been accessed through traditional thermal activation routes.<sup>42,227</sup> More recently, Dincă and colleagues presented the use of chemical reduction as a route for accessing divalent vanadium sites within the closely related MOF framework, MIL-101.<sup>407</sup> Specifically, Mashima's reagent (1,4-bis(trimethylsilyl)-2,3,5,6-tetramethyl-1,4-dihydropyrazine)<sup>408,409</sup> was used to react with terminal chloride anions and produce coordinatively unsaturated V<sup>2+</sup> open-metal sites, offering another potential route for accessing seemingly elusive divalent metal sites within a wider range of MIL-type MOF frameworks. Moreover, results of our own work (presented in Chapter 2) suggest that the nature of the anionic ligand (X<sup>-</sup>) in MIL-100 may play an important role in the capability to access divalent open-metal sites

through facile thermal treatment.<sup>227</sup> Specifically, Cr<sup>2+</sup> open-metal site densities in exclusively (OH<sup>-</sup>)-containing MIL-100(Cr) were found to significantly exceed those reported previously for MIL-100(Cr) containing predominantly F<sup>-</sup> anions.<sup>59</sup> Furthermore, the synthesis of MIL-100 featuring more labile anionic ligands, specifically OH<sup>-</sup>, may allow for achieving higher M<sup>2+</sup> open-metal site densities in a broader range of transition metal compositions. In an experimental study conducted by Feng and coworkers, the use of Al(III)Cl<sub>3</sub> was used to exchange F<sup>-</sup> ions with Cl<sup>-</sup> ions in MIL-100(Cr), the later of which could also be exchanged with OH<sup>-</sup> through reaction with NaOH, without any significant loss of crystallinity as indicated by powder XRD measurements.<sup>410</sup> Moreover, the application of such anionic ligand exchange routes in producing MIL-100 samples in which divalent metal sites can be accessed through facile thermal activation could be a valuable method to consider for future evaluations, specifically in applications of redox catalysis where such sites are the predominant active site.

# References

- Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular Synthesis and the Design of New Materials. *Nature* 2003, *423*, 705–714.
- Janiak, C. Engineering Coordination Polymers towards Applications. *Dalt. Trans.* 2003, 0, 2781–2804.
- (3) Férey, G. Building Units Design and Scale Chemistry. J. Solid State Chem. 2000, 152, 37–48.
- (4) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. Crystallized Frameworks with Giant Pores: Are There Limits to the Possible? *Acc. Chem. Res.* 2005, *38*, 217–225.
- Yildirim, T.; Hartman, M. Direct Observation of Hydrogen Adsorption Sites and Nanocage Formation in Metal-Organic Frameworks. *Phys. Rev. Lett.* 2005, 95, 215504.
- Vitillo, J. G.; Regli, L.; Chavan, S.; Ricchiardi, G.; Spoto, G.; Dietzel, P. D. C.;
  Bordiga, S.; Zecchina, A. Role of Exposed Metal Sites in Hydrogen Storage in MOFs. J. Am. Chem. Soc. 2008, 130, 8386–8396.
- Li, H.; Wang, K.; Sun, Y.; Lollar, C. T.; Li, J.; Zhou, H.-C. Recent Advances in Gas Storage and Separation Using Metal–Organic Frameworks. *Mater. Today* 2018, *21*, 108–121.
- (8) Rieter, W. J.; Taylor, K. M. L.; Lin, W. Surface Modification and Functionalization of Nanoscale Metal-Organic Frameworks for Controlled Release and Luminescence Sensing. J. Am. Chem. Soc. 2007, 129, 9852–9853.

- (9) Chen, B.; Wang, L.; Zapata, F.; Qian, G.; Lobkovsky, E. B. A Luminescent Microporous Metal-Organic Framework for the Recognition and Sensing of Anions. J. Am. Chem. Soc. 2008, 130, 6718–6719.
- (10) Achmann, S.; Hagen, G.; Kita, J.; Malkowsky, I. M.; Kiener, C.; Moos, R. Metal-Organic Frameworks for Sensing Applications in the Gas Phase. *Sensors* 2009, *9*, 1574–1589.
- Horcajada, P.; Serre, C.; Maurin, G.; Ramsahye, N. A.; Balas, F.; Vallet-Regí, M.;
   Sebban, M.; Taulelle, F.; Férey, G. Flexible Porous Metal-Organic Frameworks for a Controlled Drug Delivery. *J. Am. Chem. Soc.* 2008, *130*, 6774–6780.
- (12) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. Metal–Organic Frameworks in Biomedicine. *Chem. Rev.* 2012, *112*, 1232–1268.
- (13) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. Metal-Organic Framework Materials as Catalysts. *Chem. Soc. Rev.* 2009, *38*, 1450–1459.
- Mueller, U.; Schubert, M.; Teich, F.; Puetter, H.; Schierle-Arndt, K.; Pastré, J.
   Metal–Organic Frameworks Prospective Industrial Applications. *J. Mater. Chem.* 2006, 16, 626–636.
- (15) Farrusseng, D.; Aguado, S.; Pinel, C. Metal-Organic Frameworks: Opportunities for Catalysis. *Angew. Chemie Int. Ed.* **2009**, *48*, 7502–7513.
- (16) Corma, A.; García, H.; Llabrés i Xamena, F. X. Engineering Metal Organic
   Frameworks for Heterogeneous Catalysis. *Chem. Rev.* 2010, *110*, 4606–4655.
- (17) Ranocchiari, M.; Bokhoven, J. A. Van. Catalysis by Metal-Organic Frameworks:

Fundamentals and Opportunities. Phys. Chem. Chem. Phys. 2011, 13, 6388–6396.

- (18) Zhao, S. N.; Song, X. Z.; Song, S. Y.; Zhang, H. J. Highly Efficient Heterogeneous Catalytic Materials Derived from Metal-Organic Framework Supports/Precursors. *Coord. Chem. Rev.* 2017, *337*, 80–96.
- (19) García-García, P.; Müller, M.; Corma, A. MOF Catalysis in Relation to Their Homogeneous Counterparts and Conventional Solid Catalysts. *Chem. Sci.* 2014, *5*, 2979–3007.
- (20) Metzger, E. D.; Brozek, C. K.; Comito, R. J.; Dinca, M. Selective Dimerization of Ethylene to 1-Butene with a Porous Catalyst. ACS Cent. Sci. 2016, 2, 148–153.
- Metzger, E. D.; Comito, R. J.; Hendon, C. H.; Dincă, M. Mechanism of Single-Site Molecule-like Catalytic Ethylene Dimerization in Ni-MFU-4l. *J. Am. Chem. Soc.*2017, 139, 757–762.
- (22) Comito, R. J.; Metzger, E. D.; Wu, Z.; Zhang, G.; Hendon, C. H.; Miller, J. T.;
   Dincă, M. Selective Dimerization of Propylene with Ni-MFU-41. *Organometallics* 2017, *36*, 1681–1683.
- (23) Collis, A. E. C.; Horvath, Istvan, T. Heterogenization of Homogeneous Catalytic Systems. *Catal. Sci. Technol.* 2011, *1*, 912–919.
- (24) Ikuno, T.; Zheng, J.; Vjunov, A.; Sanchez-Sanchez, M.; Ortuño, M. A.; Pahls, D. R.; Fulton, J. L.; Camaioni, D. M.; Li, Z.; Ray, D.; Mehdi, B. L.; Browning, N. D.; Farha, O. K.; Hupp, J. T.; Cramer, C. J.; Gagliardi, L.; Lercher, J. A. Methane Oxidation to Methanol Catalyzed by Cu-Oxo Clusters Stabilized in NU-1000 Metal-Organic Framework. *J. Am. Chem. Soc.* 2017, *139*, 10294–10301.

- (25) Goetjen, T. A.; Knapp, J. G.; Syed, Z. H.; Hackler, R. A.; Zhang, X.; Delferro, M.; Hupp, J. T.; Farha, O. K. Ethylene Polymerization with a Crystallographically Well-Defined Metal–Organic Framework Supported Catalyst. *Catal. Sci. Technol.* 2022, *12*, 1619–1627.
- (26) Yeh, B.; Vicchio, S. P.; Chheda, S.; Zheng, J.; Schmid, J.; Löbbert, L.; Bermejo-Deval, R.; Gutiérrez, O. Y.; Lercher, J. A.; Lu, C. C.; Neurock, M.; Getman, R. B.; Gagliardi, L.; Bhan, A. Site Densities, Rates, and Mechanism of Stable Ni/UiO-66 Ethylene Oligomerization Catalysts. *J. Am. Chem. Soc.* 2021, *143*, 20274–20280.
- (27) Zhang, Y.; Yang, X.; Zhou, H. C. Synthesis of MOFs for Heterogeneous Catalysis via Linker Design. *Polyhedron* 2018, *154*, 189–201.
- (28) Jiang, J.; Yaghi, O. M. Brønsted Acidity in Metal-Organic Frameworks. *Chem. Rev.* 2015, *115*, 6966–6997.
- (29) Xu, C.; Sun, K.; Zhou, Y. X.; Ma, X.; Jiang, H. L. Light-Enhanced Acid Catalysis over a Metal–Organic Framework. *Chem. Commun.* 2018, *54*, 2498–2501.
- (30) Goesten, M. G.; Juan-Alcañiz, J.; Ramos-Fernandez, E. V.; Sai Sankar Gupta, K.
  B.; Stavitski, E.; Van Bekkum, H.; Gascon, J.; Kapteijn, F. Sulfation of Metal–
  Organic Frameworks: Opportunities for Acid Catalysis and Proton Conductivity. *J. Catal.* 2011, 281, 177–187.
- (31) Navalón, S.; Álvaro, M.; Dhakshinamoorthy, A.; García, H. Encapsulation of Metal Nanoparticles within Metal–Organic Frameworks for the Reduction of Nitro Compounds. *Molecules* 2019, 24, 3050.
- (32) Rösler, C.; Dissegna, S.; Rechac, V. L.; Kauer, M.; Guo, P.; Turner, S.; Ollegott,
K.; Kobayashi, H.; Yamamoto, T.; Peeters, D.; Wang, Y.; Matsumura, S.; van Tendeloo, G.; Kitagawa, H.; Muhler, M.; Llabrés I Xamena, F. X.; Fischer, R. A. Encapsulation of Bimetallic Metal Nanoparticles into Robust Zirconium-Based Metal–Organic Frameworks: Evaluation of the Catalytic Potential for Size-Selective Hydrogenation. *Chem. – A Eur. J.* **2017**, *23*, 3583–3594.

- Pachfule, P.; Yang, X.; Zhu, Q. L.; Tsumori, N.; Uchida, T.; Xu, Q. From Ru
   Nanoparticle-Encapsulated Metal–Organic Frameworks to Highly Catalytically
   Active Cu/Ru Nanoparticle-Embedded Porous Carbon. *J. Mater. Chem. A* 2017, *5*, 4835–4841.
- (34) Han, L.; Qi, H.; Zhang, D.; Ye, G.; Zhou, W.; Hou, C.; Xu, W.; Sun, Y. A Facile and Green Synthesis of MIL-100(Fe) with High-Yield and Its Catalytic Performance. *New J. Chem.* 2017, *41*, 13504–13509.
- (35) Yepez, R.; Garcí, S.; Schachat, P.; Sánchez-Sánchez, M.; González-Estefan, J. H.;
  González-Zamora, E.; Ibarra, I. A.; Aguilar-Pliego, J.; Bartolo Atepehuacan, S.
  Catalytic Activity of HKUST-1 in the Oxidation of Trans-Ferulic Acid to Vanillin. *New J. Chem.* 2015, *39*, 5112–5115.
- (36) Akiyama, G.; Matsuda, R.; Sato, H.; Kitagawa, S. Catalytic Glucose Isomerization by Porous Coordination Polymers with Open Metal Sites. *Chem. An Asian J.* **2014**, *9*, 2772–2777.
- (37) Chen, B.; Eddaoudi, M.; Reineke, T. M.; Kampf, J. W.; O'Keeffe, M.; Yaghi, O.
  M. Cu<sub>2</sub>(ATC)·6H<sub>2</sub>O: Design of Open Metal Sites in Porous Metal–Organic
  Crystals (ATC: 1,3,5,7-Adamantane Tetracarboxylate). J. Am. Chem. Soc. 2000,

122, 11559–11560.

- (38) S-Y Chui, S.; M-F Lo, S.; H Charmant, J. P.; Guy Orpen, A.; Williams, I. D. A Chemically Functionalizable Nanoporous Material [Cu<sub>3</sub>(TMA)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>] N. *Science* 1999, 283, 1148–1150.
- (39) Karra, J. R.; Walton, K. S. Effect of Open Metal Sites on Adsorption of Polar and Nonpolar Molecules in Metal-Organic Framework Cu-BTC. *Langmuir* 2008, 24.
- (40) Hailian Li; Charles E. Davis; Thomas L. Groy; Kelley, D. G.; Yaghi, O. M.
  Coordinatively Unsaturated Metal Centers in the Extended Porous Framework of Zn<sub>3</sub>(BDC)<sub>3</sub>·6CH<sub>3</sub>OH (BDC = 1,4-Benzenedicarboxylate). *J. Am. Chem. Soc.* 1998, *120*, 2186–2187.
- (41) Hong, D. Y.; Hwang, Y. K.; Serre, C.; Férey, G.; Chang, J. S. Porous Chromium Terephthalate MIL-101 with Coordinatively Unsaturated Sites: Surface Functionalization, Encapsulation, Sorption and Catalysis. *Adv. Funct. Mater.* 2009, *19*, 1537–1552.
- (42) Yoon, J. W.; Seo, Y.-K.; Hwang, Y. K.; Chang, J.-S.; Leclerc, H.; Wuttke, S.;
  Bazin, P.; Vimont, A.; Daturi, M.; Bloch, E.; Llewellyn, P. L.; Serre, C.;
  Horcajada, P.; Grenèche, J.-M.; Rodrigues, A. E.; Férey, G. Controlled
  Reducibility of a Metal-Organic Framework with Coordinatively Unsaturated Sites
  for Preferential Gas Sorption. *Angew. Chem. Int. Ed.* 2010, *49*, 5949–5952.
- (43) Férey, G.; Serre, C.; Mellot-Draznieks, C.; Millange, F.; Surblé, S.; Dutour, J.;
   Margiolaki, I. A Hybrid Solid with Giant Pores Prepared by a Combination of
   Targeted Chemistry, Simulation, and Powder Diffraction. *Angew. Chem. Int. Ed.*

**2004**, *43*, 6296–6301.

- (44) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.;
  Lillerud, K. P. A New Zirconium Inorganic Building Brick Forming Metal
  Organic Frameworks with Exceptional Stability. *J. Am. Chem. Soc.* 2008, *130*, 13850–13851.
- (45) Dietzel, P. D. C.; Panella, B.; Hirscher, M.; Blom, R.; Fjellvåg, H. Hydrogen
   Adsorption in a Nickel Based Coordination Polymer with Open Metal Sites in the
   Cylindrical Cavities of the Desolvated Framework. *Chem. Commun.* 2006, *9*, 959.
- (46) Kim, H. K.; Yun, W. S.; Kim, M.-B.; Kim, J. Y.; Bae, Y.-S.; Lee, J.; Jeong, N. C. A Chemical Route to Activation of Open Metal Sites in the Copper-Based Metal–Organic Framework Materials HKUST-1 and Cu-MOF-2. *J. Am. Chem. Soc.* 2015, *137*, 10009–10015.
- (47) Mitchell, L.; Gonzalez-Santiago, B.; Mowat, J. P. S.; Gunn, M. E.; Williamson, P.;
  Acerbi, N.; Clarke, M. L.; Wright, P. A. Remarkable Lewis Acid Catalytic
  Performance of the Scandium Trimesate Metal Organic Framework MIL-100(Sc)
  for C-C and C=N Bond-Forming Reactions. *Catal. Sci. Technol.* 2013, *3*, 606–617.
- (48) Chen, L.; Morrison, C. A.; Düren, T. Improving Predictions of Gas Adsorption in Metal–Organic Frameworks with Coordinatively Unsaturated Metal Sites: Model Potentials, Ab Initio Parameterization, and GCMC Simulations. *J. Phys. Chem. C* 2012, *116*, 18899.
- (49) Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. Exceptional H2 Saturation Uptake in Microporous Metal–Organic Frameworks. J. Am. Chem. Soc. 2006, 128, 3494–

3495.

- (50) Zhou, W.; Wu, H.; Yildirim, T. Enhanced H<sub>2</sub> Adsorption in Isostructural Metal–Organic Frameworks with Open Metal Sites: Strong Dependence of the Binding Strength on Metal Ions. J. Am. Chem. Soc. 2008, 130, 15268–15269.
- (51) Yazaydın, A. O.; Snurr, R. Q.; Park, T.-H.; Koh, K.; Liu, J.; LeVan, M. D.; Benin, A. I.; Jakubczak, P.; Lanuza, M.; Galloway, D. B.; Low, J. J.; Willis, R. R. Screening of Metal–Organic Frameworks for Carbon Dioxide Capture from Flue Gas Using a Combined Experimental and Modeling Approach. *J. Am. Chem. Soc.* 2009, *131*, 18198–18199.
- (52) Chowdhury, P.; Bikkina, C.; Meister, D.; Dreisbach, F.; Gumma, S. Comparison of Adsorption Isotherms on Cu-BTC Metal Organic Frameworks Synthesized from Different Routes. *Microporous Mesoporous Mater.* 2008, *117*, 406–413.
- (53) Gascon, J.; Corma, A.; Kapteijn, F.; Llabrés I Xamena, F. X. Metal Organic
   Framework Catalysis: Quo Vadis? ACS Catal. 2014, 4, 361–378.
- (54) Hall, J. N.; Bollini, P. Structure, Characterization, and Catalytic Properties of Open-Metal Sites in Metal Organic Frameworks. *React. Chem. Eng.* 2019, 4.
- (55) Horike, S.; Dincă, M.; Tamaki, K.; Long, J. R. Size-Selective Lewis Acid
   Catalysis in a Microporous Metal-Organic Framework with Exposed Mn 2+
   Coordination Sites. J. Am. Chem. Soc. 2008, 130, 5854–5855.
- (56) Alaerts, L.; Séguin, E.; Poelman, H.; Thibault-Starzyk, F.; Jacobs, P. A.; De Vos,
  D. E. Probing the Lewis Acidity and Catalytic Activity of the Metal-Organic
  Framework [Cu<sub>3</sub>(Btc)<sub>2</sub>] (BTC = Benzene-1,3,5-Tricarboxylate). *Chem. A Eur. J.*

**2006**, *12*, 7353–7363.

- (57) Wenge, Q.; Yu, W.; Chuanqiang, L.; Zongcheng, Z.; Xuehong, Z.; Guizhen, Z.;
  Rui, W.; Hong, H. Effect of Activation Temperature on Catalytic Performance of CuBTC for CO Oxidation. *Chinese J. Catal.* 2012, *33*, 986–992.
- (58) Hamon, L.; Heymans, N.; Llewellyn, P. L.; Guillerm, V.; Ghoufi, A.; Vaesen, S.;
  Maurin, G.; Serre, C.; De Weireld, G.; Pirngruber, G. D. Separation of CO<sub>2</sub>–CH<sub>4</sub>
  Mixtures in the Mesoporous MIL-100(Cr) MOF: Experimental and Modelling
  Approaches. *Dalt. Trans.* 2012, *41*, 4052.
- Yoon, J. W.; Chang, H.; Lee, S.-J.; Hwang, Y. K.; Hong, D.-Y.; Lee, S.-K.; Lee, J. S.; Jang, S.; Yoon, T.-U.; Kwac, K.; Jung, Y.; Pillai, R. S.; Faucher, F.; Vimont, A.; Daturi, M.; Férey, G.; Serre, C.; Maurin, G.; Bae, Y.-S.; Chang, J.-S. Selective Nitrogen Capture by Porous Hybrid Materials Containing Accessible Transition Metal Ion Sites. *Nat. Mater.* 2017, *16*, 526–531.
- (60) Wuttke, S.; Bazin, P.; Vimont, A.; Serre, C.; Seo, Y. K.; Hwang, Y. K.; Chang, J. S.; Férey, G.; Daturi, M. Discovering the Active Sites for C3 Separation in MIL-100(Fe) by Using Operando IR Spectroscopy. *Chem. A Eur. J.* 2012, *18*, 11959–11967.
- (61) Yoon, J. W.; Lee, J. S.; Lee, S.; Cho, K. H.; Hwang, Y. K.; Daturi, M.; Jun, C.-H.; Krishna, R.; Chang, J.-S. Adsorptive Separation of Acetylene from Light Hydrocarbons by Mesoporous Iron Trimesate MIL-100(Fe). *Chem. A Eur. J.* **2015**, *21*, 18431–18438.
- (62) Latroche, M.; Surblé, S.; Serre, C.; Mellot-Draznieks, C.; Llewellyn, P. L.; Lee, J.

H.; Chang, J. S.; Sung, H. J.; Férey, G. Hydrogen Storage in the Giant-Pore Metal-Organic Frameworks MIL-100 and MIL-101. *Angew. Chemie - Int. Ed.* **2006**, *45*, 8227–8231.

- (63) Cabello, C. P.; Rumori, P.; Palomino, G. T. Carbon Dioxide Adsorption on MIL-100(M) (M = Cr, V, Sc) Metal–Organic Frameworks: IR Spectroscopic and Thermodynamic Studies. *Microporous Mesoporous Mater.* 2014, 190, 234–239.
- (64) Hamon, L.; Serre, C.; Devic, T.; Loiseau, T.; Millange, F.; Rard Fé Rey, G.; De Weireld, G. Comparative Study of Hydrogen Sulfide Adsorption in the MIL-53(Al, Cr, Fe), MIL-47(V), MIL-100(Cr), and MIL-101(Cr) Metal-Organic Frameworks at Room Temperature. *J. Am. Chem. Soc.* 2009, *131*, 8775–8777.
- (65) Soubeyrand-Lenoir, E.; Vagner, C.; Yoon, J. W.; Bazin, P.; Ragon, F.; Hwang, Y. K.; Serre, C.; Chang, J.-S.; Llewellyn, P. L. How Water Fosters a Remarkable 5-Fold Increase in Low-Pressure CO<sub>2</sub> Uptake within Mesoporous MIL-100(Fe). *J. Am. Chem. Soc.* 2012, *134*, 10174–10181.
- (66) Zhang, F.; Shi, J.; Jin, Y.; Fu, Y.; Zhong, Y.; Zhu, W. Facile Synthesis of MIL-100(Fe) under HF-Free Conditions and Its Application in the Acetalization of Aldehydes with Diols. *Chem. Eng. J.* 2015, 259, 183–190.
- (67) Opanasenko, M. Catalytic Behavior of Metal-Organic Frameworks and Zeolites:
   Rationalization and Comparative Analysis. *Catal. Today* 2015, 243, 2–9.
- (68) Horcajada, P.; Surblé, S.; Serre, C.; Hong, D. Y.; Seo, Y. K.; Chang, J. S.;
  Grenèche, J. M.; Margiolaki, I.; Férey, G. Synthesis and Catalytic Properties of MIL-100(Fe), an Iron(III) Carboxylate with Large Pores. *Chem. Commun.* 2007,

100, 2820–2822.

- (69) Dhakshinamoorthy, A.; Alvaro, M.; Horcajada, P.; Gibson, E.; Vishnuvarthan, M.;
  Vimont, A.; Grene, J.; Serre, C.; Daturi, M. Comparison of Porous Iron Trimesates
  Basolite F300 and MIL-100(Fe) As Heterogeneous Catalysts for Lewis Acid and
  Oxidation Reactions: Roles of Structural Defects and Stability. *ACS Catal.* 2012, 2, 2060–2065.
- (70) Han, Y.; Zhang, Y.; Zhang, Y.; Cheng, A.; Hu, Y.; Wang, Z. Selective Ethylene Tetramerization with Iron-Based Metal–organic Framework MIL-100 to Obtain C8 Alkanes. *Appl. Catal. A Gen.* 2018, *564*, 183–189.
- (71) Liu, S.; Zhang, Y.; Han, Y.; Feng, G.; Gao, F.; Wang, H.; Qiu, P. Selective
   Ethylene Oligomerization with Chromium-Based Metal-Organic Framework MIL 100 Evacuated under Different Temperatures. *Organometallics* 2017, *36*, 632–638.
- (72) Vitillo, J. G.; Bhan, A.; Cramer, C. J.; Lu, C. C.; Gagliardi, L. Quantum Chemical Characterization of Structural Single Fe(II) Sites in MIL-Type Metal–Organic Frameworks for the Oxidation of Methane to Methanol and Ethane to Ethanol. *ACS Catal.* 2019, *9*, 2870–2879.
- (73) Simons, M. C.; Vitillo, J. G.; Babucci, M.; Hoffman, A. S.; Boubnov, A.;
  Beauvais, M. L.; Chen, Z.; Cramer, C. J.; Chapman, K. W.; Bare, S. R.; Gates, B.
  C.; Lu, C. C.; Gagliardi, L.; Bhan, A. Structure, Dynamics, and Reactivity for
  Light Alkane Oxidation of Fe(II) Sites Situated in the Nodes of a Metal–Organic
  Framework. J. Am. Chem. Soc. 2019, 141, 18142–18151.
- (74) Barona, M.; Snurr, R. Q. Exploring the Tunability of Trimetallic MOF Nodes for

Partial Oxidation of Methane to Methanol. *ACS Appl. Mater. Interfaces* **2020**, *12*, 28217–28231.

- (75) Gunay, A.; Theopold, K. H. C-H Bond Activations by Metal Oxo Compounds. *Chem. Rev.* 2010, *110*, 1060–1081.
- (76) Sharpless, K. B.; Flood, T. C. Oxotransition Metal Oxidants as Mimics for the Action of Mixed-Function Oxygenases."NIH Shift" with Chromyl Reagents. J. Am. Chem. Soc. 1971, 93, 2316–2318.
- (77) Ortiz De Montellano, P. R. Hydrocarbon Hydroxylation by Cytochrome P450 Enzymes. *Chem. Rev.* 2010, *110*, 932–948.
- (78) Mahyuddin, M. H.; Shiota, Y.; Yoshizawa, K. Methane Selective Oxidation to Methanol by Metal-Exchanged Zeolites: A Review of Active Sites and Their Reactivity. *Catal. Sci. Technol.* **2019**, *9*, 1744–1768.
- (79) Crabtree, R. H. Alkane C-H Activation and Functionalization with Homogeneous Transition Metal Catalysts: A Century of Progress - A New Millennium in Prospect. *Daltron Trans.* 2001, *17*, 2437–2450.
- (80) Dong, Y.; Fujii, H.; Hendrich, M. P.; Leising, R. A.; Pan, G.; Randall, C. R.;
  Wilkinson, E. C.; Zang, Y.; Que, L.; Fox, B. G.; Kauffmann, K.; Münck, E. A
  High-Valent Nonheme Iron Intermediate. Structure and Properties of [Fe<sub>2</sub>(μ-O)<sub>2</sub>(5Me-TPA)<sub>2</sub>] (ClO<sub>4</sub>)<sub>3</sub>. *J. Am. Chem. Soc.* **1995**, *117*, 2778–2792.
- (81) Sturgeon, B. E.; Burdi, D.; Chen, S.; Huynh, B. H.; Edmondson, D. E.; Stubbe, J.
   A.; Hoffman, B. M. Reconsideration of X, the Diiron Intermediate Formed during Cofactor Assembly in E. Coli Ribonucleotide Reductase. *J. Am. Chem. Soc.* 1996,

118, 7551–7557.

- (82) Lee, S.-K.; Nesheim, J. C.; Lipscomb\$, J. D. Transient Intermediates of the Methane Monooxygenase Catalytic Cycle. *J. Biol. Chem.* 1993, 268, 21569– 21577.
- (83) Liu, K. E.; Salifoglou, A.; Wang, D.; Huynh, B. H.; Edmondson, D. E.; Lippard, S. J. Spectroscopic Detection of Intermediates in the Reaction of Dioxygen with the Reduced Methane Monooxygenase Hydroxylase from Methylococcus Capsulatus (Bath). *J. Am. Chem. Soc.* **1994**, *116*, 7465–7466.
- (84) Kaserer, H. Ueber Die Oxydation Des Wasserstofes Und Des Methane Durch Mikroorganismen. Z. landv. Versuchsw. Deut. Oesterr., 1905, 8, 789.
- (85) Sohngen, N. L. Ueber Bakterien, Welch Methan Als Kohlenstoffnahrung Und Energiequelle Gebrauchen. Zentr. Bakt. Parasitenk., 1906, 15, 513–517.
- (86) Ross, M. O.; Rosenzweig, A. C. A Tale of Two Methane Monooxygenases. J.
   *Biol. Inorg. Chem.* 2017, 22, 307–319.
- (87) Kopp, D. A.; Lippard, S. J. Soluble Methane Monooxygenase: Activation of Dioxygen and Methane. *Curr. Opin. Chem. Biol.* 2002, *6*, 568–576.
- (88) Dinh, K. T.; Sullivan, M. M.; Narsimhan, K.; Serna, P.; Meyer, R. J.; Dincă, M.; Román-Leshkov, Y. Continuous Partial Oxidation of Methane to Methanol Catalyzed by Diffusion-Paired Copper Dimers in Copper-Exchanged Zeolites. *J. Am. Chem. Soc.* 2019, *141*, 11641–11650.
- (89) Narsimhan, K.; Iyoki, K.; Dinh, K.; Román-Leshkov, Y. Catalytic Oxidation of Methane into Methanol over Copper-Exchanged Zeolites with Oxygen at Low

Temperature. ACS Cent. Sci. 2016, 2, 424–429.

- (90) Panov, G. I.; Sobolev, V. I.; Dubkov, K. A.; Parmon, V. N.; Ovanesyan, N. S.;
  Shilov, A. E.; Shteinman, A. A. Iron Complexes in Zeolites as a New Model of Methane Monooxygenase. *React. Kinet. Catal. Lett.* **1997**, *61*, 251–258.
- (91) Starokon, E. V.; Parfenov, M. V.; Arzumanov, S. S.; Pirutko, L. V.; Stepanov, A. G.; Panov, G. I. Oxidation of Methane to Methanol on the Surface of FeZSM-5 Zeolite. *J. Catal.* 2013, *300*, 47–54.
- (92) Snyder, B. E. R.; Vanelderen, P.; Bols, M. L.; Hallaert, S. D.; Böttger, L. H.;
  Ungur, L.; Pierloot, K.; Schoonheydt, R. A.; Sels, B. F.; Solomon, E. I. The Active Site of Low-Temperature Methane Hydroxylation in Iron-Containing Zeolites. *Nature* 2016, *536*, 317–321.
- (93) Bols, M. L.; Hallaert, S. D.; Snyder, B. E. R.; Devos, J.; Plessers, D.; Rhoda, H. M.; Dusselier, M.; Schoonheydt, R. A.; Pierloot, K.; Solomon, E. I.; Sels, B. F. Spectroscopic Identification of the α-Fe/α-O Active Site in Fe-CHA Zeolite for the Low-Temperature Activation of the Methane C–H Bond. *J. Am. Chem. Soc.* 2018, *140*, 12021–12032.
- (94) Markovits, M. A. C.; Jentys, A.; Tromp, M.; Sanchez-Sanchez, M.; Lercher, J. A. Effect of Location and Distribution of Al Sites in ZSM-5 on the Formation of Cu-Oxo Clusters Active for Direct Conversion of Methane to Methanol. *Top. Catal.* 2016, *59*, 1554–1563.
- (95) Beznis, N. V.; Weckhuysen, B. M.; Bitter, J. H. Cu-ZSM-5 Zeolites for the Formation of Methanol from Methane and Oxygen: Probing the Active Sites and

Spectator Species. Catal. Letters 2010, 138, 14–22.

- Li, H.; Paolucci, C.; Khurana, I.; Wilcox, L. N.; Göltl, F.; Albarracin-Caballero, J. D.; Shih, A. J.; Ribeiro, F. H.; Gounder, R.; Schneider, W. F. Consequences of Exchange-Site Heterogeneity and Dynamics on the UV-Visible Spectrum of Cu-Exchanged SSZ-13. *Chem. Sci.* 2019, *10*, 2373–2384.
- (97) Zecchina, A.; Rivallan, M.; Berlier, G.; Lamberti, C.; Ricchiardi, G. Structure and Nuclearity of Active Sites in Fe-Zeolites: Comparison with Iron Sites in Enzymes and Homogeneous Catalysts. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3483–3499.
- (98) Pirngruber, G. D.; Roy, P. K.; Weiher, N. An in Situ X-Ray Absorption
   Spectroscopy Study of N<sub>2</sub>O Decomposition over Fe-ZSM-5 Prepared by Chemical
   Vapor Deposition of FeCl<sub>3</sub>. J. Phys. Chem. B 2004, 108, 13746–13754.
- (99) Nechita, M. T.; Berlier, G.; Ricchiardi, G.; Bordiga, S.; Zecchina, A. New
   Precursor for the Post-Synthesis Preparation of Fe-ZSM-5 Zeolites with Low Iron
   Content. *Catal. Letters* 2005, *103*, 33–41.
- Babucci, M.; Guntida, A.; Gates, B. C. Atomically Dispersed Metals on Well-Defined Supports Including Zeolites and Metal-Organic Frameworks: Structure, Bonding, Reactivity, and Catalysis. *Chem. Rev.* 2020, *120*, 11956–11985.
- (101) Zhang, T.; Chen, Z.; Walsh, A. G.; Li, Y.; Zhang, P. Single-Atom Catalysts Supported by Crystalline Porous Materials: Views from the Inside. *Adv. Mater.* **2020**, *32*, 2002910.
- (102) Katz, M. J.; Mondloch, J. E.; Totten, R. K.; Park, J. K.; Nguyen, S. T.; Farha, O. K.; Hupp, J. T. Simple and Compelling Biomimetic Metal-Organic Framework

Catalyst for the Degradation of Nerve Agent Simulants. *Angew. Chem. Int. Ed.* **2014**, *53*, 497–501.

- (103) Chen, Y.; Ma, S. Biomimetic Catalysis of Metal–Organic Frameworks. *Dalt. Trans.* 2016, 45, 9744–9753.
- (104) Chen, K.; Wu, C. De. Designed Fabrication of Biomimetic Metal–Organic
   Frameworks for Catalytic Applications. *Coord. Chem. Rev.* 2019, *378*, 445–465.
- (105) Phan, A.; Czaja, A. U.; Gándara, F.; Knobler, C. B.; Yaghi, O. M. Metal-Organic Frameworks of Vanadium as Catalysts for Conversion of Methane to Acetic Acid. *Inorg. Chem.* 2011, 50, 7388–7390.
- (106) Xiao, D. J.; Bloch, E. D.; Mason, J. A.; Queen, W. L.; Hudson, M. R.; Planas, N.; Borycz, J.; Dzubak, A. L.; Verma, P.; Lee, K.; Bonino, F.; Crocellà, V.; Yano, J.; Bordiga, S.; Truhlar, D. G.; Gagliardi, L.; Brown, C. M.; Long, J. R. Oxidation of Ethane to Ethanol by N<sub>2</sub>O in a Metal–Organic Framework with Coordinatively Unsaturated Iron(II) Sites. *Nat. Chem.* 2014, *6*, 590–595.
- (107) Vogiatzis, K. D.; Haldoupis, E.; Xiao, D. J.; Long, J. R.; Siepmann, J. I.;
  Gagliardi, L. Accelerated Computational Analysis of Metal-Organic Frameworks for Oxidation Catalysis. *J. Phys. Chem. C* 2016, *120*, 18707–18712.
- (108) Osadchii, D. Y.; Olivos-Suarez, A. I.; Szécsényi, Á.; Li, G.; Nasalevich, M. A.;
  Dugulan, I. A.; Crespo, P. S.; Hensen, E. J. M.; Veber, S. L.; Fedin, M. V.; Sankar,
  G.; Pidko, E. A.; Gascon, J. Isolated Fe Sites in Metal Organic Frameworks
  Catalyze the Direct Conversion of Methane to Methanol. *ACS Catal.* 2018, *8*, 5542–5548.

- (109) Hall, J. N.; Bollini, P. Low-Temperature, Ambient Pressure Oxidation of Methane to Methanol Over Every Tri-Iron Node in a Metal–Organic Framework Material. *Chem. – A Eur. J.* 2020, *26*, 16639–16643.
- (110) Baek, J.; Rungtaweevoranit, B.; Pei, X.; Park, M.; Fakra, S. C.; Liu, Y.-S.;
  Matheu, R.; Alshmimri, S. A.; Alshehri, S.; Trickett, C. A.; Somorjai, G. A.;
  Yaghi, O. M. Bioinspired Metal–Organic Framework Catalysts for Selective
  Methane Oxidation to Methanol. *J. Am. Chem. Soc.* 2018, *140*, 18208–18216.
- (111) Zheng, J.; Ye, J.; Ortuño, M. A.; Fulton, J. L.; Gutiérrez, O. Y.; Camaioni, D. M.; Motkuri, R. K.; Li, Z.; Webber, T. E.; Mehdi, B. L.; Browning, N. D.; Penn, R. L.; Farha, O. K.; Hupp, J. T.; Truhlar, D. G.; Cramer, C. J.; Lercher, J. A. Selective Methane Oxidation to Methanol on Cu-Oxo Dimers Stabilized by Zirconia Nodes of an NU-1000 Metal-Organic Framework. *J. Am. Chem. Soc.* 2019, *141*, 9292– 9304.
- (112) Hall, J. N.; Bollini, P. Role of Metal Identity and Speciation in the Low-Temperature Oxidation of Methane over Tri-Metal Oxo Clusters. *AIChE J.* 2021, 67, e17496.
- (113) Rosen, A. S.; Notestein, J. M.; Snurr, R. Q. Identifying Promising Metal–Organic Frameworks for Heterogeneous Catalysis via High-Throughput Periodic Density Functional Theory. J. Comput. Chem. 2019, 40, 1305–1318.
- (114) Rosen, A. S.; Notestein, J. M.; Snurr, R. Q. Structure–Activity Relationships That Identify Metal–Organic Framework Catalysts for Methane Activation. *ACS Catal.* 2019, 9, 3576–3587.

- (115) Ma, S.; Zhou, H.-C. A Metal-Organic Framework with Entatic Metal Centers Exhibiting High Gas Adsorption Affinity. *J. Am. Chem. Soc.* 2006, *128*, 11734– 11735.
- (116) Llabrés i Xamena, F.; Corma, A.; Garcia, H. Applications for Metal–Organic
   Frameworks (MOFs) as Quantum Dot Semiconductors. J. Phys. Chem. C 2007, 111, 80–85.
- (117) Canivet, J.; Vandichel, M.; Farrusseng, D. Origin of Highly Active Metal-Organic
   Framework Catalysts: Defects? Defects! *Dalt. Trans.* 2016, 45, 4090–4099.
- (118) Britt, D.; Furukawa, H.; Wang, B.; Glover, T. G.; Yaghi, O. M. Highly Efficient Separation of Carbon Dioxide by a Metal-Organic Framework Replete with Open Metal Sites. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 20637–20640.
- (119) Min Wang, Q.; Shen, D.; Bulow, M.; Ling Lau, M.; Deng, S.; Fitch, F. R.;
   Lemcoff, N. O.; Semanscin, J. Metallo-Organic Molecular Sieve for Gas
   Separation and Purification. *Microporous Mesoporous Mater.* 2002, 55, 217–230.
- (120) Bae, Y.-S.; Farha, O. K.; Spokoyny, A. M.; Mirkin, C. A.; Hupp, J. T.; Snurr, R.
  Q. Carborane-Based Metal–Organic Frameworks as Highly Selective Sorbents for CO2 over Methane. *Chem. Commun.* 2008, *35*, 4135.
- (121) Hu, Z.; Zhao, D. Metal–Organic Frameworks with Lewis Acidity: Synthesis, Characterization, and Catalytic Applications. *CrystEngComm* 2017, *19*, 4066–4081.
- (122) Hidalgo, C. V.; Itoh, H.; Hattori, T.; Niwa, M.; Murakami, Y. Measurement of the Acidity of Various Zeolites by Temperature-Programmed Desorption of

Ammonia. J. Catal. 1984, 85, 362–369.

- (123) Centi, G.; Perathoner, S.; Trifiro, F.; Aboukais, A.; Aissi, C. F.; Guelton, M.
  Physicochemical Characterization of V-Silicalite. *J. Phys. Chem.* 1992, *96*, 2617–2629.
- (124) Lónyi, F.; Valyon, J. On the Interpretation of the NH3-TPD Patterns of H-ZSM-5 and H-Mordenite. *Microporous Mesoporous Mater.* 2001, 47, 293–301.
- (125) Jiang, H.; Wang, Q.; Wang, H.; Chen, Y.; Zhang, M. MOF-74 as an Efficient Catalyst for the Low-Temperature Selective Catalytic Reduction of NOx with NH<sub>3</sub>. ACS Appl. Mater. Interfaces **2016**, *8*, 26817–26826.
- (126) Kim, J.; Kim, S.-N.; Jang, H.-G.; Seo, G.; Ahn, W.-S. CO2 Cycloaddition of Styrene Oxide over MOF Catalysts. *Appl. Catal. A Gen.* **2013**, *453*, 175–180.
- (127) Kim, D.-W.; Kim, H.-G.; Cho, D.-H. Catalytic Performance of MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr) in the Isomerization of Endo- to Exo-Dicyclopentadiene.
   *Catal. Commun.* 2016, *73*, 69–73.
- (128) Vimont, A.; Thibault-Starzyk, F.; Daturi, M. Analysing and Understanding the Active Site by IR Spectroscopy. *Chem. Soc. Rev.* **2010**, *39*, 4928.
- (129) Harris, J. W.; Cordon, M. J.; Di Iorio, J. R.; Vega-Vila, J. C.; Ribeiro, F. H.;
  Gounder, R. Titration and Quantification of Open and Closed Lewis Acid Sites in
  Sn-Beta Zeolites That Catalyze Glucose Isomerization. *J. Catal.* 2016, *335*, 141–154.
- (130) Matyshak, V. A.; Krylov, O. V. Problems of Quantitative SpectroscopicMeasurements in Heterogeneous Catalysis: Molar Absorption Coefficients of

Vibrations in Adsorbed Substances. Kinet. Catal. 2002, 43, 391-407.

- (131) Volkringer, C.; Leclerc, H.; Lavalley, J. C.; Loiseau, T.; Férey, G.; Daturi, M.;
  Vimont, A. Infrared Spectroscopy Investigation of the Acid Sites in the MetalOrganic Framework Aluminum Trimesate MIL-100(Al). *J. Phys. Chem. C* 2012, *116*, 5710–5719.
- (132) Vimont, A.; Goupil, J.-M.; Lavalley, J.-C.; Daturi, M.; Surblé, S.; Serre, C.;
  Millange, F.; Fé, G.; Audebrand, N. Investigation of Acid Sites in a Zeotypic Giant
  Pores Chromium(III) Carboxylate. *J. Am. Chem. Soc.* 2006, *128*, 3218–3227.
- (133) Nijem, N.; Veyan, J.-F.; Kong, L.; Li, K.; Pramanik, S.; Zhao, Y.; Li, J.; Langreth, D.; Chabal, Y. J. Interaction of Molecular Hydrogen with Microporous Metal Organic Framework Materials at Room Temperature. *J. Am. Chem. Soc.* 2010, *132*, 1654.
- (134) Dawody, J.; Eurenius, L.; Abdulhamid, H.; Skoglundh, M.; Olsson, E.; Fridell, E.
   Platinum Dispersion Measurements for Pt/BaO/Al<sub>2</sub>O<sub>3</sub>, NOx Storage Catalysts.
   *Appl. Catal. A Gen.* 2005, 296, 157–168.
- (135) Lif, J.; Skoglundh, M.; Löwendahl, L. Sintering of Nickel Particles Supported on γ-Alumina in Ammonia. *Appl. Catal. A Gen.* **2002**, 228, 145–154.
- (136) Holmgren, A.; Andersson, B. Oxygen Storage Dynamics in Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>Catalysts. J. Catal. 1998, 178, 14–25.
- (137) Scholten, J. J. F.; Pijpers, A. P.; Hustings, A. M. L. Surface Characterization of Supported and Nonsupported Hydrogenation Catalysts. *Catal. Rev.* 1985, 27, 151– 206.

- (138) Webb, P. A. Introduction to Chemical Adsorption Analytical Techniques and Their Applications to Catalysis. *MIC Tech. Publ.* 2003.
- (139) Mao, Y.; Qi, H.; Ye, G.; Han, L.; Zhou, W.; Xu, W.; Sun, Y. Green and Time-Saving Synthesis of MIL-100(Cr) and Its Catalytic Performance. *Microporous Mesoporous Mater.* 2019, 274, 70–75.
- (140) Vokringer, C.; Popov, D.; Loiseau, T.; Ferey, G.; Burghammer, M.; Riekel, C.;
  Haouas, M.; Taulelle, F. Synthesis, Single-Crystal X-Ray Microdiffraction, and
  NMR Characterizations of the Giant Pore Metal-Organic Framework Aluminum
  Trimesate MIL-100. *Chem. Mater.* 2009, *21*, 5695–5697.
- (141) Jeremias, F.; Khutia, A.; Henninger, S. K.; Janiak, C. MIL-100(Al, Fe) as Water Adsorbents for Heat Transformation Purposes - A Promising Application. J. Mater. Chem. 2012, 22, 10148–10151.
- (142) Wickenheisser, M.; Jeremias, F.; Henninger, S. K.; Janiak, C. Grafting of Hydrophilic Ethylene Glycols or Ethylenediamine on Coordinatively Unsaturated Metal Sites in MIL-100(Cr) for Improved Water Adsorption Characteristics. *Inorganica Chim. Acta* 2013, 407, 145–152.
- (143) Mileo, P. G. M.; Ho Cho, K.; Park, J.; Devautour-Vinot, S.; Chang, J.-S.; Maurin,
  G. Unraveling the Water Adsorption Mechanism in the Mesoporous MIL-100(Fe)
  Metal–Organic Framework. *J. Phys. Chem. C* 2019, *123*, 23014–23025.
- (144) Mei, L.; Wu, Y.; Zhou, X.; Yan, J.; Xu, F.; Li, Z. Adsorption Performance of MIL-100(Fe) for Separation of Olefin–Paraffin Mixtures. *J. Taiwan Inst. Chem. Eng.*2017, 70, 74–78.

- (145) Valenzano, L.; Civalleri, B.; Chavan, S.; Bordiga, S.; Nilsen, M. H.; Jakobsen, S.;
  Lillerud, K. P.; Lamberti, C. Disclosing the Complex Structure of UiO-66 Metal
  Organic Framework: A Synergic Combination of Experiment and Theory. *Chem. Mater.* 2011, 23, 1700–1718.
- (146) Dissegna, S.; Epp, K.; Heinz, W. R.; Kieslich, G.; Fischer, R. A. Defective Metal-Organic Frameworks. *Adv. Mater.* 2018, *30*, 1704501.
- (147) Wu, H.; Chua, Y. S.; Krungleviciute, V.; Tyagi, M.; Chen, P.; Yildirim, T.; Zhou, W. Unusual and Highly Tunable Missing-Linker Defects in Zirconium Metal–
  Organic Framework UiO-66 and Their Important Effects on Gas Adsorption. *J. Am. Chem. Soc.* 2013, *135*, 10525–10532.
- (148) Ghosh, P.; Colón, Y. J.; Snurr, R. Q. Water Adsorption in UiO-66: The Importance of Defects. *Chem. Commun.* 2014, 50, 11329–11331.
- (149) Liang, W.; Coghlan, C. J.; Ragon, F.; Rubio-Martinez, M.; D'Alessandro, D. M.;
  Babarao, R. Defect Engineering of UiO-66 for CO<sub>2</sub> and H<sub>2</sub>O Uptake a Combined
  Experimental and Simulation Study. *Dalt. Trans.* 2016, 45, 4496–4500.
- (150) Akiyama, G.; Matsuda, R.; Kitagawa, S. Highly Porous and Stable Coordination Polymers as Water Sorption Materials. 2010, *39*, 360–361.
- (151) Seo, Y.-K.; Yoon, J. W.; Lee, J. S.; Lee, U.-H.; Hwang, Y. K.; Jun, C.-H.;
  Horcajada, P.; Serre, C.; Chang, J.-S. Large Scale Fluorine-Free Synthesis of
  Hierarchically Porous Iron(III) Trimestate MIL-100(Fe) with a Zeolite MTN
  Topology. *Microporous Mesoporous Mater.* 2012, 157, 137–145.
- (152) Tong, M.; Liu, D.; Yang, Q.; Devautour-Vinot, S.; Maurin, G.; Zhong, C.

Influence of Framework Metal Ions on the Dye Capture Behavior of MIL-100 (Fe, Cr) MOF Type Solids. *J. Mater. Chem. A* **2013**, *1*, 8534.

- (153) Wang, C.; Zhang, F.; Yang, J.; Li, J. Rapid and HF-Free Synthesis of MIL-100(Cr) via Steam-Assisted Method. *Mater. Lett.* **2019**, 252, 286–288.
- (154) Leclerc, H.; Vimont, A.; Lavalley, J. C.; Daturi, M.; Wiersum, A. D.; Llwellyn, P. L.; Horcajada, P.; Férey, G.; Serre, C. Infrared Study of the Influence of Reducible Iron(III) Metal Sites on the Adsorption of CO, CO<sub>2</sub>, Propane, Propene and Propyne in the Mesoporous Metalorganic Framework MIL-100. *Phys. Chem. Chem. Phys.* 2011, *13*, 11748–11756.
- (155) Vimont, A.; Leclerc, H.; Maugé, F.; Daturi, M.; Lavalley, J.-C.; Surblé, S.; Serre,
  C.; Férey, G. Creation of Controlled Brønsted Acidity on a Zeotypic Mesoporous
  Chromium(III) Carboxylate by Grafting Water and Alcohol Molecules. *J. Phys. Chem. C* 2007, *111*, 383–388.
- (156) Küsgens, P.; Rose, M.; Senkovska, I.; Fröde, H.; Henschel, A.; Siegle, S.; Kaskel,
  S. Characterization of Metal-Organic Frameworks by Water Adsorption. *Microporous Mesoporous Mater.* 2009, *120*, 325–330.
- (157) De Lange, M. F.; Gutierrez-Sevillano, J. J.; Hamad, S.; Vlugt, T. J. H.; Calero, S.;
  Gascon, J.; Kapteijn, F. Understanding Adsorption of Highly Polar Vapors on
  Mesoporous MIL-100(Cr) and MIL-101(Cr): Experiments and Molecular
  Simulations. J. Phys. Chem. C 2013, 117, 7613–7622.
- (158) Kolokathis, P. D.; Pantatosaki, E.; Papadopoulos, G. K. Atomistic Modeling ofWater Thermodynamics and Kinetics within MIL-100(Fe). *J. Phys. Chem. C* 2015,

119, 20074–20084.

- (159) Splith, T.; Pantatosaki, E.; Kolokathis, P. D.; Fröhlich, D.; Zhang, K.; Füldner, G.; Chmelik, C.; Jiang, J.; Henninger, S. K.; Stallmach, F.; Papadopoulos, G. K.
  Molecular Dynamics Phenomena of Water in the Metalorganic Framework MIL-100(Al), as Revealed by Pulsed Field Gradient NMR and Atomistic Simulation. *J. Phys. Chem. C* 2017, *121*, 18065–18074.
- (160) Chen, Y.-R.; Liou, K.-H.; Kang, D.-Y.; Chen, J.-J.; Lin, L.-C. Investigation of the Water Adsorption Properties and Structural Stability of MIL-100(Fe) with Different Anions. *Langmuir* **2018**, *34*, 4180–4187.
- (161) Küsgens, P.; Rose, M.; Senkovska, I.; Fröde, H.; Henschel, A.; Siegle, S.; Kaskel,
   S. Characterization of Metal-Organic Frameworks by Water Adsorption.
   *Microporous Mesoporous Mater.* 2009, 120, 325–330.
- (162) Haouas, M.; Volkringer, C.; Loiseau, T.; Férey, G.; Taulelle, F. Monitoring the Activation Process of the Giant Pore MIL-100(Al) by Solid State NMR. *J. Phys. Chem. C* 2011, *115*, 17934–17944.
- (163) Shearer, G. C.; Forselv, S.; Chavan, S.; Bordiga, S.; Mathisen, K.; Bjørgen, M.;
  Svelle, S.; Lillerud, K. P. In Situ Infrared Spectroscopic and Gravimetric
  Characterisation of the Solvent Removal and Dehydroxylation of the Metal
  Organic Frameworks UiO-66 and UiO-67. *Top. Catal.* 2013, *56*, 770–782.
- (164) Khan, A. H.; Barth, B.; Hartmann, M.; Haase, R.; Bertmer, M. Nitric Oxide Adsorption in MIL-100(Al) MOF Studied by Solid-State NMR. *J. Phys. Chem. C* 2018, *122*, 12723.

- (165) Yang, Q.; Zhong, C. Understanding Hydrogen Adsorption in Metal-Organic Frameworks with Open Metal Sites: A Computational Study. *J. Phys. Chem. B* 2006, *110*, 655–658.
- (166) Sun, J.; Yu, G.; Huo, Q.; Kan, Q.; Guan, J. Epoxidation of Styrene over Fe(Cr)-MIL-101 Metal-Organic Frameworks. *RSC Adv.* 2014, *4*, 38048–38054.
- (167) Pu, M.; Ma, Y.; Wan, J.; Wang, Y.; Wang, J.; Brusseau, M. L. Activation
  Performance and Mechanism of a Novel Heterogeneous Persulfate Catalyst:
  Metal-Organic Framework MIL-53(Fe) with FeII/FeIII Mixed-Valence
  Coordinatively Unsaturated Iron Center. *Catal. Sci. Technol.* 2017, *7*, 1129–1140.
- (168) Wu, X.; Bao, Z.; Yuan, B.; Wang, J.; Sun, Y.; Luo, H.; Deng, S. Microwave Synthesis and Characterization of MOF-74 (M = Ni, Mg) for Gas Separation. *Microporous Mesoporous Mater.* 2013, *180*, 114–122.
- (169) Zhang, Z.; Zhao, Y.; Gong, Q.; Li, Z.; Li, J. MOFs for CO2 Capture and Separation from Flue Gas Mixtures: The Effect of Multifunctional Sites on Their Adsorption Capacity and Selectivity. *Chem. Commun.* 2013, 49, 653–661.
- (170) Millward, A. R.; Yaghi, O. M. Metal-Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature. *J. Am. Chem. Soc.* 2005, *127*, 17998–17999.
- (171) Li, L.; Lin, R. B.; Krishna, R.; Li, H.; Xiang, S.; Wu, H.; Li, J.; Zhou, W.; Chen,
  B. Ethane/Ethylene Separation in a Metal-Organic Framework with Iron-Peroxo
  Sites. *Science* 2018, *362*, 443–446.
- (172) Mowat, J. P. S.; Miller, S. R.; Slawin, A. M. Z.; Seymour, V. R.; Ashbrook, S. E.;

Wright, P. A. Synthesis, Characterisation and Adsorption Properties of
Microporous Scandium Carboxylates with Rigid and Flexible Frameworks. *Microporous Mesoporous Mater.* 2011, *142*, 322–333.

- (173) Lieb, A.; Leclerc, H.; Devic, T.; Serre, C.; Margiolaki, I.; Mahjoubi, F.; Lee, J. S.;
  Vimont, A.; Daturi, M.; Chang, J. S. MIL-100(V) A Mesoporous Vanadium
  Metal Organic Framework with Accessible Metal Sites. *Microporous Mesoporous Mater.* 2012, 157, 18–23.
- (174) Reinsch, H.; Stock, N. Formation and Characterisation of Mn-MIL-100. *CrystEngComm* 2013, *15*, 544–550.
- (175) Fubini, B.; Ghiotti, G.; Stradella, L.; Garrone, E.; Morterra, C. The Chemistry of Silica-Supported Cr Ions: A Characterization of the Reduced and Oxidized Forms of Chromia/Silica Catalyst by Calorimetry and Ultraviolet-Visible Spectroscopy. *J. Catal.* **1980**, *66*, 200–213.
- (176) Gaspar, A. B.; Martins, R. L.; Schmal, M.; Dieguez, L. C. Characterization of Cr<sup>2+</sup> and Ethylene Polymerization on Cr/SiO<sub>2</sub> Catalysts. *J. Mol. Catal. A Chem.* 2001, *169*, 105–112.
- (177) Zecchina, A.; Spoto, G.; Ghiotti, G.; Garrone, E. Cr<sup>2+</sup> Ions Grafted to Silica and Silicalite Surfaces: FTIR Characterization and Ethylene Polymerization Activity. *J. Mol. Catal.* 1994, *86*, 423–446.
- (178) Ketrat, S.; Maihom, T.; Wannakao, S.; Probst, M.; Nokbin, S.; Limtrakul, J.
   Coordinatively Unsaturated Metal-Organic Frameworks M<sub>3</sub>(Btc)<sub>2</sub> (M = Cr, Fe, Co, Ni, Cu, and Zn) Catalyzing the Oxidation of CO by N<sub>2</sub>O: Insight from DFT

Calculations. Inorg. Chem. 2017, 56, 14005–14012.

- (179) Murray, L. J.; Dinca, M.; Yano, J.; Chavan, S.; Bordiga, S.; Brown, C. M.; Long, J. R. Highly-Selective and Reversible O<sub>2</sub> Binding in Cr<sub>3</sub>(1,3,5-Benzenetricarboxylate)<sub>2</sub>. J. Am. Chem. Soc. 2010, 132, 7856–7857.
- (180) Yang, L.; Zhou, W.; Li, H.; Alsalme, A.; Jia, L.; Yang, J.; Li, J.; Li, L.; Chen, B. Reversed Ethane/Ethylene Adsorption in a Metal–Organic Framework via Introduction of Oxygen. *Chinese J. Chem. Eng.* **2019**.
- (181) Hall, J. N.; Bollini, P. Quantification of Open-Metal Sites in Metal-Organic
   Frameworks Using Irreversible Water Adsorption. *Langmuir* 2020, *36*, 1345–1356.
- (182) Hall, J. N.; Bollini, P. Quantification of Open-Metal Sites in Metal–Organic
   Frameworks Using Irreversible Water Adsorption. *Langmuir* 2020, *36*, 1345–1356.
- (183) Eubank, J. F.; Wheatley, P. S.; Lebars, G.; McKinlay, A. C.; Leclerc, H.;
  Horcajada, P.; Daturi, M.; Vimont, A.; Morris, R. E.; Serre, C. Porous, Rigid
  Metal(III)-Carboxylate Metal-Organic Frameworks for the Delivery of Nitric
  Oxide. *APL Mater.* 2014, 2, 124112–1.
- (184) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 5th ed.;John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2009.
- (185) Miessler, G. L.; Fischer, P. J.; Tarr, D. A. *Inorganic Chemistry*, 5th ed.; Pearson Education Inc., 2014.
- (186) Frenking, G.; Fröhlich, N. The Nature of the Bonding in Transition-Metal

Compounds. Chem. Rev. 2000, 100, 717–774.

- (187) Lupinetti, A. J.; Fau, S.; Frenking, G.; Strauss, S. H. Theoretical Analysis of the Bonding between CO and Positively Charged Atoms. *J. Phys. Chem. A* 1997, *101*, 9551–9559.
- (188) Kung, M. C.; Kung, H. H. IR Studies of NH<sub>3</sub>, Pyridine, CO, and NO Adsorbed on Transition Metal Oxides. *Catal. Rev.* **1985**, *27*, 425–460.
- (189) Hadjiivanov, K.; Busca, G. Surface Chemistry of Oxidized and Reduced Chromia: A Fourier Transform Infrared Spectroscopy Study. *Langmuir* 1994, 10, 4534– 4541.
- (190) Ford, R. R. Carbon Monoxide Adsorption on the Transition Metals. *Adv. Catal.***1970**, *21*, 51–150.
- (191) Zecchina, A.; Garrone, E.; Ghiotti, G.; Coluccia, S. On the Chemistry of Silica Supported Chromium Ions. II. One-Ligand Complexes. Adsorption of Carbon Monoxide, Carbon Dioxide, and Pyridine. *J. Phys. Chem.* **1975**, *79*, 972–978.
- (192) Zecchina, A.; Garrone, E.; Morterra, C.; Coluccia, S. On the Chemistry of Silica Supported Chromium Ions. III Two-Ligand Complexes. Nitric Oxide Adsorption. *J. Phys. Chem.* 1975, 79, 978–983.
- (193) Peri, J. B. Infrared Study of Nitric Oxide and Carbon Monoxide Adsorbed on Chromia/Alumina. J. Phys. Chem. 1974, 78, 588–594.
- (194) Kazusaka, A.; Howe, R. F. Interaction of Nitric Oxide with Supported Chromium, Molybdenum, and Tungsten Catalysts. J. Catal. 1980, 63, 447–455.
- (195) Kugler, E. L.; Kadet, A. B.; Gryder, J. W. The Nature of NO Adsorption on

Chromia. J. Catal. 1976, 41, 72–81.

- (196) Ziegler, T.; Rauk, A. Carbon Monoxide, Carbon Monosulfide, Molecular Nitrogen, Phosphorus Trifluoride, and Methyl Isocyanide as Sigma Donors and Pi Acceptors. A Theoretical Study by the Hartree-Fock-Slater Transition-State Method. *Inorg. Chem.* **1979**, *18*, 1755–1759.
- (197) Hadjiivanov, K. I.; Vayssilov, G. N. Characterization of Oxide Surfaces and Zeolites by Carbon Monoxide as an IR Probe Molecule. *Adv. Catal.* 2002, *47*, 307–511.
- (198) Kim, A.; Ahn, S.; Yoon, T.; Notestein, J. M.; Farha, O. K.; Bae, Y. Fast Cyclohexane Oxidation Under Mild Reaction Conditions Through a Controlled Creation of Redox-Active Fe(II/III) Sites in a Metal–Organic Framework. *ChemCatChem* **2019**, *11*, 5650–5656.
- (199) Espelid, Ø.; Børve, K. J. Theoretical Models of Ethylene Polymerization over a Mononuclear Chromium(II)/Silica Site. J. Catal. 2000, 195, 125–139.
- (200) Bloch, E. D.; Queen, W. L.; Krishna, R.; Zadrozny, J. M.; Brown, C. M.; Long, J. R. Hydrocarbon Separations in a Metal-Organic Framework with Open Iron(II) Coordination Sites. *Science* 2012, *335*, 1606–1610.
- (201) Zhang, L.; Li, L.; Hu, E.; Yang, L.; Shao, K.; Yao, L.; Jiang, K.; Cui, Y.; Yang, Y.; Li, B.; Chen, B.; Qian, G. Boosting Ethylene/Ethane Separation within Copper(I)-Chelated Metal–Organic Frameworks through Tailor-Made Aperture and Specific π-Complexation. *Adv. Sci.* 2020, *7*, 1901918.
- (202) Geier, S. J.; Mason, J. A.; Bloch, E. D.; Queen, W. L.; Hudson, M. R.; Brown, C.

M.; Long, J. R. Selective Adsorption of Ethylene over Ethane and Propylene over Propane in the Metal-Organic Frameworks  $M_2$ (Dobdc) (M = Mg, Mn, Fe, Co, Ni, Zn). *Chem. Sci.* **2013**, *4*, 2054–2061.

- (203) Tang, P.; Zhu, Q.; Wu, Z.; Ma, D. Methane Activation: The Past and Future. *Energy Environ. Sci.* 2014, 7, 2580–2591.
- (204) York, A. P. E.; Xiao, T.; Green, M. L. H. Brief Overview of the Partial Oxidation of Methane to Synthesis Gas. *Top. Catal.* **2003**, *22*, 345–358.
- (205) West, N. M.; Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. Homogeneous Syngas Conversion. *Coord. Chem. Rev.* 2011, 255, 881–898.
- (206) Hausinger, R. P. Fe(II)/α-Ketoglutarate-Dependent Hydroxylases and Related Enzymes. *Crit. Rev. Biochem. Mol. Biol.* **2004**, *39*, 21–68.
- (207) Martinez, S.; Hausinger, R. P. Catalytic Mechanisms of Fe(II)- and 2 Oxoglutarate-Dependent Oxygenases. J. Biol. Chem. 2015, 290, 20702–20711.
- (208) Snyder, B. E. R.; Vanelderen, P.; Bols, M. L.; Hallaert, S. D.; Böttger, L. H.; Ungur, L.; Pierloot, K.; Schoonheydt, R. A.; Sels, B. F.; Solomon, E. I. The Active Site of Low-Temperature Methane Hydroxylation in Iron-Containing Zeolites. *Nature* **2016**, *536*, 317–321.
- (209) Sobolev, V. I.; Dubkov, K. A.; Panna, O. V.; Panov, G. I. Selective Oxidation of Methane to Methanol on a FeZSM-5 Surface. *Stud. Surf. Sci. Catal.* 1994, 81, 387–392.
- (210) Knops-Gerrits, P. P.; Goddard, W. A. Methane Partial Oxidation in Iron Zeolites: Theory versus Experiment. J. Mol. Catal. A Chem. 2001, 166, 135–145.

- (211) Hammond, C.; Forde, M. M.; Ab Rahim, M. H.; Thetford, A.; He, Q.; Jenkins, R. L.; Dimitratos, N.; Lopez-Sanchez, J. A.; Dummer, N. F.; Murphy, D. M.; Carley, A. F.; Taylor, S. H.; Willock, D. J.; Stangland, E. E.; Kang, J.; Hagen, H.; Kiely, C. J.; Hutchings, G. J. Direct Catalytic Conversion of Methane to Methanol in an Aqueous Medium by Using Copper-Promoted Fe-ZSM-5. *Angew. Chemie Int. Ed.* 2012, *51*, 5129–5133.
- (212) Göltl, F.; Michel, C.; Andrikopoulos, P. C.; Love, A. M.; Hafner, J.; Hermans, I.;
  Sautet, P. Computationally Exploring Confinement Effects in the Methane-to-Methanol Conversion over Iron-Oxo Centers in Zeolites. *ACS Catal.* 2016, *6*, 8404–8409.
- (213) Reynolds, R. A.; Dunham, W. R.; Coucouvanis, D. Kinetic Lability, Structural Diversity, and Oxidation Reactions of New Oligomeric, Anionic Carboxylate–Pyridine Complexes. *Inorg. Chem.* 2002, *37*, 1232–1241.
- (214) Stassinopoulos, A.; Caradonna, J. P. A Binuclear Non-Heme Iron Oxo-Transfer Analog Reaction System: Observations and Biological Implications. *J. Am. Chem. Soc.* **1990**, *112*, 7071–7073.
- (215) Xue, G.; Wang, D.; De Hont, R.; Fiedler, A. T.; Shan, X.; Munck, E.; Que, L. A Synthetic Precedent for the [Fe<sup>IV</sup><sub>2</sub>(O)<sub>2</sub>] Diamond Core Proposed for Methane Monooxygenase Intermediate Q. *Proc. Natl. Acad. Sci.* 2007, *104*, 20713–20718.
- (216) Mukerjee, S.; Stassinopoulus, A.; Caradonna, J. P. Iodosylbenzene Oxidation of Alkanes, Alkenes, and Sulfides Catalyzed by Binuclear Non-Heme Iron Systems: Comparison of Non-Heme Iron versus Heme Iron Oxidation Pathways. J. Am.

Chem. Soc. 1997, 119, 8097–8098.

- (217) Do, L. H.; Lippard, S. J. Evolution of Strategies to Prepare Synthetic Mimics of Carboxylate-Bridged Diiron Protein Active Sites. J. Inorg. Biochem. 2011, 105, 1774–1785.
- (218) Watton, S. P.; Fuhrmann, P.; Pence, L. E.; Caneschi, A.; Cornia, A.; Abbati, G. L.; Lippard, S. J. A Cyclic Octadecairon(III) Complex, the Molecular 18-Wheeler. *Angew. Chem. Int. Ed.* **1997**, *36*, 2774–2776.
- (219) Vincent, J. B.; Huffman, J. C.; Christou, G.; Li, Q.; Nanny, M. A.; Hendrickson,
  D. N.; Fong, R. H.; Fish, R. H. Modeling the Dinuclear Sites of Iron Biomolecules: Synthesis and Properties of Fe2O(OAc)2Cl2(Bipy)2 and Its Use as an Alkane
  Activation Catalyst. J. Am. Chem. Soc. 1988, 110, 6898–6900.
- (220) Armstrong, W. H.; Roth, M. E.; Lippard, S. J. Tetranuclear Iron—Oxo Complexes. Synthesis, Structure, and Properties of Species Containing The Nonplanar {Fe<sub>4</sub>O<sub>2</sub>}<sup>8+</sup> Core and Seven Bridging Carboxvlate Ligands. *J. Am. Chem. Soc.* **1987**, *109*, 6318–6326.
- (221) Terminal, L.; Dicarboxylate, B. A General Method for Assembling
   (MOxo)Bis(Mcarboxylato)Diiron(III) Complexes with Labile Terminal Sites
   Using a Bridging Dicarboxylate Ligand. *Inorg. Chem.* 1989, 28, 4557–4558.
- (222) Zecchina, A.; Rivallan, M.; Berlier, G.; Lamberti, C.; Ricchiardi, G. Structure and Nuclearity of Active Sites in Fe-Zeolites: Comparison with Iron Sites in Enzymes and Homogeneous Catalysts. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3483–3499.
- (223) Baek, J.; Rungtaweevoranit, B.; Pei, X.; Park, M.; Fakra, S. C.; Liu, Y.-S.;

Matheu, R.; Alshmimri, S. A.; Alshehri, S.; Trickett, C. A.; Somorjai, G. A.; Yaghi, O. M. Bioinspired Metal–Organic Framework Catalysts for Selective Methane Oxidation to Methanol. *J. Am. Chem. Soc.* **2018**, *140*, 18208–18216.

- (224) Verma, P.; Vogiatzis, K. D.; Planas, N.; Borycz, J.; Xiao, D. J.; Long, J. R.;
  Gagliardi, L.; Truhlar, D. G. Mechanism of Oxidation of Ethane to Ethanol at Iron(IV)-Oxo Sites in Magnesium-Diluted Fe<sub>2</sub>(Dobdc). *J. Am. Chem. Soc.* 2015, *137*, 5770–5781.
- (225) Hirao, H.; Ng, W. K. H.; Moeljadi, A. M. P.; Bureekaew, S. Multiscale Model for a Metal-Organic Framework: High-Spin Rebound Mechanism in the Reaction of the Oxoiron(IV) Species of Fe-MOF-74. ACS Catal. 2015, 5, 3287–3291.
- (226) Yuan, S.; Feng, L.; Wang, K.; Pang, J.; Bosch, M.; Lollar, C.; Sun, Y.; Qin, J.;
  Yang, X.; Zhang, P.; Wang, Q.; Zou, L.; Zhang, Y.; Zhang, L.; Fang, Y.; Li, J.;
  Zhou, H.-C. Stable Metal–Organic Frameworks: Design, Synthesis, and
  Applications. *Adv. Mater.* 2018, *30*, 1704303.
- (227) Hall, J. N.; Bollini, P. Enabling Access to Reduced Open-Metal Sites in Metal-Organic Framework Materials through Choice of Anion Identity: The Case of MIL-100(Cr). ACS Mater. Lett. 2020, 2, 838–844.
- (228) Yuranov, I.; Bulushev, D. A.; Renken, A.; Kiwi-Minsker, L. Benzene Hydroxylation over FeZSM-5 Catalysts: Which Fe Sites Are Active? *J. Catal.*2004, 227, 138–147.
- (229) Pirngruber, G. D.; Roy, P. K.; Weiher, N. An in Situ X-Ray Absorption Spectroscopy Study of N<sub>2</sub>O Decomposition over Fe-ZSM-5 Prepared by Chemical

Vapor Deposition of FeCl<sub>3</sub>. J. Phys. Chem. B. 2004, 108, 13746–13754.

- (230) Wood, B. R.; Reimer, J. A.; Bell, A. T.; Janicke, M. T.; Ott, K. C. Methanol Formation on Fe/Al-MFI via the Oxidation of Methaneby Nitrous Oxide. *J. Catal.* **2004**, 225, 300–306.
- (231) Rana, B. S.; Singh, B.; Kumar, R.; Verma, D.; Bhunia, M. K.; Bhaumik, A.; Sinha,
  A. K. Hierarchical Mesoporous Fe/ZSM-5 with Tunable Porosity for Selective
  Hydroxylation of Benzene to Phenol. *J. Mater. Chem.* 2010, 20, 8575–8581.
- (232) Cho, K. Bin; Wu, X.; Lee, Y. M.; Kwon, Y. H.; Shaik, S.; Nam, W. Evidence for an Alternative to the Oxygen Rebound Mechanism in C-H Bond Activation by Non-Heme Fe<sup>IV</sup>O Complexes. *J. Am. Chem. Soc.* **2012**, *134*, 20222–20225.
- (233) Cho, K. Bin; Hirao, H.; Shaik, S.; Nam, W. To Rebound or Dissociate? This Is the Mechanistic Question in C-H Hydroxylation by Heme and Nonheme Metal-Oxo Complexes. *Chem. Soc. Rev.* 2016, 45, 1197–1210.
- (234) Starokon, E. V.; Parfenov, M. V.; Pirutko, L. V.; Abornev, S. I.; Panov, G. I. Room-Temperature Oxidation of Methane by α-Oxygen and Extraction of Products from the FeZSM-5 Surface. J. Phys. Chem. C 2011, 115, 2155–2161.
- (235) Baek, J.; Rungtaweevoranit, B.; Pei, X.; Park, M.; Fakra, S. C.; Liu, Y.-S.;
  Matheu, R.; Alshmimri, S. A.; Alshehri, S.; Trickett, C. A.; Somorjai, G. A.;
  Yaghi, O. M. Bioinspired Metal–Organic Framework Catalysts for Selective
  Methane Oxidation to Methanol. *J. Am. Chem. Soc.* 2018, *140*, 18208–18216.
- (236) Hall, J. N.; Bollini, P. Role of Metal Identity and Speciation in the Low-Temperature Oxidation of Methane over Tri-Metal Oxo Clusters. *AIChE J.* **2021**,

67, e17496.

- (237) Simons, M. C.; Prinslow, S. D.; Babucci, M.; Hoffman, A. S.; Hong, J.; Vitillo, J. G.; Bare, S. R.; Gates, B. C.; Lu, C. C.; Gagliardi, L.; Bhan, A. Beyond Radical Rebound: Methane Oxidation to Methanol Catalyzed by Iron Species in Metal–Organic Framework Nodes. *J. Am. Chem. Soc.* 2021, *143*, 12165–12174.
- (238) Rosen, A. S.; Notestein, J. M.; Snurr, R. Q. High-Valent Metal–Oxo Species at the Nodes of Metal–Triazolate Frameworks: The Effects of Ligand Exchange and Two-State Reactivity for C–H Bond Activation. *Angew. Chemie Int. Ed.* 2020, *59*, 19494–19502.
- (239) Vitillo, J. G.; Lu, C. C.; Cramer, C. J.; Bhan, A.; Gagliardi, L. Influence of First and Second Coordination Environment on Structural Fe(II) Sites in MIL-101 for C-H Bond Activation in Methane. ACS Catal. 2021, 11, 579–589.
- (240) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.;
   Margiolaki, I. A Chromium Terephthalate Based Solid with Unusually Large
   Pore Volumes and Surface Area. *Science* 2005, *309*, 2040–2042.
- (241) Horcajada, P.; Chevreau, H.; Heurtaux, D.; Benyettou, F.; Salles, F.; Devic, T.;
  Garcia-Marquez, A.; Yu, C.; Lavrard, H.; Dutson, C. L.; Magnier, E.; Maurin, G.;
  Elkaïm, E.; Serre, C. Extended and Functionalized Porous Iron(III) Tri- or
  Dicarboxylates with MIL-100/101 Topologies. *Chem. Commun.* 2014, *50*, 6872–6874.
- (242) Castells-Gil, J.; M. Padial, N.; Almora-Barrios, N.; Da Silva, I.; Mateo, D.; Albero,J.; García, H.; Martí-Gastaldo, C. De Novo Synthesis of Mesoporous Photoactive

Titanium(Iv)-Organic Frameworks with MIL-100 Topology. *Chem. Sci.* **2019**, *10*, 4313–4321.

- (243) Mason, J. A.; Darago, L. E.; Wayne W. Lukens, J.; Long, J. R. Synthesis and O2 Reactivity of a Titanium(III) Metal–Organic Framework. *Inorg. Chem.* 2015, 54, 10096–10104.
- (244) Biswas, S.; Couck, S.; Grzywa, M.; Denayer, J. F. M.; Volkmer, D.; Van Der Voort, P. Vanadium Analogues of Nonfunctionalized and Amino-Functionalized MOFs with MIL-101 Topology Synthesis, Characterization, and Gas Sorption Properties. *Eur. J. Inorg. Chem.* 2012, No. 15, 2481–2486.
- (245) Bauer, S.; Serre, C.; Devic, T.; Horcajada, P.; Me Marrot, J.; Férey, G.; Stock, N. High-Throughput Assisted Rationalization of the Formation of Metal Organic Frameworks in the Iron(III) Aminoterephthalate Solvothermal System. *Inorg. Chem.* 2008, 47, 7568–7576.
- (246) Serra-Crespo, P.; Ramos-Fernandez, E. V; Gascon, J.; Kapteijn, F. Synthesis and Characterization of an Amino Functionalized MIL-101(Al): Separation and Catalytic Properties. *Chem. Mater* **2011**, *23*, 2565–2572.
- (247) Gómez-Pozuelo, G.; Cabello, C. P.; Opanasenko, M.; Horáček, M.; Čejka, J.
  Superior Activity of Isomorphously Substituted MOFs with MIL-100(M=Al, Cr, Fe, In, Sc, V) Structure in the Prins Reaction: Impact of Metal Type. *Chempluschem* 2017, 82, 152–159.
- (248) Mali, G.; Mazaj, M.; Arčon, I.; Hanžel, D.; Arčon, D.; Jagličić, Z. Unraveling the Arrangement of Al and Fe within the Framework Explains the Magnetism of

Mixed-Metal MIL-100(Al,Fe). J. Phys. Chem. Lett. 2019, 10, 1464–1470.

- (249) Giménez-Marqués, M.; Santiago-Portillo, A.; Navalón, S.; Álvaro, M.; Briois, V.;
  Nouar, F.; Garcia, H.; Serre, C. Exploring the Catalytic Performance of a Series of Bimetallic MIL-100(Fe, Ni) MOFs. *J. Mater. Chem. A* 2019, *7*, 20285–20292.
- (250) Mitchell, L.; Williamson, P.; Ehrlichová, B.; Anderson, A. E.; Seymour, V. R.; Ashbrook, S. E.; Acerbi, N.; Daniels, L. M.; Walton, R. I.; Clarke, M. L.; Wright, P. A. Mixed-Metal MIL-100(Sc,M) (M=Al, Cr, Fe) for Lewis Acid Catalysis and Tandem C-C Bond Formation and Alcohol Oxidation. *Chem. - A Eur. J.* 2014, 20, 17185–17197.
- (251) Vallés-García, C.; Gkaniatsou, E.; Santiago-Portillo, A.; Giménez-Marqués, M.;
  Álvaro, M.; Greneche, J.-M.; Steunou, N.; Sicard, C.; Navalón, S.; Serre, C.;
  García, H. Design of Stable Mixed-Metal MIL-101(Cr/Fe) Materials with
  Enhanced Catalytic Activity for the Prins Reaction. *J. Mater. Chem. A* 2020, *8*, 17002–17011.
- (252) Li, X.; Wang, J.; Liu, X.; Liu, L.; Cha, D.; Zheng, X.; Yousef, A. A.; Song, K.;
  Zhu, Y.; Zhang, D.; Han, Y. Direct Imaging of Tunable Crystal Surface Structures of MOF MIL-101 Using High-Resolution Electron Microscopy. *J. Am. Chem. Soc.* **2019**, *141*, 12021–12028.
- (253) Kraft, S.; Stümpel, J.; Becker, P.; Kuetgens, U. High Resolution X-ray Absorption Spectroscopy with Absolute Energy Calibration for the Determination of Absorption Edge Energies. *Rev. Sci. Instrum.* **1998**, 67, 681.
- (254) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for

X-Ray Absorption Spectroscopy Using IFEFFIT. J. Synchrotron Rad. 2005, 12, 537–541.

- (255) Zabinsky, S. I.; Rehr, J. J.; Ankudinov, A.; Albers, R. C.; Eller, M. J. Multiple-Scattering Calculations of x-Ray-Absorption Spectra. *Phys. Rev. B* 1995, *52*, 2995.
- (256) NIST Chemistry WebBook, *National Institute of Standards and Technology* (https://webbook.nist.gov/chemistry).
- (257) Baertsch, C. D.; Komala, K. T.; Chua, Y. H.; Iglesia, E. Genesis of Brønsted Acid Sites during Dehydration of 2-Butanol on Tungsten Oxide Catalysts. *J. Catal.*2002, 205, 44–57.
- (258) Langmuir, I. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403.
- (259) Carabineiro, S. A. C.; Van Noort, W. D.; Nieuwenhuys, B. E. A Comparative Study of the N<sub>2</sub>O-CO and N<sub>2</sub>O-H<sub>2</sub> Reactions on the Ir(110) Surface with Emphasis on the Oscillatory Behavior. *Catal. Lett.* **2002**, *84*, 135–142.
- (260) Rossi, S. De; Ferraris, G.; Mancini, R. Comparison of Carbon Monoxide and Nitrous Oxide Adsorption on Copper/Zinc Oxide Catalysts. *Appl. Catal.* **1988**, *38*, 359–364.
- (261) Randall, H.; Doepper, R.; Renken, A. Model Discrimination by Unsteady-State Operation: Application to the Reduction of NO with CO on Iron Oxide. *Can. J. Chem. Eng.* **1996**, *74*, 586–593.
- (262) Pai, M. R.; Banerjee, A. M.; Kartha, K.; Pai, R. V.; Kamble, V. S.; Bharadwaj, S.
  R. Mechanism of CO + N2O Reaction via Transient CO<sub>3</sub><sup>2-</sup> Species over

Crystalline Fe-Substituted Lanthanum Titanates. *J. Phys. Chem. B* **2010**, *114*, 6943–6953.

- (263) Pérez-Ramírez, J.; Kondratenko, E. V.; Debbagh, M. N. Transient Studies on the Mechanism of N<sub>2</sub>O Activation and Reaction with CO and C<sub>3</sub>H<sub>8</sub> over Fe-Silicalite. *J. Catal.* 2005, 233, 442–452.
- (264) Dandekar, A.; Vannice, M. A. Decomposition and Reduction of N<sub>2</sub>O over Copper Catalysts. *Appl. Catal. B Environ.* **1999**, *22*, 179–200.
- (265) Sadhankar, R. R.; Lynch, D. T. N2O Reduction by CO over an Alumina-Supported Pt Catalyst: Forced Composition Cycling. *J. Catal.* **1994**, *149*, 278–291.
- (266) Granger, P.; Malfoy, P.; Esteves, P.; Leclercq, L.; Leclercq, G. Kinetics of the CO+N<sub>2</sub>O Reaction over Noble Metals: I. Pt/Al<sub>2</sub>O<sub>3</sub>. J. Catal. **1999**, *187*, 321–331.
- (267) McCabe, R. W.; Wong, C. Steady-State Kinetics of the CO-N2O Reaction over an Alumina-Supported Rhodium Catalyst. J. Catal. 1990, 121, 422–431.
- (268) Tanaka, K.-I.; Blyholder, G. Photocatalytic Reaction on Zinc Oxide II. Oxidation of Carbon Monoxide with Nitrous Oxide and Oxygen. J. Phys. Chem. 1972, 76, 1807–1814.
- (269) Krupay, B. W.; Ross, R. A. The Reaction of Carbon Monoxide with Nitrous Oxide Over Nickel(II) Oxide in the Néel Transition Temperature Region. *Zeitschrift fur Phys. Chemie* **1977**, *106*, 83–94.
- (270) Hori, B.; Takezawa, N. Mechanism of Reduction of Dinitrogen Monoxide by Carbon Monoxide over Magnesium Oxide—Role of Surface Formate Species. *Catal. Lett.* 1992 124 1992, 12, 383–388.

- (271) García-Diéguez, M.; Chin, Y. H. C.; Iglesia, E. Catalytic Reactions of Dioxygen with Ethane and Methane on Platinum Clusters: Mechanistic Connections, Site Requirements, and Consequences of Chemisorbed Oxygen. *J. Catal.* 2012, 285, 260–272.
- (272) Chin, Y. H.; Buda, C.; Neurock, M.; Iglesia, E. Reactivity of Chemisorbed Oxygen Atoms and Their Catalytic Consequences during CH<sub>4</sub>-O<sub>2</sub> Catalysis on Supported Pt Clusters. *J. Am. Chem. Soc.* 2011, *133*, 15958–15978.
- (273) Allian, A. D.; Takanabe, K.; Fujdala, K. L.; Hao, X.; Truex, T. J.; Cai, J.; Buda, C.; Neurock, M.; Iglesia, E. Chemisorption of CO and Mechanism of CO Oxidation on Supported Platinum Nanoclusters. *J. Am. Chem. Soc.* 2011, *133*, 4498–4517.
- (274) Weiss, B. M.; Iglesia, E. No Oxidation Catalysis on Pt Clusters: Elementary Steps, Structural Requirements, and Synergistic Effects of NO<sub>2</sub> Adsorption Sites. *J. Phys. Chem. C* 2009, *113*, 13331–13340.
- (275) Carnisio, G.; Garbassi, F.; Petrini, G.; Parravano, G. Isotopic Mixing in Carbon Monoxide Catalyzed by Zinc Oxide. J. Catal. 1978, 54, 66–80.
- (276) Belton, D. N.; Schmieg, S. J. Kinetics of CO Oxidation by N<sub>2</sub>O over Rh(111). J.
   *Catal.* 1992, 138, 70–78.
- (277) Kapteijn, F.; Marban, G.; Mirasol-Rodriguez, J.; Moulijn, J. A. Kinetic Analysis of the Decomposition of Nitrous Oxide over ZSM-5 Catalysts. J. Catal. 1997, 167, 256–265.
- (278) Obalová, L.; Fíla, V. Kinetic Analysis of N2O Decomposition over Calcined
Hydrotalcites. Appl. Catal. B Environ. 2007, 70, 353–359.

- (279) Eley, D. D.; Knights, C. F. The Decomposition of Nitrous Oxide Catalysed by Palladium-Gold Alloy Wires. *Proc. R. Soc. A* **1966**, *294*, 1–19.
- (280) Sastri, V. R.; Pitchai, R.; Swamy, C. S. Nitrous Oxide Decomposition on La<sub>2</sub>TiMO<sub>6</sub> (M = Cu Ni & Zn): Pressure Effect on Kinetics. *Indian J. Chem.* 1979, *18A*, 213–216.
- (281) Fanson, P. T.; Stradt, M. W.; Lauterbach, J.; Delgass, W. N. The Effect of Si/Al Ratio and Copper Exchange Level on Isothermal Kinetic Rate Oscillations for N<sub>2</sub>O Decomposition over Cu-ZSM-5: A Transient FTIR Study. *Appl. Catal. B Environ.* 2002, *38*, 331–347.
- (282) Leglise, J.; Petunchi, J. O.; Hall, W. K. N<sub>2</sub>O Decomposition over Iron-Exchanged Mordenite. J. Catal. 1984, 86, 392–399.
- (283) Sastri, V. R.; Pitchai, R.; Swamy, C. S. Nitrous Oxide Decomposition on La<sub>2</sub>TiMO<sub>6</sub>. *Indian J. Chem.* **1979**, *18A*, 213–216.
- (284) Dubkov, K. A.; Starokon', E. V.; Paukshtis, E. A.; Volodin, A. M.; Panov, G. I. Mechanism of the Low-Temperature Interaction of Hydrogen with α-Oxygen on FeZSM-5 Zeolite. *Kinet. Catal.* 2004 452 2004, 45, 202–208.
- (285) Westre, T. E.; Kennepohl, P.; DeWitt, J. G.; Hedman, B.; Hodgson, K. O.;
  Solomon, E. I. A Multiplet Analysis of Fe K-Edge 1s → 3d Pre-Edge Features of Iron Complexes. J. Am. Chem. Soc. 1997, 119, 6297–6314.
- (286) Hanna, L.; Kucheryavy, P.; Lahanas, N.; Lockard, J. V. Spectroscopic Characterization of Metal Ligation in Trinuclear Iron-µ<sub>3</sub>-Oxo-Based Complexes

and Metal-Organic Frameworks. J. Chem. Phys. 2019, 150, 174707.

- (287) Rosen, A. S.; Notestein, J. M.; Snurr, R. Q. High-Valent Metal–Oxo Species at the Nodes of Metal–Triazolate Frameworks: The Effects of Ligand Exchange and Two-State Reactivity for C–H Bond Activation. *Angew. Chemie* 2020, ange.202004458.
- (288) Cannon, R. D.; White, R. P. Cannon Inorganic Chem. *Prog. Inorg. Chem.* **1988**, *36*, 195–298.
- (289) Anson, C. E.; Bourke, J. P.; Cannon, R. D; Jayasooriya, U. A.; Molinier, M.;
  Powell, A. K. Crystal Structures of the Isomorphous Prototypic Oxo-Centered Trinuclear Complexes [Cr<sub>3</sub>O(OOCCH<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl·6H<sub>2</sub>O and [Fe<sub>3</sub>O(OOCCH<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl·6H<sub>2</sub>O. *Inorg. Chem.* **1997**, *36*, 1265–1267.
- (290) Uemura, S.; Spencer, A.; Wilkinson, G. μ<sub>3</sub>-Oxotrimetal Acetato-Complexes of Chromium, Manganese, Iron, Cobalt, Rhodium, and Iridium. *J. Chem. Soc. Dalt. Trans.* 1973, No. 23, 2565–2571.
- (291) Blake, A. B.; Yavari, A.; Hatfield, W. E.; Sethulekshmi, C. N. Magnetic and Spectroscopic Properties of Some Heterotrinuclear Basic Acetates of Chromium(III), Iron(III), and Divalent Metal Ions. *J. Chem. Soc. Dalt. Trans.* 1985, No. 12, 2509–2520.
- (292) Belmore, K.; Madison, X. J.; Harton, A.; Vincent, J. B. Carbon-13 NMR Studies of Oxo-Centered Trinuclear Chromium(III) Complexes of the General Formula [Cr<sub>3</sub>O(O<sub>2</sub>CR)<sub>6</sub>(L)<sub>3</sub>]<sup>+</sup> (R = Me, Ph; L = H2O, Py). *Spectrochim. Acta Part A Mol. Spectrosc.* 1994, *50*, 2365–2370.

- (293) Blake, A. B.; Sinn, E.; Yavari, A.; Murray, K. S.; Moubaraki, B. Oxo-Centred Trinuclear Acetate Complexes Containing Mixed-Metal Clusters. Crystal Structure of a Chromium(III)Iron(III)Nickel(II) Complex and Magnetic Properties of a Dichromium(III)Magnesium(II) Complex. *Dalt. Trans.* **1998**, *1*, 45–50.
- (294) Lang, J.; Hewer, J. M.; Meyer, J.; Schuchmann, J.; Van Wüllen, C.; Niedner-Schatteburg, G. Magnetostructural Correlation in Isolated Trinuclear Iron(III) Oxo Acetate Complexes. *Phys. Chem. Chem. Phys.* **2018**, *20*, 16673–16685.
- (295) Baumann, J. A.; Salmon, D. J.; Wilson, S. T.; Meyer, T. J.; Hatfield, W. E.
   Electronic Structure and Redox Properties of the Clusters [Ru<sub>3</sub>O(CH<sub>3</sub>CO<sub>2</sub>)<sub>6</sub>L<sub>3</sub>]<sup>N+</sup>.
   *Inorg. Chem.* 1978, *17*, 3342–3350.
- (296) Jang, H. G.; Geib, S. J.; Kaneko, Y.; Nakano, M.; Sorai, M.; Rheingold, A. L.;
  Montez, B.; Hendrickson, D. N. Lattice-Engineered Micromodulation of Intramolecular Electron-Transfer Rates in Trinuclear Mixed-Valence Iron Acetate Complexes. J. Am. Chem. Soc. 1989, 111, 173–186.
- (297) Wu, R.; Poyraz, M.; Sowrey, F. E.; Anson, C. E.; Wocadlo, S.; Powell, A. K.; Jayasooriya, U. A.; Cannon, R. D.; Nakamoto, T.; Katada, M.; Sano, H. Electron Localization and Delocalization in Mixed-Valence Transition Metal Clusters: Structural and Spectroscopic Studies of Oxo-Centered Trinuclear Complexes [Fe<sub>3</sub>O(OOCCMe<sub>3</sub>)<sub>6</sub>(Py)<sub>3</sub>]<sup>+/0</sup> and [Mn<sub>3</sub>O(OOCCMe<sub>3</sub>)<sub>6</sub>(Py)<sub>3</sub>]<sup>+/0</sup>. *Inorg. Chem.* 1998, *37*, 1913–1921.
- (298) Stadler, C.; Daub, J.; Köhler, J.; Saalfrank, R. W.; Coropceanu, V.; Schünemann,V.; Ober, C.; Trautwein, A. X.; Parker, S. F.; Poyraz, M.; Inomata, T.; Cannon, R.

D. Electron Transfer in a Trinuclear Oxo-Centred Mixed-Valence Iron Complex, in Solid and Solution States. *J. Chem. Soc. Dalt. Trans.* **2001**, No. 22, 3373–3383.

- (299) Overgaard, J.; Larsen, F. K.; Schiøtt, B.; Iversen, B. B. Electron Density Distributions of Redox Active Mixed Valence Carboxylate Bridged Trinuclear Iron Complexes. J. Am. Chem. Soc. 2003, 125, 11088–11099.
- (300) Harton, A.; Nagi, M. K.; Glass, M. M.; Junk, P. C.; Atwood, J. L.; Vincent, J. B. Synthesis and Characterization of Symmetric and Unsymmetric Oxo-Bridged Trinuclear Chromium Benzoate Complexes: Crystal and Molecular Structure of [Cr<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(Py)<sub>3</sub>]ClO<sub>4</sub>. *Inorganica Chim. Acta* **1994**, *217*, 171–179.
- (301) Kou, N.; Tadashi, Y.; Yoichi, S.; Tasuku, I. Synthesis of Trinuclear Molybdenum Cluster Complex with Novel Skeleton, [Mo<sub>3</sub>(μ<sub>3</sub>-CCH<sub>3</sub>)(μ<sub>3</sub>-O)(μ-C<sub>6</sub>H<sub>5</sub>COO)<sub>6</sub>(CH<sub>3</sub>OH)<sub>3</sub>]Cl through Bridging Carboxylate Ligand Substitution. *Chem. Lett.* **1992**, *21*, 983–986.
- (302) Ito, S.; Inoue, K.; Mastumoto, M. [Fe<sub>3</sub>O(OCOR)<sub>6</sub>L<sub>3</sub>]<sup>+</sup>-Catalyzed Epoxidation of Olefinic Alcohol Acetates by Molecular Oxygen. *J. Am. Chem. Soc.* 1982, *104*, 6450–6452.
- (303) Fouda, S. A.; Rempel, G. L. μ<sub>3</sub>-Oxo-Triruthenium Acetate Cluster Complexes as Catalysts for Olefin Hydrogenation. *Inorg. Chem.* **1979**, *18*, 1–8.
- (304) Nunes, G. S.; Alexiou, A. D. P.; Toma, H. E. Catalytic Oxidation of Hydrocarbons by Trinuclear μ-Oxo-Bridged Ruthenium-Acetate Clusters: Radical versus Non-Radical Mechanisms. J. Catal. 2008, 260, 188–192.
- (305) Sudik, A. C.; Cô Té, A. P.; Yaghi, O. M. Metal-Organic Frameworks Based on

Trigonal Prismatic Building Blocks and the New "Acs" Topology. *Inorg. Chem.* **2005**, *44*, 2998–3000.

- (306) Fujihara, T.; Aonahata, J.; Kumakura, S.; Nagasawa, A.; Murakami, K.; Ito, T. Kinetic Study on the Substitution of Dimethylacetamide for the Terminal Aqua Ligands in the Trinuclear Chromium(III) Complexes [Cr<sub>3</sub>(μ<sub>3</sub>-O)(μ-RCO<sub>2</sub>)<sub>6</sub>(H 2O)<sub>3</sub>]<sup>+</sup> (R = H, CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, CH<sub>2</sub>Cl, CHCl<sub>2</sub>, CH<sub>3</sub>OCH<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>C, *Inorg. Chem.* **1998**, *37*, 3779–3784.
- (307) Sasaki, Y.; Nagasawa, A.; Tokiwa-Yamamoto, A.; Ito, T. Substitution of Methanol-D4 for the Coordinated Water in the Trinuclear Complexes, [M<sub>3</sub>(μ<sub>3</sub>-O)(μ-CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> (M<sub>3</sub>=Ru<sub>3</sub>, Rh<sub>3</sub> or Ru<sub>2</sub>Rh) in Methanol-D4. *Inorganica Chim. Acta* **1993**, *212*, 175–182.
- (308) Lawrence, M. A. W.; Maragh, P. T.; Dasgupta, T. P. Kinetics and Mechanism of Aquation of a Series of Mixed-Metal Oxo-Centered Trinuclear Cations. *J. Coord. Chem.* 2010, 63, 2517–2527.
- (309) Jackson, T. A.; Rohde, J. U.; Mi, S. S.; Sastri, C. V.; DeHont, R.; Stubna, A.;
  Ohta, T.; Kitagawa, T.; Münck, E.; Nam, W.; Que, L. Axial Ligand Effects on the Geometric and Electronic Structures of Nonheme Oxoiron(IV) Complexes. *J. Am. Chem. Soc.* 2008, *130*, 12394–12407.
- (310) Zhang, L. L.; Wang, X. Y.; Jiang, K. Y.; Zhao, B. Y.; Yan, H. M.; Zhang, X. Y.;
  Zhang, Z. X.; Guo, Z.; Che, C. M. A Theoretical Study on the Oxidation of
  Alkenes to Aldehydes Catalyzed by Ruthenium Porphyrins Using O<sub>2</sub> as the Sole
  Oxidant. *Dalt. Trans.* 2018, 47, 5286–5297.

- (311) Snyder, B. E. R.; Böttger, L. H.; Bols, M. L.; Yan, J. J.; Rhoda, H. M.; Jacobs, A. B.; Hu, M. Y.; Zhao, J.; Ercan Alp, E.; Hedman, B.; Hodgson, K. O.; Schoonheydt, R. A.; Sels, B. F.; Solomon, E. I. Structural Characterization of a Non-Heme Iron Active Site in Zeolites That Hydroxylates Methane. *Proc. Natl. Acad. Sci. U. S. A.* 2018, *115*, 4565–4570.
- (312) Roy, L. Theoretical Identification of the Factors Governing the Reactivity of C–H
   Bond Activation by Non-Heme Iron(IV)-Oxo Complexes. *Chempluschem* 2019, 84, 893–906.
- (313) Kumar, D.; Sastry, G. N.; De Visser, S. P. Axial Ligand Effect on the Rate Constant of Aromatic Hydroxylation by Iron(IV)-Oxo Complexes Mimicking Cytochrome P450 Enzymes. J. Phys. Chem. B 2012, 116, 718–730.
- (314) Chantarojsiri, T.; Sun, Y.; Long, J. R.; Chang, C. J. Water-Soluble Iron(IV)-Oxo Complexes Supported by Pentapyridine Ligands: Axial Ligand Effects on Hydrogen Atom and Oxygen Atom Transfer Reactivity. *Inorg. Chem.* 2015, *54*, 5879–5887.
- (315) Vogel, K. M.; Kozlowski, P. M.; Zgierski, M. Z.; Spiro, T. G. Determinants of the FeXO (X = C, N, O) Vibrational Frequencies in Heme Adducts from Experiment and Density Functional Theory. *J. Am. Chem. Soc.* **1999**, *121*, 9915–9921.
- (316) Spiro, T. G.; Soldatova, A. V.; Balakrishnan, G. CO, NO and O<sub>2</sub> as Vibrational Probes of Heme Protein Interactions. *Coord. Chem. Rev.* 2013, 257, 511.
- (317) Goodrich, L. E.; Paulat, F.; Praneeth, V. K. K.; Lehnert, N. Electronic Structure of Heme-Nitrosyls and Its Significance for Nitric Oxide Reactivity, Sensing,

Transport, and Toxicity in Biological Systems. Inorg. Chem. 2010, 49, 6293-6316.

- (318) Rivallan, M.; Bromley, B.; Kiwi-Minsker, L. Do Synthetic Fe-Zeolites Mimic
   Biological Fe-Porphyrins in Reactions with Nitric Oxide? *Catal. Today* 2010, *157*, 223–230.
- (319) Vitillo, J. G.; Gagliardi, L. Thermal Treatment Effect on CO and NO Adsorption on Fe(II) and Fe(III) Species in Fe<sub>3</sub>O-Based MIL-Type Metal-Organic Frameworks: A Density Functional Theory Study. *Inorg. Chem.* 2021, 60, 11813– 11824.
- (320) Li, Y.; Yang, R. T. Hydrogen Storage in Metal-Organic and Covalent-Organic Frameworks by Spillover. AIChE J 2007, 54, 269–279.
- (321) Zornoza, B.; Martinez-Joaristi, A.; Serra-Crespo, P.; Tellez, C.; Coronas, J.;
  Gascon, J.; Kapteijn, F. Functionalized Flexible MOFs as Fillers in Mixed Matrix
  Membranes for Highly Selective Separation of CO<sub>2</sub> from CH<sub>4</sub> at Elevated
  Pressures. *Chem. Commun.* 2011, 47, 9522–9524.
- (322) Sun, C. Y.; Qin, C.; Wang, X. L.; Yang, G. S.; Shao, K. Z.; Lan, Y. Q.; Su, Z. M.;
  Huang, P.; Wang, C. G.; Wang, E. B. Zeolitic Imidazolate Framework-8 as
  Efficient PH-Sensitive Drug Delivery Vehicle. *Dalt. Trans.* 2012, *41*, 6906–6909.
- (323) Tan, L.-L.; Li, H.; Zhou, Y.; Zhang, Y.; Feng, X.; Wang, B.; Yang, Y.-W. Zn<sup>2+</sup> -Triggered Drug Release from Biocompatible Zirconium MOFs Equipped with Supramolecular Gates. *Small* **2015**, *11*, 3807–3813.
- (324) Zhao, M.; Ou, S.; Wu, C. De. Porous Metal-Organic Frameworks for Heterogeneous Biomimetic Catalysis. *Acc. Chem. Res.* 2014, 47, 1199–1207.

- (325) Yang, D.; Ortuño, M. A.; Bernales, V.; Cramer, C. J.; Gagliardi, L.; Gates, B. C. Structure and Dynamics of Zr<sub>6</sub>O<sub>8</sub> Metal-Organic Framework Node Surfaces
  Probed with Ethanol Dehydration as a Catalytic Test Reaction. *J. Am. Chem. Soc.*2018, *140*, 3751–3759.
- (326) Long, J. R.; Yaghi, O. M. The Pervasive Chemistry of Metal-Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1213–1214.
- (327) Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. Assembly of Metal-Organic Frameworks from Large Organic and Inorganic Secondary Building Units: New Examples and Simplifying Principles for Complex Structures. *J. Am. Chem. Soc.* 2001, *123*, 8239–8247.
- (328) Vermoortele, F.; Vandichel, M.; Van De Voorde, B.; Ameloot, R.; Waroquier, M.;
  Van Speybroeck, V.; De Vos, D. E. Electronic Effects of Linker Substitution on
  Lewis Acid Catalysis with Metal-Organic Frameworks. *Angew. Chemie Int. Ed.*2012, *124*, 4971–4974.
- (329) Bermejo-Deval, R.; Gounder, R.; Davis, M. E. Framework and Extraframework Tin Sites in Zeolite Beta React Glucose Differently. *ACS Catal.* 2012, *2*, 2705– 2713.
- (330) Herbst, A.; Janiak, C. MOF Catalysts in Biomass Upgrading towards Value-Added Fine Chemicals. *CrystEngComm*. Royal Society of Chemistry July 27, 2017, pp 4092–4117.
- (331) Dhakshinamoorthy, A.; Alvaro, M.; Chevreau, H.; Horcajada, P.; Devic, T.; Serre,C.; Garcia, H. Iron(III) Metal–Organic Frameworks as Solid Lewis Acids for the

Isomerization of α-Pinene Oxide. *Catal. Sci. Technol.* **2012**, *2*, 324–330.

- (332) Arrozi, U. S. F.; Wijaya, H. W.; Patah, A.; Permana, Y. Efficient Acetalization of Benzaldehydes Using UiO-66 and UiO-67: Substrates Accessibility or Lewis Acidity of Zirconium. *Appl. Catal. A Gen.* **2015**, *506*, 77–84.
- (333) Rivera-Torrente, M.; Pletcher, P. D.; Jongkind, M. K.; Nikolopoulos, N.;
  Weckhuysen, B. M. Ethylene Polymerization over Metal–Organic Framework Crystallites and the Influence of Linkers on Their Fracturing Process. *ACS Catal.* 2019, *9*, 3059–3069.
- (334) Kholdeeva, O. A.; Skobelev, I. Y.; Ivanchikova, I. D.; Kovalenko, K. A.; Fedin, V. P.; Sorokin, A. B. Hydrocarbon Oxidation over Fe- and Cr-Containing Metal-Organic Frameworks MIL-100 and MIL-101-a Comparative Study. *Catal. Today* 2014, 238, 54–61.
- (335) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. Metal Organic Frameworks as Solid Acid Catalysts for Acetalization of Aldehydes with Methanol. *Adv. Synth. Catal.* 2010, *352*, 3022–3030.
- (336) Dhakshinamoorthy, A.; Alvaro, M.; Horcajada, P.; Gibson, E.; Vishnuvarthan, M.;
  Vimont, A.; Grenèche, J. M.; Serre, C.; Daturi, M.; Garcia, H. Comparison of
  Porous Iron Trimesates Basolite F300 and MIL-100(Fe) as Heterogeneous
  Catalysts for Lewis Acid and Oxidation Reactions: Roles of Structural Defects and
  Stability. ACS Catal. 2012, 2, 2060–2065.
- (337) Jin, Y.; Shi, J.; Zhang, F.; Zhong, Y.; Zhu, W. Synthesis of Sulfonic Acid-Functionalized MIL-101 for Acetalization of Aldehydes with Diols. *J. Mol. Catal.*

A Chem. 2014, 383–384, 167–171.

- (338) Herbst, A.; Khutia, A.; Janiak, C. Brønsted Instead of Lewis Acidity in Functionalized MIL-101Cr MOFs for Efficient Heterogeneous (Nano-MOF) Catalysis in the Condensation Reaction of Aldehydes with Alcohols. *Inorg. Chem.* 2014, *53*, 7319–7333.
- (339) Bromberg, L.; Hatton, T. A. Aldehyde-Alcohol Reactions Catalyzed under Mild Conditions by Chromium(III) Terephthalate Metal Organic Framework (MIL-101) and Phosphotungstic Acid Composites. *ACS Appl. Mater. Interfaces* 2011, *3*, 4756–4764.
- (340) Zhang, F.; Jin, Y.; Shi, J.; Zhong, Y.; Zhu, W.; El-Shall, M. S. Polyoxometalates Confined in the Mesoporous Cages of Metal-Organic Framework MIL-100(Fe): Efficient Heterogeneous Catalysts for Esterification and Acetalization Reactions. *Chem. Eng. J.* 2015, 269, 236–244.
- (341) Kim, M. J.; Park, S. M.; Song, S.-J.; Won, J.; Lee, J. Y.; Yoon, M.; Kim, K.; Seo,
  G. Adsorption of Pyridine onto the Metal Organic Framework MIL-101. *J. Colloid Interface Sci.* 2011, *361*, 612–617.
- (342) Woolery, G. L.; Kuehl, G. H. On the Nature of Framework Brønsted and Lewis Acid Sites in ZSM-5. Zeolites 1997, 19, 288–296.
- (343) Parry, E. P. An Infrared Study of Pyridine Adsorbed on Acidic Solids.Characterization of Surface Acidity. J. Catal. 1963, 2, 371–379.
- (344) Clerici, A.; Pastori, N.; Porta, O. Efficient Acetalisation of Aldehydes Catalyzed by Titanium Tetrachloride in a Basic Medium. *Tetrahedron* **1998**, *54*, 15679–

15690.

- (345) Jiang, Q.; Rüegger, H.; Venanzi, L. M. Some New Chain-like Terdentate Phosphines, Their Ruthenium(II) Coordination Chemistry and the Activity of the Cations [Ru(MeCN)<sub>3</sub>(PhP{CH<sub>2</sub>CH<sub>2</sub>P(p-X-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>}<sub>2</sub>)]<sup>2+</sup> (X=H, F, Me and OMe) as Acetalization Catalysts. *Inorganica Chim. Acta* **1999**, 290, 64–79.
- (346) Vermoortele, F.; Ameloot, R.; Vimont, A.; Serre, C.; De Vos, D. An Amino-Modified Zr-Terephthalate Metal-Organic Framework as an Acid-Base Catalyst for Cross-Aldol Condensation. *Chem. Commun.* **2011**, *47*, 1521–1523.
- (347) Vermoortele, F.; Bueken, B.; Le Bars, G.; Van de Voorde, B.; Vandichel, M.;
  Houthoofd, K.; Vimont, A.; Daturi, M.; Waroquier, M.; Van Speybroeck, V.;
  Kirschhock, C.; De Vos, D. E. Synthesis Modulation as a Tool To Increase the
  Catalytic Activity of Metal–Organic Frameworks: The Unique Case of UiO66(Zr). J. Am. Chem. Soc. 2013, 135, 11465–11468.
- (348) Li, L.; Korányi, T. I.; Sels, B. F.; Pescarmona, P. P. Highly-Efficient Conversion of Glycerol to Solketal over Heterogeneous Lewis Acid Catalysts. *Green Chem.* 2012, *14*, 1611–1619.
- (349) Priya, S. S.; Selvakannan, P. R.; Chary, K. V. R.; Kantam, M. L.; Bhargava, S. K. Solvent-Free Microwave-Assisted Synthesis of Solketal from Glycerol Using Transition Metal Ions Promoted Mordenite Solid Acid Catalysts. *Mol. Catal.* 2017, 434, 184–193.
- (350) Zhang, J.; Bao, S. H.; Yang, J. G. Synthesis of a Novel Multi-SO<sub>3</sub>H Functionalized Strong Brønsted Acidic Ionic Liquid and Its Catalytic Activities for Acetalization.

Chinese Sci. Bull. 2009, 54, 3958–3964.

- (351) Miao, J.; Wan, H.; Shao, Y.; Guan, G.; Xu, B. Acetalization of Carbonyl Compounds Catalyzed by Acidic Ionic Liquid Immobilized on Silica Gel. *J. Mol. Catal. A Chem.* 2011, 348, 77–82.
- (352) Leng, K.; Sun, Y.; Li, X.; Sun, S.; Xu, W. Rapid Synthesis of Metal–Organic Frameworks MIL-101(Cr) Without the Addition of Solvent and Hydrofluoric Acid. *Cryst. Growth Des.* 2016, *16*, 1168–1171.
- (353) Richardson, J. M.; Jones, C. W. Strong Evidence of Solution-Phase Catalysis Associated with Palladium Leaching from Immobilized Thiols during Heck and Suzuki Coupling of Aryl Iodides, Bromides, and Chlorides. *J. Catal.* 2007, 251, 80–93.
- (354) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. On the Nature of the Active Species in Palladium Catalyzed Mizoroki–Heck and Suzuki–Miyaura Couplings – Homogeneous or Heterogeneous Catalysis, A Critical Review. *Adv. Synth. Catal.* 2006, 348, 609–679.
- (355) Gruber-Woelfler, H.; Radaschitz, P. F.; Feenstra, P. W.; Haas, W.; Khinast, J. G. Synthesis, Catalytic Activity, and Leaching Studies of a Heterogeneous Pd-Catalyst Including an Immobilized Bis(Oxazoline) Ligand. *J. Catal.* 2012, 286, 30–40.
- (356) Basila, M. R.; Kantner, T. R.; Rhee, K. H. The Nature of the Acidic Sites on a Silica-Alumina. Characterization by Infrared Spectroscopic Studies of Trimethylamine and Pyridine Chemisorption. J. Phys. Chem. 1964, 68, 3197–

3207.

- (357) Itoh, M.; Hattori, H.; Tanabe, K. The Acidic Properties of TiO<sub>2</sub>-SiO<sub>2</sub> and Its Catalytic Activities for the Amination of Phenol, the Hydration of Ethylene and the Isomerization of Butene. *J. Catal.* **1974**, *35*, 225–231.
- (358) Opanasenko, M.; Dhakshinamoorthy, A.; Shamzhy, M.; Nachtigall, P.; Horáček, M.; Garcia, H.; Čejka, J. Comparison of the Catalytic Activity of MOFs and Zeolites in Knoevenagel Condensation. *Catal. Sci. Technol.* 2013, *3*, 500–507.
- (359) Meloni, D.; Laforge, S.; Martin, D.; Guisnet, M.; Rombi, E.; Solinas, V. Acidic and Catalytic Properties of H-MCM-22 Zeolites: 1. Characterization of the Acidity by Pyridine Adsorption. *Appl. Catal. A Gen.* 2001, 215, 55–66.
- (360) Brown, H. C.; Kanner, B. 2,6-Di-Butylpyridine—An Unusual Pyridine Base. J. Am. Chem. Soc. **1953**, 75, 3865–3865.
- (361) Dewing, J.; Monks, G. T.; Youll, B. Competitive Adsorption of Pyridine and Sterically Hindered Pyridines on Alumina. *J. Catal.* **1976**, *44*, 226–235.
- (362) Sullivan, M. M.; Bhan, A. Acetone Hydrodeoxygenation over Bifunctional Metallic-Acidic Molybdenum Carbide Catalysts. ACS Catal. 2016, 6, 1145–1152.
- (363) Soled, S. L.; McVicker, G. B.; Murrell, L. L.; Sherman, L. G.; Dispenziere, N. C.;
  Hsu, S. L.; Waldman, D. Comparison of the Acidities of WO<sub>3</sub> Al<sub>2</sub>O<sub>3</sub> and
  Ultrastable Faujasite Catalysts. *J. Catal.* **1988**, *111*, 286–295.
- (364) Santiesteban, J. G.; Vartuli, J. C.; Han, S.; Bastian, R. D.; Chang, C. D. Influence of the Preparative Method on the Activity of Highly Acidic WO<sub>x</sub> /ZrO<sub>2</sub> and the Relative Acid Activity Compared with Zeolites. *J. Catal.* **1997**, *168*, 431–441.

- (365) Corma, A.; Fornés, V.; Forni, L.; Márquez, F.; Martínez-Triguero, J.; Moscotti, D.
  2,6-Di-Tert-Butyl-Pyridine as a Probe Molecule to Measure External Acidity of Zeolites. *J. Catal.* 1998, 179, 451–458.
- (366) Gounder, R.; Jones, A. J.; Carr, R. T.; Iglesia, E. Solvation and Acid Strength Effects on Catalysis by Faujasite Zeolites. J. Catal. 2012, 286, 214–223.
- (367) Zheng, S.; Heydenrych, H. R.; Jentys, A.; Lercher, J. A. Influence of Surface Modification on the Acid Site Distribution of HZSM-5. *J. Phys. Chem. B* 2002, *106*, 9552–9558.
- (368) Góra-Marek, K.; Tarach, K.; Choi, M. 2,6-Di-Tert-Butylpyridine Sorption
   Approach to Quantify the External Acidity in Hierarchical Zeolites. *J. Phys. Chem. C* 2014, *118*, 12266–12274.
- (369) Tang, J.; Wang, J. Metal Organic Framework with Coordinatively Unsaturated Sites as Efficient Fenton-like Catalyst for Enhanced Degradation of Sulfamethazine. *Environ. Sci. Technol.* 2018, *52*, 5367–5377.
- (370) Rostamnia, S.; Alamgholiloo, · Hassan; Rostamnia, S.; Alamgholiloo, H.
   Synthesis and Catalytic Application of Mixed Valence Iron (Fe<sup>II</sup> /Fe<sup>III</sup>)-Based
   OMS-MIL-100(Fe) as an Efficient Green Catalyst for the Aza-Michael Reaction.
   *Catal. Letters* 2018, 148, 2918–2929.
- (371) Paukshtis, E. A.; Yurchenko, E. N. Study of the Acid–Base Properties of Heterogeneous Catalysts by Infrared Spectroscopy. *Russ. Chem. Rev.* 1983, 52, 242–258.
- (372) Cairon, O.; Thomas, K.; Chevreau, T. FTIR Studies of Unusual OH Groups in

Steamed HNaY Zeolites: Preparation and Acid Properties. *Microporous Mesoporous Mater.* **2001**, *46*, 327–340.

- (373) Zaki, M. I.; Knözlngem, H. Characterization of Oxide Surfaces by Adsorption of Carbon Monoxide—a Low Temperature Infrared Spectroscopy Study. *Spectrochim. Acta - Part A Mol. Spectrosc.* **1987**, *43*, 1455–1459.
- (374) Lavalley, J.-C.; Jolly-Feaugas, S.; Janin, A.; Saussey, J. In Situ Fourier Transform Infrared Studies of Active Sites and Reaction Mechanisms in Heterogeneous Catalysis: Hydrocarbon Conversion on H-Zeolites. In *Progress in Fourier Transform Spectroscopy*; Springer Vienna, 1997; Vol. 14, pp 51–56.
- (375) Zecchina, A.; Bordiga, S.; Spoto, G.; Marchese, L.; Petrini, G.; Leofanti, G.;
  Padovan, M. Silicalite Characterization. 1. Structure, Adsorptive Capacity, and IR
  Spectroscopy of the Framework and Hydroxyl Modes. *J. Phys. Chem.* 1992, *96*, 4985–4990.
- (376) Bezverkhyy, I.; Weber, G.; Bellat, J. P. Degradation of Fluoride-Free MIL-100(Fe) and MIL-53(Fe) in Water: Effect of Temperature and PH. *Microporous Mesoporous Mater.* 2016, 219, 117–124.
- (377) Bellido, E.; Guillevic, M.; Hidalgo, T.; Santander-Ortega, M. J.; Serre, C.;
  Horcajada, P. Understanding the Colloidal Stability of the Mesoporous MIL-100(Fe) Nanoparticles in Physiological Media. *Langmuir* 2014, *30*, 5911–5920.
- (378) Küsgens, P.; Rose, M.; Senkovska, I.; Fröde, H.; Henschel, A.; Siegle, S.; Kaskel,
  S. Characterization of Metal-Organic Frameworks by Water Adsorption. *Microporous Mesoporous Mater.* 2009, 120, 325–330.

- (379) Mileo, P. G. M.; Ho Cho, K.; Park, J.; Devautour-Vinot, S.; Chang, J.-S.; Maurin,
  G. Unraveling the Water Adsorption Mechanism in the Mesoporous MIL-100(Fe)
  Metal–Organic Framework. *J. Phys. Chem. C* 2019, *123*, 23014–23025.
- (380) Maache, M.; Janin, A.; Lavalley, J. C.; Benazzi, E. FT Infrared Study of Brønsted Acidity of H-Mordenites: Heterogeneity and Effect of Dealumination. *Zeolites* 1995, 15, 507–516.
- (381) Oliviero, L.; Vimont, A.; Lavalley, J. C.; Sarria, F. R.; Gaillard, M.; Maugé, F.
  2,6-Dimethylpyridine as a Probe of the Strength of Brønsted Acid Sites: Study on Zeolites. Application to Alumina. *Phys. Chem. Chem. Phys.* 2005, *7*, 1861–1869.
- (382) Makarova, M. A.; Al-Ghefaili, K. M.; Dwyer, J. Brønsted Acid Strength in US-Y:
   FTIR Study of CO Adsorption. J. Chem. Soc. Faraday Trans. 1994, 90, 383–386.
- (383) Lord, R. C.; Merrifield, R. E. Strong Hydrogen Bonds in Crystals. J. Chem. Phys. 1953, 21, 166–167.
- (384) Evans, R. F.; Kynaston, W. 188. Infrared Spectra and Hydrogen Bonding in Pyridine Derivatives. J. Chem. Soc. 1962, 0, 1005–1008.
- (385) Burnett, L.; Rysakova, M.; Wang, K.; González-Carballo, J.; Tooze, R. P.; García-García, F. R. Isothermal Cyclic Conversion of Methane to Methanol Using Copper-Exchanged ZSM-5 Zeolite Materials under Mild Conditions. *Appl. Catal. A Gen.* 2019, *587*, 117272.
- (386) Göltl, F.; Bhandari, S.; Mavrikakis, M. Thermodynamics Perspective on the Stepwise Conversion of Methane to Methanol over Cu-Exchanged SSZ-13. ACS Catal. 2021, 11, 7719–7734.

- (387) Dinh, K. T.; Sullivan, M. M.; Serna, P.; Meyer, R. J.; Dincă, M.; Román-Leshkov,
  Y. Viewpoint on the Partial Oxidation of Methane to Methanol Using Cu- and Fe-Exchanged Zeolites. *ACS Catal.* 2018, *8*, 8306–8313.
- (388) Latimer, A. A.; Kakekhani, A.; Kulkarni, A. R.; Nørskov, J. K. Direct Methane to Methanol: The Selectivity-Conversion Limit and Design Strategies. *ACS Catal.* **2018**, 8, 6894–6907.
- (389) Szécsényi, Á.; Li, G.; Gascon, J.; Pidko, E. A. Unraveling Reaction Networks behind the Catalytic Oxidation of Methane with H<sub>2</sub>O<sub>2</sub> over a Mixed-Metal MIL-53(Al,Fe) MOF Catalyst. *Chem. Sci.* **2018**, *9*, 6765–6773.
- (390) Konsolakis, M. Recent Advances on Nitrous Oxide (N<sub>2</sub>O) Decomposition over Non-Noble-Metal Oxide Catalysts: Catalytic Performance, Mechanistic Considerations, and Surface Chemistry Aspects. ACS Catal. 2015, 5, 6397–6421.
- (391) Overview of Greenhouse Gases | US EPA https://www.epa.gov/ghgemissions/overview-greenhouse-gases (accessed 2022 -03 -20).
- (392) Colby, J.; Stirling, D. I.; Dalton, H. The Soluble Methane Mono Oxygenase of Methylococcus Capsulatus (Bath). Its Ability to Oxygenate n Alkanes, n Alkenes, Ethers, and Alicyclic, Aromatic and Heterocyclic Compounds. *Biochem. J.* 1977, 165, 395–402.
- (393) Tinberg, C. E.; Lippard, S. J. Dioxygen Activation in Soluble Methane Monooxygenase. Acc. Chem. Res. 2011, 44, 280–288.
- (394) Groothaert, M. H.; Smeets, P. J.; Sels, B. F.; Jacobs, P. A.; Schoonheydt, R. A.

Selective Oxidation of Methane by the Bis(μ-Oxo)Dicopper Core Stabilized on ZSM-5 and Mordenite Zeolites. *J. Am. Chem. Soc.* **2005**, *127*, 1394–1395.

- (395) Panov, G. I.; Sobolev, V. I.; Dubkov, K. A.; Parmon, V. N.; Ovanesyan, N. S.;
  Shilov, A. E.; Shteinman, A. A. Iron Complexes in Zeolites as a New Model of Methane Monooxygenase. *React. Kinet. Catal. Lett.* **1997**, *61*, 251–258.
- (396) Parfenov, M. V.; Starokon, E. V.; Pirutko, L. V.; Panov, G. I. Quasicatalytic and Catalytic Oxidation of Methane to Methanol by Nitrous Oxide over FeZSM-5 Zeolite. *J. Catal.* 2014, *318*, 14–21.
- (397) Tabor, E.; Dedecek, J.; Mlekodaj, K.; Sobalik, Z.; Andrikopoulos, P. C.; Sklenak,
   S. Dioxygen Dissociation over Man-Made System at Room Temperature to Form
   the Active α-Oxygen for Methane Oxidation. *Sci. Adv.* 2020, *6*, eaaz9776.
- (398) Maksimchuk, N. V.; Kovalenko, K. A.; Fedin, V. P.; Kholdeeva, O. A.
  Cyclohexane Selective Oxidation over Metal-Organic Frameworks of MIL-101
  Family: Superior Catalytic Activity and Selectivity. *Chem. Commun.* 2012, 48, 6812–6814.
- (399) Skobelev, I. Y.; Sorokin, A. B.; Kovalenko, K. A.; Fedin, V. P.; Kholdeeva, O. A. Solvent-Free Allylic Oxidation of Alkenes with O<sub>2</sub> Mediated by Fe- and Cr-MIL-101. *J. Catal.* **2013**, 298, 61–69.
- (400) Kholdeeva, O. A.; Skobelev, I. Y.; Ivanchikova, I. D.; Kovalenko, K. A.; Fedin, V. P.; Sorokin, A. B. Hydrocarbon Oxidation over Fe- and Cr-Containing Metal-Organic Frameworks MIL-100 and MIL-101-a Comparative Study. *Catal. Today* 2014, 238, 54–61.

- (401) Jaffe, A.; Ziebel, M. E.; Halat, D. M.; Biggins, N.; Murphy, R. A.; Chakarawet, K.; Reimer, J. A.; Long, J. R. Selective, High-Temperature O<sub>2</sub> Adsorption in Chemically Reduced, Redox-Active Iron-Pyrazolate Metal–Organic Frameworks . *J. Am. Chem. Soc.* 2020, *142*, 14627–14637.
- (402) Bloch, E. D.; Murray, L. J.; Queen, W. L.; Chavan, S.; Maximoff, S. N.; Bigi, J. P.; Krishna, R.; Peterson, V. K.; Grandjean, F.; Long, G. J.; Smit, B.; Bordiga, S.; Brown, C. M.; Long, J. R. Selective Binding of O<sub>2</sub> over N<sub>2</sub> in a Redox-Active Metal-Organic Framework with Open Iron(II) Coordination Sites. *J. Am. Chem. Soc.* 2011, *133*, 14814–14822.
- (403) Kholdeeva, O. A.; Skobelev, I. Y.; Ivanchikova, I. D.; Kovalenko, K. A.; Fedin, V. P.; Sorokin, A. B. Hydrocarbon Oxidation over Fe- and Cr-Containing Metal-Organic Frameworks MIL-100 and MIL-101–a Comparative Study. *Catal. Today* 2014, 238, 54–61.
- (404) Barona, M.; Snurr, R. Q. Exploring the Tunability of Trimetallic MOF Nodes for Partial Oxidation of Methane to Methanol. *ACS Appl. Mater. Interfaces* 2020, *12*, 28217–28231.
- (405) Chaemchuen, S.; Xiao, X.; Klomkliang, N.; Yusubov, M. S.; Verpoort, F. Tunable Metal-Organic Frameworks for Heat Transformation Applications. *Nanomaterials* 2018, *8*, 661.
- (406) Barth, B.; Mendt, M.; Pöppl, A.; Hartmann, M. Adsorption of Nitric Oxide in Metal-Organic Frameworks: Low Temperature IR and EPR Spectroscopic Evaluation of the Role of Open Metal Sites. *Microporous Mesoporous Mater*.

**2015**, *216*, 97–110.

- (407) Oppenheim, J. J.; Bagi, S.; Chen, T.; Sun, C.; Yang, L.; Müller, P.; Román-Leshkov, Y.; Dincă, M. Isolation of a Side-On V(III)-(N<sub>2</sub>-O<sub>2</sub>) through the Intermediacy of a Low-Valent V(II) in a Metal-Organic Framework. *Inorg. Chem.* 2021, *60*, 18205–18210.
- (408) Saito, T.; Nishiyama, H.; Tanahashi, H.; Kawakita, K.; Tsurugi, H.; Mashima, K.
  1,4-Bis(Trimethylsilyl)-1,4-Diaza-2,5-Cyclohexadienes as Strong Salt-Free
  Reductants for Generating Low-Valent Early Transition Metals with ElectronDonating Ligands. J. Am. Chem. Soc. 2014, 136, 5161–5170.
- (409) Mougel, V.; Chan, K. W.; Siddiqi, G.; Kawakita, K.; Nagae, H.; Tsurugi, H.;
  Mashima, K.; Safonova, O.; Copéret, C. Low Temperature Activation of
  Supported Metathesis Catalysts by Organosilicon Reducing Agents. *ACS Cent. Sci.*2016, 2, 569–576.
- (410) Mao, C.; Kudla, R. A.; Zuo, F.; Zhao, X.; Mueller, L. J.; Bu, X.; Feng, P. Anion Stripping as a General Method to Create Cationic Porous Framework with Mobile Anions. J. Am. Chem. Soc. 2014, 136, 7579–7582.
- (411) Akiyama, G.; Matsuda, R.; Kitagawa, S. Highly Porous and Stable Coordination Polymers as Water Sorption Materials. 2010.
- (412) Guesh, K.; Caiuby, C. A. D.; Mayoral, Á.; Díaz-García, M.; Díaz, I.; Sanchez-Sanchez, M. Sustainable Preparation of MIL-100(Fe) and Its Photocatalytic Behavior in the Degradation of Methyl Orange in Water. *Cryst. Growth Des.* 2017, *17*, 1806–1813.

- (413) Kispersky, V. F.; Kropf, A. J.; Ribeiro, F. H.; Miller, J. T. Low Absorption Vitreous Carbon Reactors for OperandoXAS: A Case Study on Cu/Zeolites for Selective Catalytic Reduction of NO<sub>x</sub> by NH<sub>3</sub>. *Phys. Chem. Chem. Phys.* 2012, *14*, 2229–2238.
- (414) Fingland, B. R.; Ribeiro, F. H.; Miller, J. T. Simultaneous Measurement of X-Ray Absorption Spectra and Kinetics: A Fixed-Bed, Plug-Flow Operando Reactor. *Catal. Letters* 2009, *131*, 1–6.
- (415) Chupas, P. J.; Chapman, K. W.; Kurtz, C.; Hanson, J. C.; Lee, P. L.; Grey, C. P. A Versatile Sample-Environment Cell for Non-Ambient X-Ray Scattering Experiments. J. Appl. Cryst. 2008, 41, 822–824.
- (416) Figueroa, S. J. A.; Gibson, D.; Mairs, T.; Pasternak, S.; Newton, M. A.; Di Michiel, M.; Andrieux, J.; Christoforidis, K. C.; Iglesias-Juez, A.; Fernández-García, M.; Prestipino, C. Innovative Insights in a Plug Flow Microreactor for Operando X-Ray Studies. J. Appl. Crystallogr. 2013, 46, 1523–1527.
- (417) Andersen, P. C.; Cooper, G.; Houlding, V. H. The Cylinder's Impact on Metal Impurities in CO. Semicond. Int. 1998, 21, 127–129.
- (418) Stolzenberg, A. M. Iron Compounds. Kirk-Othmer Encycl. Chem. Technol. 2004.
- (419) Sullivan, M. M.; Bhan, A. Acetone Hydrodeoxygenation over Bifunctional Metallic-Acidic Molybdenum Carbide Catalysts. ACS Catal. 2016, 6, 1145–1152.
- (420) Mina-Camilde, N.; Manzanares I., C.; Caballero, J. F. Molecular Constants of Carbon Monoxide at v = 0, 1, 2, and 3: A Vibrational Spectroscopy Experiment in Physical Chemistry. J. Chem. Educ. 1996, 73, 804–807.

(421) Little, L. H.; Amberg, C. H. Infrared Spectra of Carbon monoxide and Carbon Dioxide Adsorbed on Chromia–Alumina and on Alumina. *Can. J. Chem.* 1962, 40, 1997-2006.

### APPENDICES

## A. Supporting Information for Section 2

### **A1. Material Characterization**

### A1.1 MIL-100(Cr) Characterization Results



Figure A1. XRD diffraction pattern (a), nitrogen physisorption isotherm (b), and TGA curve of MIL-100(Cr) (c).

### A1.2. MIL-100(Al) Synthesis and Characterization Results

Comparison of the XRD pattern with the simulated pattern for MIL-100(Al) comfirms the crystal structure of the synthesized sample (Figure A2a).<sup>140</sup> The sample displays a type-II nitrogen adsorption isotherm, as expected for this material (Figure A2b). The corresponding BET surface area is approximately  $1550 \text{ m}^2/\text{g}_{cat}$ , which is slightly lower than that reported in the literature following the same synthesis proceudre.<sup>140</sup> The TGA curve of MIL-100(Al) features two weight losses, similarly to MIL-100(Cr) (Figure A2c). The first weight loss (~ 13 wt.%) below 673 K corresponds to the removal of guest molecules including H<sub>2</sub>O and possibly DMF left over from the synthesis procedure. It is well known that in the synthesis of MIL-100(Al), significant quantities of organic linkers may persist through the washing procedures with DMF and water.<sup>131,140,164</sup> Therefore, the second weight loss step may include both framework organic molecules and occluded species present as guest molecules or at defect sites. Additionally, MIL-100(Al) shows high thermal stability up to 673 K under air.



**Figure A2.** XRD diffraction pattern (a), nitrogen physisorption isotherm (b), and TGA curve of MIL-100(Al) (c).

# A2. Results and Discussion

## A2.1. Irreversible Water Adsorption on MIL-100(Cr)



Figure A3. Water adsorption isotherm (296 K) of MIL-100(Cr) evacuated (P < 6.7 x 10-5 bar) at 523 K for 6 hours (●) and the repeat adsorption isotherm obtained immediately after evacuation for 12 hours at the analysis temperature (○).</p>



Figure A4. Open-metal site density obtained using the water adsorption isotherm method as a function of the evacuation time between the first and repeat water adsorption experiments ( $P < 6.7 \times 10^{-5}$  bar, 296 K).



**Figure A5.** Comparison of the water adsorption isotherms obtained over MIL-100(Cr) in four consecutive experiments (Trial 1-4) providing no indication of structural changes which could impact the results in this work.



Figure A6. (a) Water adsorption isotherm obtained for MIL-100(Cr) activated at 303 K for 6 hours under vacuum (●) and the repeat adsorption isotherm obtained immediately after evacuation for 12 hours at 296 K (○). (b) Linear regression of the water adsorption isotherms.



Figure A7. (a) Water adsorption isotherm obtained for MIL-100(Cr) activated at 323 K for 6 hours under vacuum (●) and the repeat adsorption isotherm obtained immediately after evacuation for 12 hours at 296 K (○). (b) Linear regression of the water adsorption isotherms.



Figure A8. (a) Water adsorption isotherm obtained for MIL-100(Cr) activated at 373 K for 6 hours under vacuum (●) and the repeat adsorption isotherm obtained immediately after evacuation for 12 hours at 296 K (○). (b) Linear regression of the water adsorption isotherms.



Figure A9. (a) Water adsorption isotherm obtained for MIL-100(Cr) activated at 423 K for 6 hours under vacuum (●) and the repeat adsorption isotherm obtained immediately after evacuation for 12 hours at 296 K (○). (b) Linear regression of the water adsorption isotherm.



Figure A10. (a) Water adsorption isotherm obtained for MIL-100(Cr) activated at 473 K for 6 hours under vacuum (●) and the repeat adsorption isotherm obtained immediately after evacuation for 12 hours at 296 K (○). (b) Linear regression of the water adsorption isotherm.

#### A2.2. Irreversible Water Adsorption on MIL-100(Al)

The water adsorption isotherm for MIL-100(Al) (Figure A11) activated at 523 K displays a type-V shaped isotherm of similar shape to that obtained for MIL-100(Cr) and is characteristic of MIL-100 from previous reports.<sup>141,161,411</sup> Figure A12 provides a comparison of the water adsorption isotherms obtained for MIL-100(Al) activated at temperatures ranging from 303 - 523 K. Data points at pressures  $\geq 0.016$  bar are shown as this region is that which is applied for determing the open-metal site fraction. Similarly to MIL-100(Cr), the adsorption capacity increases systematically with increasing activation temperature. Furthermore, the repeat adsorption isotherms (Figure A12(B)) obtained for each of the analyses are identical, providing evidence that the sample returns to the same

unactivated state following water adsorption and evacuation at the analysis temperature (296 K) with no indication of structural deterioration between analyses.



Figure A11. Water adsorption isotherm obtained for MIL-100(Al) activated at 523 K for 6 hours under vacuum (●) and the repeat adsorption isotherm obtained immediately after evacuation for 12 hours at the 296 K (○).



**Figure A12.** (a) Water adsorption isotherms obtained for MIL-100(Al) activated at 523 K for 6 hours under vacuum. (b) Repeat adsorption isotherms obtained immediately after evacuation for 12 hours at 296 K.



Figure A13. Linear regression of the water adsorption isotherms obtained for MIL-100(Al) activated at (a) 303 K, (b) 323 K, (c) 373 K, (d) 423 K, (e) 473 K, and (f) 523 K for 6 hours under vacuum (●) and the repeat adsorption isotherm (○).

# **B.** Supporting Information for Section 3

# **B1.** Supplementary Results & Discussion

## **B1.1. Literature Comparison**



**Figure B1.** Open-metal site densities measured for MIL-100(Cr) in this report (anion = OH<sup>-</sup>) and reported by Vimont *et al.* for MIL-100(Cr) synthesized with HF.<sup>132</sup> Samples were outgassed at the temperature (RT = 303 K in this study) prior to open-metal site quantification.





Figure B2. (a) IR spectra of MIL-100(Cr) following activation at the indicated temperature. (b) IR spectra at the same conditions when exposed to 10% NO in  $N_2$  (c) Comparison of the reduction in coordinated water (3672, 3649 cm<sup>-1</sup> bands) and increase in the area of the NO-Cr<sup>2+</sup> species.

### **B1.3. CO Adsorption**

The dual-site Langmuir adsorption model was fit to the experimental adsorption isotherms

using the following equation

Р

q

bi

$$q = q_{A,sat} \frac{b_A P}{1 + b_A P} + q_{B,sat} \frac{b_B P}{1 + b_B P}$$

where,

pressure / bar, quantity adsorbed / mol (mol Cr)<sup>-1</sup>, saturation capacity of site i, q<sub>i,sat</sub>

affinity parameter for site i.

and

Temperature	<b>Q</b> A,sat	<b>Q</b> B,sat	bA	bв	R <sup>2</sup>
250 °C	0.332	0.275	800	1.462	0.93
200 °C	0.265	0.277	800	1.462	0.98
150 °C	0.035	0.220	800	1.462	0.63
100 °C	0.005	0.120	800	1.462	0.97
50 °C	0	0.069	800	1.462	0.99
30 °C	0	0.044	800	1.462	0.97

**Table B1.** Summary of Fitting the Dual-Site Langmuir Adsorption Model to the Experimental

 Adsorption Isotherms for Samples Activated at the Indicated Temperature.



Figure B3. (a) Dual-site Langmuir adsorption model (dashed line) compared to the experimental data (●). (b) Adsorption model including only the parameters associated with site A. (c) Adsorption model including only the parameters associated with site B.



**Figure B4.** (a) CO adsorption isotherms (303 K) following activation at elevated temperature. Estimation of the  $Cr^{2+}$  site density based on y-intercept of the fitted line for (b) activation temperatures of (b) 303 - 373 K and (c) 423 - 523 K.



**Figure B5.** (a) CO adsorption isotherms (303 K) following activation at elevated temperature (b) Comparison of the total open-metal site density determined via irreversible water adsorption to the amount of CO adsorbed at 0.1 bar.

## C. Supporting Information for Section 4

### **C1. Experimental Methods**

### C1.1. MIL-100(Fe) Synthesis

MIL-100(Fe) was synthesized following a procedure developed by Zhang and colleagues.<sup>66</sup> A mixture of 16.16 g of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Alfa Aesar, > 98%), 7.56 g of trimesic acid (Alfa Aesar, 98%), and 24 cm<sup>3</sup> of deionized water (18.3 MΩ) were stirred at 600 rpm for 12 h at 368 K in a 250 cm<sup>3</sup> round-bottom flask. The resulting product was purified by subsequent washing with deionized water (18.3 MΩ) and ethanol (Decon Laboratories Inc., 200 Proof) in 160 cm<sup>3</sup> quantities at 343 K. A total of six washing steps, alternating between water and ethanol, were conducted over a period of 20 h. The sample was then collected with fresh ethanol and dried at 353 K overnight in an oven. Finally, the product was treated at 423 K for 10 h in a vacuum oven (MTI Corporation, P < 0.3 kPa).

### C1.2. MIL-100(Cr) Synthesis

MIL-100(Cr) was synthesized using a procedure reported previously by Mao et al.<sup>139</sup> A total of 9 g of CrCl<sub>3</sub>·6H<sub>2</sub>O (Sigma-Aldrich  $\geq$  98%) and 3.55 g of trimesic acid (Alfa Aesar, 98%) were ground using a mortar and pestle at room temperature for 30 minutes. The mixture was transferred to a 45 cm<sup>3</sup> PTFE-lined stainless steel autoclave and heated at 493 K for 15 h under rotation. The resulting product was washed with 500 cm<sup>3</sup> of deionized water (18.3 MΩ) and then with 500 cm<sup>3</sup> of ethanol (Decon Laboratories Inc., 200 Proof) for 3 h at 343 K and 338 K, respectively, within a 500 cm<sup>3</sup> Erlenmeyer flask fitted with a reflux condenser. The solid sample, collected with fresh ethanol, was dried at 343 K overnight in an oven. Lastly, the sample was treated in a vacuum oven (MTI Corporation,
P < 0.1 kPa) at 423 K for 12 h. Several catalyst batches were combined to produce a quantity of material necessary for all of the analyses in this work.

#### **C1.3.** Material Characterization

Powder X-ray diffraction (XRD) patterns were collected using an Empyrean Malvern Panalytical diffractometer equipped with a Cu K $\alpha$  X-ray source ( $\lambda = 0.15$  nm) with approximately 0.02 g of sample loaded on a glass sample holder (Rigaku, 0.2 mm indentation). Diffraction patterns were collected from 2.5-20° with a step size of 0.013° and speed of 23.8 s per step. Nitrogen physisorption experiments were conducted with a Micromeritics 3Flex Surface Characterization Analyzer. Prior to analysis, samples (~ 0.05 g) were outgassed (P < 0.01 kPa) for 15 h at 423 K using a Micromeritics VacPrep degassing system. Thermogravimetric analyses (TGA) were completed on a Targus TG 209 F3 instrument under the flow of air (40 cm<sup>3</sup> min<sup>-1</sup>, Matheson, zero-grade) and at a heating rate of 1 K min<sup>-1</sup>.

#### C1.4. Procedure for the Oxidation of CH<sub>4</sub> with N<sub>2</sub>O

Samples of MIL-100 were pelletized, crushed, sieved to  $180 - 245 \,\mu$ m particles, and loaded into a stainless steel tube (4.572 mm inner diameter) using quartz wool (CE Elantech) as support. The reactor tube was mounted vertically within a single-zone insulated furnace (1060 W/115 V, Applied Test System Series 3210). The reaction temperature was determined by the placement of a K-type thermocouple (Omega) at the top of the catalyst bed. Samples were pretreated at 523-523 K for 12 h under either inert flow (50 cm<sup>3</sup> min<sup>-1</sup> He, Matheson, Ultra High Purity) or vacuum (P < 0.01 kPa, Pfeiffer Pascal 2005 SD rotary vane vacuum pump). Reactant mixtures were stabilized in a

bypassing gas line prior to reaction. Using Ar as an internal standard and He as a carrier, gas-phase product and reactant concentrations were determined using a gas chromatograph (Agilent 7890 B) equipped with an HP-PLOT-Q capillary column (30 m x 320 µm x 0.2 µm) and a thermal conductivity detector. To initiate the reaction, a 4-port valve (Valco Instruments Co. Inc.) was switched to send the reactant gas stream to the reactor with 1.5 kPa CH<sub>4</sub> (Matheson, Research Purity), 2.9-14.5 kPa N<sub>2</sub>O (Matheson, Research Purity), and 2.9 kPa Ar (Matheson, Ultrahigh Purity) balanced with He to maintain a total flow rate of 65 cm<sup>3</sup> min<sup>-1</sup>. Following reaction, the catalyst bed was purged with He for 1-2 hours at the reaction temperature, or as indicated elsewhere. Liquid solvents necessary to extract surface-bound reaction products were fed into a He stream (50 cm<sup>3</sup> min<sup>-1</sup>) using a syringe pump (KD Scientific, Model 100). Product extraction fluids included H<sub>2</sub>O (deionized, 18.3 M $\Omega$ ), D<sub>2</sub>O (Sigma-Aldrich, 99.9 atom% D), H<sub>2</sub><sup>18</sup>O (Sigma-Aldrich, 97 atom% <sup>18</sup>O), and CH<sub>3</sub>OH (Macron Fine Chemicals,  $\geq$  99.8%). Gas lines were maintained at 383 K to prevent condensation of reactants/products. After a 1 h stabilization period, the solvent/He stream was introduced to the reactor at a temperature between 373 and 473 K. Product formation rates were measured using an online mass spectrometer (MKS Cirrus 2).

## C1.5. Procedure for the Ethanol Dehydrogenation over MIL-100

Ethanol dehydrogenation experiments were conducted using the reactor setup described in Section C1.4. Samples were treated under inert flow (50 mL min<sup>-1</sup> He, Ultra High Purity, Matheson) or in vacuum (P < 0.01 kPa, Pfeiffer Pascal 2005 SD rotary vane vacuum pump) at 373 – 523 K for 12 h prior to reaction. Liquid C<sub>2</sub>H<sub>5</sub>OH (Decon Laboratories Inc., 200 Proof) or C<sub>2</sub>D<sub>5</sub>OD (Acros Organics, 99 atom% D) was fed into a He

stream (50 cm<sup>3</sup> min<sup>-1</sup>) using a syringe pump (KD Scientific, Model 100) with gas lines maintained at 383 K to prevent condensation. After a 1 h stabilization period, a 4-port valve (Valco Instruments Co. Inc.) was switched to send the ethanol gas mixture through the reactor at 373 K. Outlet concentrations of ethanol, water, and acetaldehyde were determined using an online mass spectrometer (MKS Cirrus 2).

## **C1.6. Infrared Spectroscopy Experiments**

Transmission infrared (IR) spectroscopy measurements were obtained using a Nicolet iS50 FT-IR Spectrometer (Thermo Scientific) equipped with a Harrick Dewar Transmission/Reflection Accessory featuring ZnSe windows (25 x 2, 32 x 3 mm). An empty cell reference was used as a background reference under the given flow conditions. MIL-100-Cr samples (15-20 mg) and MIL-100-Fe (20-30 mg) samples mixed with KBr powder were pressed into self-supporting wafers and thermally treated under the flow of Ar (56 cm<sup>3</sup> min<sup>-1</sup>, Matheson, Ultra High Purity) or in vacuum (P < 0.01 kPa, Pfeiffer Pascal 2005 SD rotary vane vacuum pump). When measuring NO adsorption in MIL-100, a background reference of the thermally-activated sample was used prior to the introduction of NO. IR spectra for a given analysis were collected using the same catalyst wafer and reported without normalization. Baseline corrections and peak area estimates were carried out using Origin 8.5.

## **C2. Results and Discussion**

### **C2.1.** Characterization Results – MIL-100(Fe)

MIL-100(Fe) was synthesized according to a previously published procedure,<sup>66</sup> as described in Section C1.1. The x-ray diffraction pattern is consistent with the simulated pattern,<sup>68</sup> confirming the crystallization into an MTN (Mobile Thirty Nine) topology (Figure C1a). Quantities of nitrogen adsorption and the shape of the physisorption isotherm are consistent with previous reports (Figure C1b).<sup>66,151,412</sup> Furthermore, the TGA profile for MIL-100(Fe) exhibits two significant weight losses: the first below 250 °C (15.7 wt.%) is attributed to the removal of guest molecules and the second above 250 °C (59.6 wt.%) corresponds to oxidation of the organic linkers (Figure C1c). The weight losses measured suggest that the material composition is consistent with previous reports,<sup>66</sup> and provides a theoretical formula of (Fe<sub>3</sub>O(H<sub>2</sub>O)<sub>2</sub>(OH)[C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>3</sub>]<sub>2</sub>·nH<sub>2</sub>O,  $n \approx 3.1$ ).



**Figure C1**. (a) X-ray diffraction pattern (b) N<sub>2</sub> physisorption isotherm (77 K), and (c) TGA profile for MIL-100(Fe).

### C2.2. Characterization Results – MIL-100(Cr)

MIL-100(Cr) was synthesized following the procedure described in Section C1.2. The XRD pattern of the synthesized sample is consistent with the simulated pattern (Figure C2a) and an MTN topology.<sup>43</sup> The sample displays a nitrogen physisorption isotherm shape and quantity adsorbed consistent with literature reports and the mesoporous structure of the material (Figure C2b).<sup>6-8</sup> Additionally, the TGA curve of MIL-100(Cr) features two weight losses, similar to MIL-100(Fe) (Section C2.1, Figure C2c). Weight losses corresponding to the departure of guest molecules (~ 12 wt.%) and the oxidation of the organic ligands (~ 57 wt.%) are similar to the values reported previously for MIL-100(Cr),<sup>139</sup> suggesting composition close а to that expected theoretically  $(Cr_3O(H_2O)_2(OH)[C_6H_3(CO_2)_3]_2 \cdot nH_2O, n \approx 5.5).$ 



**Figure C2.** (a) X-ray diffraction pattern (b) N<sub>2</sub> physisorption isotherm (77 K), and (c) TGA profile of MIL-100(Cr).

## C2.3. MIL-100(Fe) IR Spectroscopy Analysis



12 hours and then (b) exposed to 0.5 kPa NO in Ar. (c) Comparison of the area of the v(HO-Fe) and  $v(NO-Fe^{2+})$  band areas for each pretreatment temperature (as indicated).

Figure C3 displays the IR spectra of MIL-100(Fe) reproduced from our previous work.<sup>109</sup> The presence of two sharp bands in the O-H stretch region (Figure C3a) that have been assigned to the asymmetric stretching vibration of coordinated water molecules (Fe-H<sub>2</sub>O) and terminal hydroxides (Fe-OH<sup>-</sup>) near 3658 and 3581 cm<sup>-1</sup>.<sup>60,131,132,154</sup> Upon increasing the activation temperature between 423 to 523 K, there is a progressive decrease in the abundance of these species as indicated by the relative intensity, indicating the formation of open-metal sites. The introduction of NO (0.5 kPa) at 423 K reveals the presence of a massif centered at 1810 cm<sup>-1</sup>, indicative of NO coordinated to Fe<sup>2+</sup> open-metal sites in MIL-100(Fe) (Figure C3b).<sup>60,73,183</sup> Significantly, under the tested conditions, no absorbance is observed in the range of 1895 - 1901 cm<sup>-1</sup> that would, if present, have indicated the interaction of NO with Fe<sup>3+</sup> open-metal sites (based on previous assignments

for NO adsorbed on MIL-100(Fe) at room temperature).<sup>60,183</sup> Additionally, there is a strong, linear correlation between the v(HO-Fe) and v(NO-Fe) band areas (Figure C3c), consistent with the selective adsorption of NO onto Fe<sup>2+</sup> open-metal sites created through anion removal.<sup>42</sup>



**C2.4. NO Breakthrough Measurements** 

**Figure C4.** (a) NO (0.5 kPa) breakthrough curves at 423 K in MIL-100(Fe) thermally activated under inert flow at 423 – 523 K. (b) Comparison of the area of the v(NO-Fe<sup>2+</sup>) IR band area (from Figure C3b) to the quantity of NO adsorbed by breakthrough adsorption measurements.

Activation Temperature / K	NO Adsorbed / mol·(mol total Fe) <sup>-1</sup>
423	0.12
448	0.15
473	0.19
498	0.22
523	0.29

**Table C1.** Quantity of NO adsorbed per total Fe in MIL-100(Fe) at 0.5 kPa NO and 423 K following thermal treatment at the indicated temperature for 12 h. Reproduced from Ref 9.

#### C2.5. D<sub>2</sub>O Breakthrough Measurements

D<sub>2</sub>O equilibrium adsorption measurements were conducted to quantify Fe<sup>3+</sup> and Fe<sup>2+</sup> open-metal site densities at various activation temperatures between 423 and 523 K (Figure C5). Introduction of D<sub>2</sub>O vapor (0.9 kPa) at 373 K over MIL-100(Fe) reveals that the total quantity of D<sub>2</sub>O adsorbed, as measured by the breakthrough curve, is independent of the extent of activation (Table C2). Conversely, the quantification of H<sub>2</sub>O and HDO at the reactor outlet decreases systematically with activation temperature. This result suggests that, under the tested conditions, D<sub>2</sub>O will adsorb onto every available open-metal site in MIL-100(Fe) and will both (a) displace any coordinated H<sub>2</sub>O (Fe-H<sub>2</sub>O) and (b) exchange with any hydroxide (Fe-OH<sup>-</sup>) to form HDO and Fe-OD<sup>-</sup>. Thus, Fe<sup>2+</sup> and Fe<sup>3+</sup> open-metal sites can be estimated by the total quantity of H<sub>2</sub>O and HDO evolved by the relationships given in Equation C.1 and C.2. Fe<sup>2+</sup> site densities enumerated are consistent with Fe<sup>2+</sup> site densities measured by equilibrium NO adsorption measurements (Table C1) and the relative fraction of v(Fe<sup>3+</sup>-OH) species as a function of activation temperature (Figure 304

C6b). Additionally,  $Fe^{3+}$  site densities determined show a strong linear correlation with the fraction of coordinated water species (Figure C6b), validating the use of this method in quantifying the fraction of open-metal  $Fe^{3+}$  sites at various activation conditions.

Estimated  $\text{Fe}^{3+}$  Site Density =  $[0.66 / \text{mol (mol Fe})^{-1}] - [\text{H}_2\text{O} \text{ Desorbed } / \text{mol (mol Fe})^{-1}]$  (C.1) Estimated  $\text{Fe}^{2+}$  Site Density =  $[0.33 / \text{mol (mol Fe})^{-1}] - [\text{HDO Desorbed } / \text{mol (mol Fe})^{-1}]$  (C.2)



**Figure C5.** Normalized molar flow rates of D<sub>2</sub>O, H<sub>2</sub>O, and HDO when D<sub>2</sub>O is introduced at 373 K over MIL-100(Fe) thermally activated at (a) 423 K and (b) 523 K under inert flow. (0.9 kPa D<sub>2</sub>O, total flow: 116 cm<sup>3</sup> min<sup>-1</sup>).

Activation Temperature / K	D2O Adsorbed mol·(mol total Fe) <sup>-1</sup>	H2O Desorbed mol·(mol total Fe) <sup>-1</sup>	HDO Desorbed mol·(mol total Fe) <sup>-1</sup>
423	1.01	0.187	0.219
448	0.99	0.122	0.171
473	1.02	0.035	0.129
498	0.98	0.012	0.102
523	0.96	0.004	0.033

**Table C2.** Quantity of D<sub>2</sub>O adsorbed and H<sub>2</sub>O/HDO desorbed when D<sub>2</sub>O is introduced at 373 K over MIL-100(Fe) thermally activated under inert flow. (0.9 kPa D<sub>2</sub>O).

**Table C3.** Estimated  $Fe^{3+}$  and  $Fe^{2+}$  open-metal site densities using Equation S1 and Equation S2,<br/>respectively. Values for H<sub>2</sub>O/HDO desorbed are reported in Table C2.

Activation Temperature / K	Estimated Fe <sup>3+</sup> Site Density mol·(mol total Fe) <sup>-1</sup>	Estimated Fe <sup>2+</sup> Site Density mol·(mol total Fe) <sup>-1</sup>
423	0.473	0.111
448	0.538	0.159
473	0.625	0.201
498	0.648	0.228
523	0.656	0.297



Figure C6. (a) Comparison of the v(H<sub>2</sub>O-Fe) IR band area, Figure S3a, to the fraction of Fe<sup>3+</sup> openmetal sites measured by D<sub>2</sub>O adsorption measurements. (b) Comparison of the v(HO-Fe) IR band area, Figure C3a, to the fraction of Fe<sup>2+</sup> open-metal sites measured by D<sub>2</sub>O adsorption.

## C2.6. CH<sub>4</sub> Oxidation In-Situ NO Titrations



**Figure C7.** Cumulative moles of CH<sub>3</sub>OH formed per total Fe in the absence of titrant and in the presence of NO (0.5 kPa). Reaction conditions: 423 K, 14.5 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, t = 2 h, activated at 523 K for 12 h in He.

## C2.7. Correction of CO<sub>2</sub> Yields in the Presence of NO

The presence of NO (0.5 kPa) at 423 K results in a minor amount of CO<sub>2</sub> formation (0.035 mol (total mol Fe)<sup>-1</sup> in a 2 h period) over MIL-100(Fe) (Table C4), possibly due to oxidation of organic linker molecules. CO<sub>2</sub> quantities formed in the presence of NO represented approximately 16% of the cumulative moles of CO<sub>2</sub> formed over MIL-100(Fe) under 14.5 kPa N<sub>2</sub>O and 1.5 kPa CH<sub>4</sub> at 423 K for 2 h. Co-feeding 0.5 kPa NO with N<sub>2</sub>O and CH<sub>4</sub> at 423 K resulted in an approximately 18% increase in the total CO<sub>2</sub> cumulative

yield (Table C4), consistent with the contribution of  $CO_2$  formation from framework oxidation in the presence of NO. This result indicates that NO does not inhibit the oxidation

- of  $CH_4$  to  $CO_2$  under the conditions tested.
- **Table C4.** Cumulative moles of CO<sub>2</sub> formed over a 2 hour period at 473 K under 0.5 kPa NO, under standard CH<sub>4</sub> oxidation reaction conditions (14.5 kPa, 1.5 kPa CH<sub>4</sub>), and when NO is co-fed during reaction. MIL-100(Fe) activated at 523 K for 12 h in He.

Gas Composition	CO <sub>2</sub> Cumulative Yield / mol (total mol Fe) <sup>-1</sup>
0.5 kPa NO	0.0035
14.5 kPa N <sub>2</sub> O 1.5 kPa CH <sub>4</sub>	0.0219
0.5 kPa NO 14.5 kPa N2O 1.5 kPa CH4	0.0258

# C2.8. H<sub>2</sub>O as an Oxidation State-Independent Titrant



**Time / s Figure C8.** Normalized concentration of Ar and H<sub>2</sub>O (0.9 kPa) at 423 K over MIL-100(Fe) thermally activated at 523 K for 12 h under inert flow (He, 50 cm<sup>3</sup> min<sup>-1</sup>).

# C2.9. Comparison of CO<sub>2</sub> Yield with Fe<sup>2+</sup> Site Densities



**Figure C9.** Cumulative moles of  $CO_2$  formed normalized by the total iron content (left axis) and per Fe<sup>2+</sup> open-metal site (right axis) with increasing activation temperature (423 - 523 K). Reaction conditions: 473 K, 14.5 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, t = 2 h, activated at temperature for 12 h in He.

# C2.10. Subsequent CH<sub>3</sub>OH and D<sub>2</sub>O Exposure over MIL-100(Fe)



**Figure C10.** Molar flow rate of D<sub>2</sub>O, CH<sub>3</sub>OH, and CH<sub>3</sub>OD when D<sub>2</sub>O (0.4 kPa) is introduced after MIL-100(Fe) is exposed to CH<sub>3</sub>OH for 1 h at 373 K and then purged with He for 6 h at 473 K. The quantity of CH<sub>3</sub>OH desorbed upon D<sub>2</sub>O exposure is 0.21 mol (total mol Fe)<sup>-1</sup>.

## C2.11. IR Spectra of MIL-100(Fe) Exposed to Air after Activation



**Figure C11.** IR spectra of MIL-100(Fe) following thermal activation at 523 K and then following exposure to ambient air at room temperature. Results indicate the formation of coordinated water and hydroxides species as indicated by bands near 3658 and 3581 cm<sup>-1</sup>, respectively.

### C2.12. MIL-100(Cr) Open-Metal Site Quantification

Open-metal site densities in MIL-100(Cr) were estimated using IR spectroscopy measurements. Dehydration and dehydroxylation processes, leading to the formation of  $Cr^{3+}$  and  $Cr^{2+}$  open-metal site densities, respectively, can be estimated from the relive area of v(OH) bands corresponding to coordinated water (3672 – 3649 cm<sup>-1</sup>) and hydroxides (3585 cm<sup>-1</sup>) as show in Figure C12.<sup>182</sup> MIL-100(Cr) activated at 303 K in vacuum for 12 h was used as a reference spectrum, representing the area of the v(OH) band areas for coordinated water and hydroxides in the fully activated material as our previous report has indicated insignificant open-metal site densities in MIL-100(Cr) under this condition.<sup>182</sup> Table C5 lists the values estimated for the  $Cr^{2+}$  and  $Cr^{3+}$  open-metal site densities for each of the activation conditions tested.



**Figure C12.** IR spectra of MIL-100(Cr) activated under a variety of conditions. The v(OH) bands between 3672-3649 cm<sup>-1</sup> correspond to coordinated water molecules and the v(OH) band at 3585 cm<sup>-1</sup> corresponds to terminal hydroxides.

**Table C5.**  $Cr^{2+}$  and  $Cr^{3+}$  open-metal site densities estimated from the IR spectra of MIL-100(Cr) and the relative area of the v(OH) bands corresponding to coordinated water and hydroxide species to the reference spectra of MIL-100(Cr) activated at 303 K in vacuum for 12 h.

Activation Condition	Estimated Cr <sup>2+</sup> Site Density mol·(mol total Cr) <sup>-1</sup>	Estimated Cr <sup>3+</sup> Site Density mol·(mol total Cr) <sup>-1</sup>
373 K, inert flow	0.002	0.310
423 K, inert flow	0.027	0.437
473 K, inert flow	0.120	0.479
523 K, inert flow	0.157	0.503
523 K, vacuum	0.282	0.574

# C2.13. Cumulative CH<sub>4</sub> Reacted with Cr<sup>3+</sup> Site Density



**Figure C13.** Cr<sup>3+</sup> open-metal site densities estimated from IR spectroscopy measurements (Table C5) at various activation conditions and the corresponding cumulative moles of CH<sub>4</sub> reacted normalized by the Cr<sup>3+</sup> open-metal site density (473 K, 14.5 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, 2 h).



**Figure C14.** (a) NO (0.8 kPa in Ar) breakthrough adsorption measurement at 473 K over MIL-100(Cr) following thermal activation at 523 K under inert flow. (b) IR spectra of MIL-100(Cr) under the same conditions, following thermal activation at 523 K in vacuum.

## C2.15. CH<sub>4</sub> Oxidation – Product Extraction with CH<sub>3</sub>OH

Table C6. For MIL-100(Fe) and MIL-100(Cr), the M<sup>2+</sup> site density and the cumulative quantities of CH<sub>4</sub> reacted and ethanol formed when CH<sub>3</sub>OH (0.12 kPa) is fed after reaction at 373 K. (Reaction conditions: 473 K, 2.9 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>)

Material	Activation Condition	M <sup>2+</sup> Site Density / mol·(mol M) <sup>-1</sup>	CH4 Reacted / mol·(mol M) <sup>-1</sup>	Ethanol Formed / mol·(mol M) <sup>-1</sup>
Fe	Inert flow, 473 K	0.23	0.24	0.22
Cr	Vacuum, 523 K	0.28	0.26	0.25

## C2.16. Ethanol Dehydrogenation over MIL-100



**Figure C15.** Molar flow rates of ethanol, water and acetaldehyde when activated (a) MIL-100(Fe) and (b) MIL-100(Cr) are exposed to ethanol (0.11 kPa) at 373 K. (MIL-100(Fe) and MIL-100(Cr) activated at 423 and 523 K, respectively, in He for 12 h prior to reaction).

# C2.17. Tabulated Product Selectivities for MIL-100(Cr)

Table C7. Selectivity for CH<sub>3</sub>OH versus C<sub>2</sub>H<sub>4</sub>O and the water uptake (total water adsorbed/reacted) during the H<sub>2</sub>O product extraction step at 473 K. (Reaction conditions: 473 K, 2.9 kPa N<sub>2</sub>O, 1.5 kPa CH<sub>4</sub>, 2 h, activated at 523 K in He for 12 h).

Label	H2O Partial Pressure / kPa	H <sub>2</sub> O Flow Rate mol s <sup>-1</sup>	CH3OH Selectivity	C2H4O Selectivity	H2O Uptake / mol (mol Fe) <sup>-1</sup>
А	0.35	1.54 x 10 <sup>-6</sup>	0.19	0.81	0.72
В	0.53	1.54 x 10 <sup>-6</sup>	0.11	0.89	0.88
С	0.70	1.54 x 10 <sup>-6</sup>	0.03	0.97	1.02
D	0.35	2.31 x 10 <sup>-6</sup>	0.07	0.93	0.75
Е	0.53	2.31 x 10 <sup>-6</sup>	0	1	0.89
F	0.70	2.31 x 10 <sup>-6</sup>	0	1	0.97
G	0.35	3.07 x 10 <sup>-6</sup>	0	1	0.75
Н	0.53	3.07 x 10 <sup>-6</sup>	0	1	0.86
Ι	0.70	3.07 x 10 <sup>-6</sup>	0	1	0.93

## **D.** Supporting Information for Section 5

## **D1. Experimental Methods**

### **D1.1. In-Situ X-ray Spectroscopy Measurements**

Samples of MIL-100 were passed through a No. 325 stainless steel mesh to produce a fine powder with particle sizes  $\leq 45 \ \mu$ m. The catalyst was diluted with inert vitreous, or glassy, carbon (HTW, Sigradur G) to produce a desirable Fe K-edge-step and allow for sufficient X-ray transmittance near the metal edge.<sup>413</sup> Specifically, approximately 1.7 mg of MIL-100(Fe) and 5.1 mg of vitreous carbon were ground thoroughly with a mortar and pestle and then loaded into a polyimide capillary (Masterflex Transfer Tubing, Cole Parmer, 1.46 mm ID, 1.56 mm OD, 75 mm L) using quartz wool (CE Elantech) as a support. Polyimide tubing was used for the reactor due to its low absorbance in the range of edge energies for 3d transition metals and for its viability at operation temperatures less than 573 K.<sup>414</sup> The loaded sample was compressed from both ends by hand using two small wires in order to reduce void space in the packed sample bed and the capillary was loaded and mounted horizontally within a microreactor flow cell assembly (Figure D1), the design of which is inspired by plug flow in-situ cell and furnace designs proposed by Chupas *et al.*<sup>415</sup> and modified by Figueroa *et al.*<sup>416</sup> for in-situ X-ray measurements.

A schematic drawing of the gas lines and associated equipment with the microreactor can be found in (Figure D2). Brooks Instruments mass flow controllers were used to feed He, 10% N<sub>2</sub>O/He and 1% CO/He into the reactor. The CO/He gas mixture was fed through a scrubber consisting of 1/2-inch stainless steel tubing packed with quartz wool heated to approximately 443 K by a nozzle heater (McMaster-Carr) to decompose iron-carbonyl impurities in the gas stream.<sup>417,418</sup>



Figure D1. Schematic representation of the assembled flow cell for in-situ XAFS measurements. List of labelled components can be found in Table D1.

<b>Table D1.</b> List of components	labelled in	Figure I	D1 to	assemble	the flow	cell for	in-situ	XAFS
measurements.								

a	Inlet gas line	1/16 <sup>th</sup> in., stainless steel
b	Mountable base plate	Thorlabs (UBP2)
c	Assembly rod	Thorlabs (ER)
d	Bulkhead union	Swagelok (SS-200-61), stainless steel
e	Movable support with modified threaded cap	Thorlabs (CP08FP/M) and Thorlabs (SM1CP2M or SM1PL)
f	Polyimide capillary	Cole-Parmer (95820-12), 0.0575 in. ID x 0.0615 in. OD
g	Alumina ceramic two-bore rod	McMaster-Carr (87175K23), 0.052 in. ID x 0.156 in. OD
h	Kanthal A-1 annealed resistance wire	TEMCo Industrial (RW0241)
i	Movable support for heating assembly	Modified ThorLabs (SP30)
j	Union tee	Swagelok (SS-100-3)
k	K-type thermocouple	Omega XL, 0.02 in. OD
1	Outlet gas line	1/16 <sup>th</sup> in., stainless steel

For analysis of MIL-100(Fe), XAFS spectra of the as-synthesized sample were collected with the sample under helium flow (4 mL min<sup>-1</sup>) at room temperature. The sample temperature was then increased slowly to 523 K under flowing helium and held at temperature for 90 minutes. XAFS spectra were collected during the pretreatment of the

catalyst at 523 K with no measurable changes being measured between 60 and 90 minutes at 523 K. The catalyst was then cooled to 473 K and the spectra of the thermally activated sample was obtained. At 473 K, the sample was exposed to three reaction conditions (1) a low N<sub>2</sub>O/CO molar ratio (~3) (2.6 kPa N<sub>2</sub>O, 0.8 kPa CO), (2) a high N<sub>2</sub>O/CO molar ratio (~50) (8.6 kPa N<sub>2</sub>O, 0.17 kPa CO), and (3) under N<sub>2</sub>O/O<sub>2</sub> co-feed (7.6 kPa N<sub>2</sub>O, 2.7 kPa O<sub>2</sub>). The sample was allowed to dwell for at least 15 minutes before collecting the in-situ XAFS spectra at each condition and the sample was monitored as a function of time until no further changes in the spectra were observed.



Figure D2. Schematic drawing of the experimental setup used for in-situ XAFS measurements.



**Figure D3.** Scattering paths considered for EXAFS fitting including single scattering Fe-O (N = 5 -6, depending on the extent of thermal activation), Fe-C (N = 4), and F-Fe (N = 2).

## **D2.** Results and Discussion

## **D2.1.** Thermodynamic Equilibrium Calculations

The equilibrium constant for the reaction of  $N_2O$  and CO to form  $CO_2$  and  $N_2$  was estimated using the gas phase thermodynamic property values obtained from the NIST Chemistry WebBook (Table D.2).<sup>256</sup> Furthermore, these values were used to estimate  $K_{eq}$ and the approach to equilibrium with reactant conversion (Figure D4).

**Table D.2.** Gas phase thermodynamic properties of N<sub>2</sub>O, CO, CO<sub>2</sub>, and N<sub>2</sub> (obtained from: *NIST Chemistry Web-Book*).

Species	$\Delta H^{\circ}_{f}$ (kJ/mol)	S° (J/mol-K)
$N_2O_{(g)}$	89.4	239.3
$CO_{(g)}$	-105.4	211.2
$N_{2(g)}$		232.4
CO <sub>2(g)</sub>	-386.4	205.1

*Heat of reaction:* 

$$\Delta H_{rxn}^{o} = \Delta H_{f}^{o}(N_{2}) + \Delta H_{f}^{o}(CO_{2}) - \Delta H_{f}^{o}(N_{2}O) - \Delta H_{f}^{o}(CO) =$$

$$-370.4 \, kJ \, (mol)^{-1} \tag{D.1}$$

*Estimation for*  $\Delta S^{\circ}$ *:* 

$$\Delta S^{o} = \Delta S^{o}(N_{2}) + \Delta S^{o}(CO_{2}) - \Delta S^{o}(N_{2}O) - \Delta S^{o}(CO) = -13 \text{ J} (mol \cdot K)^{-1}$$
(D.2)

*Estimation for*  $\Delta G$ *:* 

$$\Delta G = \Delta H_{rxn}^o - \Delta S^o T \tag{D.3}$$

$$\Delta G = -364.3 \frac{kJ}{mol} \ at \ 473 \ K \tag{D.4}$$

*Estimation for K<sub>eq</sub>:* 

$$K_{eq} = e^{-\frac{\Delta G}{RT}} = 1.71 \ x \ 10^{40} \tag{D.5}$$

Approach to equilibrium  $(\eta)$ :

$$\eta = \frac{P_{N_2} P_{CO_2}}{P_{N_2} o P_{CO}} * \frac{1}{K_{eq}}$$
(D.6)



**Figure D4.** Approach to equilibrium ( $\eta$ ) as a function of the reactant conversion at a standard reaction condition (2 kPa CO and 2 kPa N<sub>2</sub>O) at 473 K.

## **D2.2.** Oxidation Rate with Conversion



**Figure D5.** Oxidation rate measured over MIL-100(Fe) and the reactant conversions as a function of the weight hourly space velocity (WHSV), varied by controlling the total flow rate or the catalyst mass (473 K, 4.4 kPa N<sub>2</sub>O, 1.5 kPa CO).



**Figure D6.** Oxidation rate measured over MIL-100(Cr) and the reactant conversions as a function of the weight hourly space velocity (WHSV), varied by controlling the total flow rate (473 K, 6.4 kPa N<sub>2</sub>O, 7.4 kPa CO).

## D2.3. In-Situ Co-Titration Experiment with NO and H<sub>2</sub>O



**Figure D7.** Under 0.5 kPa NO co-feed, the total quantity of H<sub>2</sub>O adsorbed over MIL-100(Fe) and the corresponding steady-state CO<sub>2</sub> formation rate (per total mol Fe) under each condition. 14.6 kPa N<sub>2</sub>O, 1.5 kPa CO, 423 K, sample activated at 523 K for 12 h under He flow.

D2.4. In-Situ NO Titration during Breakthrough Adsorption



**Figure D8.** (a) Normalized oxidation rate (a) as a function of time and (b) at a given coverage of NO, when NO is introduced to the reactant flow at t = 0 hours. Reaction conditions: 14.6 kPa N<sub>2</sub>O, 1.5 kPa CO, 0.003 kPa NO, 423 K.

### **D2.5. CO Oxidation Mechanisms Considered**

Four possible mechanisms for the oxidation of CO with N<sub>2</sub>O were considered in this study, including (1) sequential mechanism, (2) concerted mechanism (N<sub>2</sub>O binding first), (3) concerted mechanism (CO binding first), and (4) concerted mechanism (two active sites) as described on the following pages of this section. Based on the kinetic data obtained for MIL-100, the reaction mechanism, and series of elementary reaction steps must meet three main requirements:

- 1. CO adsorption is reversible
- 2. N<sub>2</sub>O reaction orders can increase with CO partial pressure
- 3. CO reaction orders can increase with N<sub>2</sub>O partial pressure

For each reaction mechanism, various rate expressions were derived and considered an appropriate model based on the requirements described above. Suitable rate expressions identified included Scheme 1(e, f), Scheme 2(d), and Scheme 4(e).

# **<u>SCHEME 1</u>**: Sequential Mechanism

1	$N_2O_{(g)}\ +\ M$	$\leftrightarrow$	$N_2O\cdots M$
2	$N_2 O \cdots M$	$\leftrightarrow$	$N_{2(g)} + M-O$
3	$M\text{-}O \ + \ CO_{(g)}$	$\leftrightarrow$	М-О…СО
4	М-О…СО	$\leftrightarrow$	$M{\cdots}CO_2$
5	$M \cdots CO_2$	$\leftrightarrow$	$M + CO_{2(g)}$

*1a)* Step 1 is the RDS, all other steps are quasi-equilibrated:

$$r = k_1 [N_2 O] [M],$$
 (D.7)

$$L=[M]+[N_2O-M]+[M-O]+[M-O-CO]+[M-CO_2],$$
(D.8)

$$[CO_2-M] = \frac{[CO_2]}{K_5} [M], \qquad (D. 9)$$

$$[M-0-C0] = \frac{[C0_2]}{K_4 K_5} [M], \qquad (D.10)$$

$$[M-O] = \frac{[CO_2]}{K_3 K_4 K_5 [CO]} [M], \qquad (D.11)$$

$$[N_2 O - M] = \frac{[N_2][M - O]}{K_2} = \frac{[N_2][CO_2]}{K_2 K_3 K_4 K_5[CO]} [M],$$
(D.12)

and 
$$r = \frac{k_1[N_2O]}{1 + \left(\frac{[N_2][CO_2]}{K_2K_3K_4K_5[CO]}\right) + \left(\frac{[CO_2]}{K_3K_4K_5[CO]}\right) + \left(\frac{[CO_2]}{K_4K_5}\right) + \frac{[CO_2]}{K_5}}$$
 (D.13)

The rate expression does not meet requirement 2 or 3

# 1b) Step 2 is the RDS, all other steps are quasi-equilibrated:

$$r = k_2[N_2 O - M],$$
 (D.14)

$$L = [M] + [N_2 O - M] + [M - O] + [M - O - CO] + [M - CO_2], \quad (D.15)$$

$$[N_2 O - M] = K_1 [N_2 O] [M], (D.16)$$

$$[M - 0] = \frac{[CO_2]}{K_3 K_4 K_5 [CO]} [M], \qquad (D.17)$$

$$[CO_2 - M] = \frac{[CO_2]}{K_5} [M], \qquad (D.18)$$

$$[M - O - CO] = \frac{[CO_2]}{K_4 K_5} [M],$$
(D.19)

and 
$$r = \frac{k_2 K_1 [N_2 O]}{1 + K_1 [N_2 O] + \left(\frac{[CO_2]}{K_3 K_4 K_5 [CO]}\right) + \left(\frac{[CO_2]}{K_4 K_5}\right) + \frac{[CO_2]}{K_5}}$$
 (D.20)

# The rate expression does not meet requirement 2 or 3

*1c) Step 4 is the RDS, all other steps are quasi-equilibrated:* 

$$r = k_4 [M - 0 - C0], (D.21)$$

$$L = [M] + [N_2 O - M] + [M - O] + [M - O - CO] + [M - CO_2], \quad (D.22)$$

$$[N_2 O - M] = K_1 [N_2 O] [M], (D.23)$$

$$[M - 0] = \frac{K_1 K_2 [N_2 0]}{[N_2]} [M], \qquad (D.24)$$

$$[CO_2 - M] = \frac{[CO_2]}{K_5} [M], \tag{D.25}$$

$$[M - O - CO] = \frac{K_1 K_2 K_3 [N_2 O] [CO]}{[N_2]} [M],$$
(D.26)

and 
$$r = \frac{k_4 \frac{K_1 K_2 K_3 [N_2 0][C0]}{[N_2]}}{1 + K_1 [N_2 0] + \frac{K_1 K_2 [N_2 0]}{[N_2]} + \frac{K_1 K_2 K_3 [N_2 0][C0]}{[N_2]} + \frac{[C0_2]}{K_5}}$$
 (D.27)

The rate expression does not meet requirements 2 or 3.

*1d) Step 5 is the RDS, all other steps are quasi-equilibrated:* 

$$r = k_5 [CO_2 - M],$$
 (D.28)

$$L = [M] + [N_2 O - M] + [M - O] + [M - O - CO] + [M - CO_2], \quad (D.29)$$

$$[N_2 O - M] = K_1 [N_2 O] [M], (D.30)$$

$$[M - 0] = \frac{K_1 K_2 [N_2 0]}{[N_2]} [M], \qquad (D.31)$$

$$[M - O - CO] = \frac{K_1 K_2 K_3 [N_2 O][CO]}{[N_2]} [M],$$
(D.32)

$$[M - O - CO_2] = \frac{K_1 K_2 K_3 K_4 [N_2 O][CO]}{[N_2]} [M],$$
(D.33)

and 
$$r = \frac{k_5 \frac{K_1 K_2 K_3 K_4 [N_2 0] [C0]}{[N_2]}}{1 + K_1 [N_2 0] + \frac{K_1 K_2 [N_2 0]}{[N_2]} + \frac{K_1 K_2 K_3 [N_2 0] [C0]}{[N_2]} + \frac{K_1 K_2 K_3 K_4 [N_2 0] [C0]}{[N_2]}}{[N_2]}}.$$
 (D.34)

The rate expression does not meet requirements 2 or 3.

*1e) Step 2 and Step 4 are irreversible, Step 1 and Step 5 are quasi-equilibrated:* 

$$r = k_2[N_2O - M] = k_4[M - O - CO],$$
 (D.35)

$$L = [M] + [N_2 O - M] + [M - O] + [M - CO_2],$$
(D.36)

$$[N_2 O - M] = K_1 [N_2 O] [M], (D.37)$$

$$[CO_2 - M] = \frac{[CO_2]}{K_5} [M], \tag{D.38}$$

$$\frac{d[M-O-CO]}{dt} = \vec{k_3}[M-O][CO] - \vec{k_3}[M-O-CO] - \vec{k_4}[M-O-CO], \quad (D.39)$$

$$[M - O - CO] = \frac{\overline{k_3}[M - O][CO]}{\overline{k_3} + \overline{k_4}},$$
 (D.40)

$$\frac{d[M-O]}{dt} = \vec{k_2}[N_2O - M] - \vec{k_3}[M - O][CO] + \vec{k_3}[M - O - CO], \quad (D.41)$$

$$[M-0] = \frac{\overline{k_2}K_1[N_20]}{\overline{k_3}[C0]\left(1 - \frac{\overline{k_3}}{\overline{k_3} + \overline{k_4}}\right)} [M], \qquad (D.42)$$

$$[M - O - CO] = \frac{\overline{k_2}K_1[N_2O]}{\overline{k_4}}[M], \qquad (D.43)$$

and 
$$r = \frac{k_2 K_1[N_2 O]}{1 + K_1[N_2 O] + \frac{\overline{k_2} K_1[N_2 O]}{\overline{k_3}[CO] \left(1 - \frac{\overline{k_3}}{\overline{k_3} + \overline{k_4}}\right)} + \frac{\overline{k_2} K_1[N_2 O]}{\overline{k_4} + \frac{[CO_2]}{K_5}}.$$
 (D.44)

# The rate expression meets all requirements

*If) Step 1 and 4 are irreversible, Step 5 is quasi-equilibrated:* 

$$r = k_1[N_20][M] = k_4[M - 0 - C0],$$
(D.45)

$$L = [M] + [N_2 O - M] + [M - O] + [M - CO_2],$$
(D.46)

$$[CO_2 - M] = \frac{[CO_2]}{K_5} [M], \qquad (D.47)$$

$$\frac{d[M-N_2O]}{dt} = k_1[N_2O][M] - \overrightarrow{k_2}[M-N_2O] + \overleftarrow{k_2}[N_2][M-O], \qquad (D.48)$$

$$\frac{d[M-O]}{dt} = \vec{k_2}[M - N_2 O] - \vec{k_2}[N_2][M - O] - \vec{k_3}[M - O][CO] + \vec{k_2}[M - O - CO], (D.49)$$

$$\frac{d[M-O-CO]}{dt} = \vec{k_3}[M-O][CO] - \vec{k_3}[M-O-CO] - \vec{k_4}[M-O-CO], \quad (D.50)$$

$$[M - O - CO] = \frac{k_1[N_2O]}{\vec{k_4}}[M], \qquad (D.51)$$

$$[M-O] = \frac{\overline{k_1}[N_2O]}{\overline{k_3}[CO]\left(1 - \frac{\overline{k_3}}{\overline{k_3} + \overline{k_4}}\right)} [M], \qquad (D.52)$$

$$[M - N_2 O] = \overrightarrow{k_1}[N_2 O][M] \left( 1 + \frac{\overleftarrow{k_2}[N_2]}{\overrightarrow{k_3}[CO]\left(1 - \frac{\overleftarrow{k_3}}{\overrightarrow{k_3} + \overrightarrow{k_4}}\right)} \right), \tag{D.53}$$

and 
$$r = \frac{k_1[N_2O]}{1 + \overline{k_1}[N_2O] \left(1 + \frac{\overline{k_2}[N_2]}{\overline{k_3}[CO] \left(1 - \frac{\overline{k_3}}{\overline{k_3} + \overline{k_4}}\right)}\right) + \frac{\overline{k_1}[N_2O]}{\overline{k_3}[CO] \left(1 - \frac{\overline{k_3}}{\overline{k_3} + \overline{k_4}}\right)} + \frac{k_1[N_2O]}{\overline{k_4}} + \frac{k_1[N_2O]}{\overline{k_5}}.$$
 (D.54)

The rate expression meets all requirements

# **<u>SCHEME 2</u>**: Concerted Mechanism (N<sub>2</sub>O Binding First)

1	$N_2O_{(g)}\ +\ M$	$\leftrightarrow$	$N_2O\cdots M$
2	$N_2O\!\cdots\!M+CO_{(g)}$	$\leftrightarrow$	$N_2O\cdots M\cdots CO$
3	$N_2O\cdots M\cdots CO$	$\leftrightarrow$	$M{\cdots}CO_2+N_2$
4	$M \cdots CO_2$	$\leftrightarrow$	$M \ + \ CO_{2(g)}$

2a) Step 1 is the RDS, all other steps are quasi-equilibrated:

$$r = k_1[N_2 0][M], (D.55)$$

$$L = [M] + [N_2 O - M] + [N_2 O - M - CO] + [M - CO_2],$$
(D.56)

$$[CO_2 - M] = \frac{[CO_2]}{K_4} [M], \qquad (D.57)$$

$$[N_2 O - M - CO] = \frac{[M - CO_2][N_2]}{K_3} = \frac{[CO_2][N_2]}{K_3 K_4} [M],$$
(D.58)

$$[N_2 O - M] = \frac{[N_2 O - M - CO]}{K_2[CO]} = \frac{[CO_2][N_2]}{K_3 K_4 K_2[CO]} [M],$$
(D.59)

and 
$$r = \frac{k_1[N_2O]}{1 + \frac{[CO_2][N_2]}{K_3K_4K_2[CO]} + \frac{[CO_2][N_2]}{K_3K_4} + \frac{[CO_2]}{K_4}}.$$
 (D.60)

The rate expression does not meet requirement 2 or 3.

2b) Step 3 is the RDS, all other steps are quasi-equilibrated:

$$r = k_3 [N_2 O - M - CO], (D.61)$$

$$L = [M] + [N_2 O - M] + [N_2 O - M - CO] + [M - CO_2],$$
(D.62)

$$[N_2 O - M] = K_1 [N_2 O] [M], (D.63)$$

$$[CO_2 - M] = \frac{[CO_2]}{K_4} [M], \qquad (D.64)$$

$$[N_2 O - M - CO] = K_2 K_1 [N_2 O] [CO] [M],$$
(D.65)

and 
$$r = \frac{k_3 K_1 K_2 [CO] [N_2 O]}{1 + K_1 [N_2 O] + K_2 K_1 [N_2 O] [CO] + \frac{[CO_2]}{K_4}}$$
 (D.66)

The rate expression does not meet requirement 2 or 3.

2c) Step 4 is the RDS, all other steps are quasi-equilibrated:

$$r = k_4 [M - CO_2],$$
 (D.67)

$$L = [M] + [N_2 O - M] + [N_2 O - M - CO] + [M - CO_2],$$
(D.68)

$$[N_2 O - M] = K_1 [N_2 O] [M], (D.69)$$

$$[N_2 O - M - CO] = K_2 K_1 [N_2 O] [CO] [M],$$
(D.70)

$$[M - CO_2] = \frac{K_1 K_2 K_3 [N_2 O][CO]}{[N_2]} [M],$$
(D.71)

and 
$$r = \frac{k_4 \frac{K_1 K_2 K_3 [N_2 0][C0]}{[N_2]}}{1 + K_1 [N_2 0] + K_2 K_1 [N_2 0][C0] + \frac{K_1 K_2 K_3 [N_2 0][C0]}{[N_2]}}.$$
 (D.72)

# The rate expression does not meet requirements 2 or 3.

2d) Step 1 and Step 3 are irreversible, Step 4 is quasi-equilibrated:

$$r = k_1[N_2O][M] = k_3[N_2O - M - CO],$$
(D.73)

$$L = [M] + [N_2 O - M] + [N_2 O - M - CO] + [M - CO_2],$$
(D.74)

$$[CO_2 - M] = \frac{[CO_2]}{K_4} [M], \tag{D.75}$$

$$\frac{d[N_2 O - M]}{dt} = \overline{k_1} [N_2 O] [M] - \overline{k_2} [N_2 O - M] [CO] + \overline{k_2} [N_2 O - M - CO], \qquad (D.76)$$

$$\frac{d[N_2O - M - CO]}{dt} = \overline{k_2}[N_2O - M][CO] - \overline{k_2}[N_2O - M - CO] - \overline{k_3}[N_2O - M - CO],$$
(D.77)  
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$$[N_2 O - M - CO] = \frac{\overline{k_2}[N_2 O - M][CO]}{\overline{k_2} + \overline{k_3}},$$
 (D.78)

$$[N_2 O - M] = \frac{\overline{k_1}[N_2 O][M]}{\overline{k_2}[CO]\left(1 - \frac{\overline{k_2}}{\overline{k_2} + \overline{k_3}}\right)},$$
(D.79)

$$[N_2 O - M - CO] = \frac{\overline{k_1}[N_2 O][M]}{\overline{k_3}},$$
 (D.80)

and 
$$r = \frac{k_1[N_2O]}{1 + \frac{\overline{k_1}[N_2O]}{\overline{k_2}[co]\left(1 - \frac{\overline{k_2}}{\overline{k_2} + \overline{k_3}}\right)} + \frac{\overline{k_1}[N_2O]}{\overline{k_3}} + \frac{[co_2]}{\overline{k_4}}}.$$
 (D.81)

The rate expression meets all requirements

# **<u>SCHEME 3</u>**: Concerted Mechanism (CO Binding First)

$$1 \qquad CO_{(g)} + M \quad \leftrightarrow \quad CO \cdots M$$

$$2 \qquad N_2O_{(g)} + CO \cdots M \quad \leftrightarrow \quad N_2O \cdots M \cdots CO$$

$$3 \qquad N_2O \cdots M \cdots CO \quad \leftrightarrow \quad M \cdots CO_2 + N_{2(g)}$$

$$4 \qquad M \cdots CO_2 \quad \leftrightarrow \quad M + CO_{2(g)}$$

*3a) Step 2 is the RDS, all other steps are quasi-equilibrated:* 

$$r = k_2 [CO - M] [N_2 O], (D.82)$$

$$L = [M] + [CO - M] + [N_2O - M - CO] + [M - CO_2],$$
(D.83)

$$[CO_2 - M] = \frac{[CO_2]}{K_4} [M], \qquad (D.84)$$

$$[CO - M] = K_1[CO][M], (D.85)$$

$$[N_2 O - M - CO] = \frac{[M - CO_2][N_2]}{K_3} = \frac{[CO_2][N_2]}{K_3 K_4} [M],$$
(D.86)

and 
$$r = \frac{k_2 K_1[CO][N_2O]}{1 + K_1[CO] + \frac{[CO_2][N_2]}{K_3 K_4} + \frac{[CO_2]}{K_4}}$$
 (D.87)

The rate expression does not meet requirements 2 or 3.

*3b) Step 3 is the RDS, all other steps are quasi-equilibrated:* 

$$r = k_3 [N_2 O - M - CO], (D.88)$$

$$L = [M] + [CO - M] + [N_2O - M - CO] + [M - CO_2],$$
(D.89)

$$[CO_2 - M] = \frac{[CO_2]}{K_4} [M], \qquad (D.90)$$

$$[CO - M] = K_1[CO][M], (D.91)$$

$$[N_2 O - M - CO] = K_1 K_2 [CO] [N_2 O] [M],$$
(D.92)

$$[N_2 O - M - CO] = \frac{[M - CO_2][N_2]}{K_3} = \frac{[CO_2][N_2]}{K_3 K_4} [M],$$
(D.93)

and 
$$r = \frac{k_3 K_1 K_2 [CO] [N_2 O]}{1 + K_1 [CO] + K_1 K_2 [CO] [N_2 O] + \frac{[CO_2]}{K_4}}$$
 (D.94)

# The rate expression does not meet requirements 2 or 3.

*3c) Step 4 is the RDS, all other steps are quasi-equilibrated:* 

$$r = k_4 [M - CO_2],$$
 (D.95)

$$L = [M] + [CO - M] + [N_2O - M - CO] + [M - CO_2],$$
(D.96)

$$[CO - M] = K_1[CO][M], (D.97)$$

$$[N_2 O - M - CO] = K_2 K_1 [N_2 O] [CO] [M],$$
(D.98)

$$[M - CO_2] = \frac{K_1 K_2 K_3 [N_2 O] [CO]}{[N_2]} [M],$$
(D.99)

and 
$$r = \frac{k_4 \frac{K_1 K_2 K_3 [N_2 0][C0]}{[N_2]}}{1 + K_1 [C0] + K_1 K_2 [C0][N_2 0] + \frac{K_1 K_2 K_3 [N_2 0][C0]}{[N_2]}}.$$
 (D.100)

## The rate expression does not meet requirements 2 or 3.

# *3e) Step 2 and Step 3 are irreversible, Step 1 and Step 4 is quasi-equilibrated:*

$$r = k_2[CO - M][N_2O] = k_3[N_2O - M - CO],$$
 (D.101)

$$L = [M] + [CO - M] + [N_2O - M - CO] + [M - CO_2],$$
(D.102)

$$[CO - M] = K_1[CO][M], (D.103)$$

$$[CO_2 - M] = \frac{[CO_2]}{K_4} [M], \qquad (D.104)$$

$$\frac{d[N_2 O - M - CO]}{dt} = \vec{k_2} [CO - M] [N_2 O] - \vec{k_3} [N_2 O - M - CO], \qquad (D.105)$$
$$[N_2 O - M - CO] = \frac{\overline{k_2} K_1 [N_2 O] [CO] [M]}{\overline{k_3}},$$
 (D.106)

and 
$$r = \frac{k_2 K_1[CO]}{1 + K_1[CO] + \frac{\overline{k_2} K_1[N_2O][CO]}{\overline{k_3}} + \frac{[CO_2]}{K_4}}$$
 (D.107)

The rate expression does not meet requirements 2 or 3.

# **<u>SCHEME 4</u>: Concerted Mechanism (Two Sites)**

$$1 \qquad N_2O_{(g)} + M_1 \quad \leftrightarrow \quad N_2O\cdots M_1$$

$$2 \qquad CO_{(g)} + M_2 \quad \leftrightarrow \quad CO\cdots M_2$$

$$3 \qquad N_2O\cdots M_1 + CO\cdots M_2 \quad \leftrightarrow \quad N_2\cdots M_1 + CO_2\cdots M_2$$

$$4 \qquad N_2\cdots M_1 \quad \leftrightarrow \quad M_1 + N_{2(g)}$$

$$5 \qquad M_2\cdots CO_2 \quad \leftrightarrow \quad M_2 + CO_{2(g)}$$

*4a) Step 1 is the RDS, all other steps are quasi-equilibrated:* 

$$r = k_1 [N_2 O] [M_1], \tag{D.108}$$

$$L_1 = [M_1] + [N_2 O - M_1] + [N_2 - M_1],$$
(D.109)

$$L_2 = [M_2] + [CO - M_2] + [CO_2 - M_2],$$
(D.110)

$$[N_2 - M_1] = \frac{[N_2]}{K_4} [M_1], \qquad (D.111)$$

$$[CO - M_2] = K_2[CO][M_2], (D.112)$$

$$[CO_2 - M_2] = \frac{[CO_2]}{K_5} [M_2], \qquad (D.113)$$

$$[N_2 O - M_1] = \frac{[N_2 - M_1][CO_2 - M_2]}{K_3[CO - M_2]} = \frac{[N_2][CO_2][M_1]}{K_2 K_3 K_4 K_5[CO]},$$
(D.114)

$$[M_1] = \frac{1}{1 + \frac{[N_2][CO_2]}{K_2 K_3 K_4 K_5[CO]} + \frac{[N_2]}{K_4}},$$
(D.115)

$$[M_2] = \frac{1}{1 + K_2[CO] + \frac{[CO_2]}{K_5}},$$
 (D.116)

$$r = k_1 [N_2 O] [M_1],$$
 (D.117)

and 
$$r = \frac{k_1[N_2O]}{1 + \frac{[N_2][CO_2]}{K_2K_3K_4K_5[CO]} + \frac{[N_2]}{K_4}}$$
 (D.118)

The rate expression does not meet requirements 2 or 3.

4b) Step 3 is the RDS, all other steps are quasi-equilibrated:

$$r = k_3 [N_2 O - M_1] [CO - M_2], (D.119)$$

$$L_1 = [M_1] + [N_2 O - M_1] + [N_2 - M_1],$$
(D.120)

$$L_2 = [M_2] + [CO - M_2] + [CO_2 - M_2],$$
(D.121)

$$[N_2 - M_1] = \frac{[N_2]}{K_4} [M_1], \qquad (D.122)$$

$$[N_2 O - M_1] = K_1 [N_2 O] [M_1], (D.123)$$

$$[CO_2 - M_2] = \frac{[CO_2]}{K_5} [M_2], \qquad (D.124)$$

$$[CO - M_2] = K_2[CO][M_2], (D.125)$$

$$r = k_3[N_2O - M_1][CO - M_2] = k_3K_1K_2[N_2O][CO][M_1][M_2], \quad (D.126)$$

and 
$$r = \frac{k_3 K_1 K_2 [N_2 O] [CO]}{\left(1 + K_1 [N_2 O] + \frac{[N_2]}{K_4}\right) \left(1 + K_2 [CO] + \frac{[CO_2]}{K_5}\right)}$$
 (D.127)

# The rate expression does not meet requirements 2 or 3.

*4c) Step 4 is the RDS, all other steps are quasi-equilibrated:* 

$$r = k_4 [N_2 - M_1], \tag{D.128}$$

$$L_1 = [M_1] + [N_2 O - M_1] + [N_2 - M_1],$$
(D.129)

$$L_2 = [M_2] + [CO - M_2] + [CO_2 - M_2],$$
(D.130)

$$[N_2 O - M_1] = K_1 [N_2 O] [M_1], (D.131)$$

$$[CO_2 - M_2] = \frac{[CO_2]}{K_5} [M_2], \qquad (D.132)$$

$$[CO - M_2] = K_2[CO][M_2], (D.133)$$

$$[N_2 - M_1] = \frac{K_3[N_2 O - M_1][CO - M_2]}{[CO_2 - M_2]} = \frac{K_1 K_2 K_3 K_5[N_2 O][CO][M_1]}{[CO_2]},$$
 (D.134)

and 
$$r = \frac{k_4 \frac{K_1 K_2 K_3 K_5[N_2 0][C0]}{[C0_2]}}{\left(1 + K_1[N_2 0] + \frac{K_1 K_2 K_3 K_5[N_2 0][C0]}{[C0_2]}\right)}.$$
 (D.135)

The rate expression does not meet requirements 2 or 3.

*4d) Step 5 is the RDS, all other steps are quasi-equilibrated:* 

$$r = k_5 [CO_2 - M_2], (D.136)$$

$$L_1 = [M_1] + [N_2 O - M_1] + [N_2 - M_1],$$
(D.137)

$$L_2 = [M_2] + [CO - M_2] + [CO_2 - M_2],$$
(D.138)

$$[N_2 O - M_1] = K_1 [N_2 O] [M_1], (D.139)$$

$$[N_2 - M_2] = \frac{[N_2]}{K_4} [M_1], \qquad (D.140)$$

$$[CO - M_2] = K_2[CO][M_2], (D.141)$$

$$[CO_2 - M_3] = \frac{K_3[N_2O - M_1][CO - M_2]}{[N_2 - M_1]} = \frac{K_1K_2K_3K_4[N_2O][CO][M_2]}{[N_2]},$$
 (D.142)

and 
$$r = \frac{k_5 \frac{K_1 K_2 K_3 K_4 [N_2 0][C0]}{[N_2]}}{\left(1 + K_2 [C0] + \frac{K_1 K_2 K_3 K_4 [N_2 0][C0]}{[N_2]}\right)}$$
 (D.143)

# The rate expression does not meet requirements 2 or 3.

# *4e) Step 1 and Step 3 are irreversible, all other steps are quasi-equilibrated:*

$$r = k_1[N_2O][M_1] = k_3[N_2O - M_1][CO - M_2],$$
(D.144)

$$L_1 = [M_1] + [N_2 O - M_1] + [N_2 - M_1],$$
(D.145)

$$L_2 = [M_2] + [CO - M_2] + [CO_2 - M_2],$$
(D.146)

$$[N_2 - M_1] = \frac{[N_2]}{K_4} [M_1], \qquad (D.147)$$

$$[CO - M_2] = K_2[CO][M_2], (D.148)$$

$$[CO_2 - M_2] = \frac{[CO_2]}{K_5} [M_2], \qquad (D.149)$$

$$\frac{d[N_2 O - M_1]}{dt} = \overrightarrow{k_1}[N_2 O][M_1] - \overrightarrow{k_3}[N_2 O - M_1][CO - M_2], \qquad (D.150)$$

$$[N_2 O - M_1] = \frac{\overline{k_1}[N_2 O][M_1]}{\overline{k_3}K_2[CO][M_2]},$$
(D.151)

$$[M_2] = \frac{1}{1 + K_2[CO] + \frac{[CO_2]}{K_5}},$$
 (D.152)

$$[M_1] = \frac{1}{1 + \frac{\overline{k_1}[N_2O]}{\overline{k_3}K_2[CO][M_2]} + \frac{[N_2]}{K_4}},$$
(D.153)

and 
$$r = \frac{\overline{k_1}[N_2O]}{1 + \frac{\overline{k_1}[N_2O](1 + K_2[CO] + \frac{[CO_2]}{K_5})}{\overline{k_3}K_2[CO]} + \frac{[N_2]}{K_4}}$$
. (D.154)

# D2.6. Quantification of Species formed in the Reaction of N2<sup>16</sup>O and C<sup>18</sup>O

During the oxidation of C<sup>18</sup>O with N<sub>2</sub><sup>16</sup>O over MIL-100, there is a multitude of isotopologues which may form with indistinct mass fragments that can be detected using a mass spectrometer (MS) as shown in Table D3. The total CO<sub>2</sub> and N<sub>2</sub> formation rates can be easily measured by analyzing the steady-state reaction effluent by gas chromatography (GC). Increases in the baseline intensity of the m/z = 28 signal measured by MS analysis will also reflect finite <sup>14</sup>N<sub>2</sub> formation rates and may also include contributions of <sup>12</sup>C<sup>16</sup>O net formation rates. Furthermore, assuming that increases in the intensity of the m/z = 28 signal correspond solely to <sup>12</sup>C<sup>16</sup>O and <sup>14</sup>N<sub>2</sub> formation, the net formation rate of C<sup>16</sup>O can be estimated by correcting for the <sup>14</sup>N<sub>2</sub> formation rate measured by GC analysis, given by the following series of equations:

$$\left(\frac{I_{14}{N_2}(28)}{I_{Ar}(40)}\right) = CF_{14}{N_2}\left(\frac{\dot{n}_{14}{N_2}}{\dot{n}_{Ar}}\right),\tag{D.155}$$

$$\left(\frac{I_{12}C^{16}O^{(28)}}{I_{Ar}(40)}\right) = CF_{12}C^{16}O\left(\frac{\dot{n}_{12}C^{16}O}{\dot{n}_{Ar}}\right),\tag{D. 156}$$

$$\left(\frac{I(28)}{I_{Ar}(40)}\right) = \left(\frac{I_{14}{N_2}(28)}{I_{Ar}(40)}\right) + \left(\frac{I_{12}{C^{16}o}(28)}{I_{Ar}(40)}\right),\tag{D.157}$$

$$I_{{}^{12}C^{16}O}(28) = I(28) - I_{{}^{14}N_2}(28),$$
 (D.158)

and 
$$\dot{n}_{12}{}_{C^{16}O} = \frac{I(28) - I_{Ar}(40) \left( CF_{14}{}_{N_2} \left( \frac{\dot{n}_{14}{}_{N_2}}{\dot{n}_{Ar}} \right) \right)}{I_{Ar}(40) \left( \frac{CF_{12}{}_{C^{16}O}}{\dot{n}_{Ar}} \right)}$$
 (D.159)

where  $I_x(z)$  corresponds to the intensity (I) of the MS signal corresponding to the primary mass fragment (z) of species (x), and *CF* is the correction factor used for calibrating MS signals for <sup>12</sup>C<sup>16</sup>O and <sup>14</sup>N<sub>2</sub> to molar flow rates ( $\dot{n}_x$ ) using Ar as an internal standard. *I*(28) represents the intensity of the MS signal under reaction conditions with <sup>14</sup>N<sub>2</sub><sup>16</sup>O and C<sup>18</sup>O that corresponds to the linear combination of contributions from  $^{14}\mathrm{N}_2$  and  $\mathrm{C}^{16}\mathrm{O}$  formation

(Equation D.157).

Isotope	Mass	Secondary Mass Fragment (1)	Secondary Mass Fragment (2)
<sup>12</sup> C <sup>18</sup> O	30	$^{12}C (m/z = 12)$	$^{18}O(m/z = 18)$
<sup>12</sup> C <sup>16</sup> O	28	$^{12}C (m/z = 12)$	$^{16}O(m/z = 16)$
$^{14}N_2^{16}O$	44	$^{14}N_2 (m/z = 28)$	$^{14}N^{16}O$ (m/z = 30)
$^{14}N_2^{18}O$	46	$^{14}N_2 (m/z = 28)$	$^{14}N^{18}O$ (m/z = 32)
$^{12}C^{18}O^{16}O$	46	${}^{12}C^{18}O (m/z = 30)$	$^{12}C^{16}O(m/z = 28)$
$^{12}C^{18}O_2$	48	$^{12}C^{18}O(m/z = 30)$	${}^{12}C (m/z = 12)$ ${}^{18}O (m/z = 18)$
$^{12}C^{16}O_2$	44	$^{12}C^{16}O(m/z = 28)$	${}^{12}C (m/z = 12)$ ${}^{16}O (m/z = 16)$
$^{14}N_2$	28	$^{14}N (m/z = 14)$	

**Table D3.** Possible isotope species which could be formed or measured under  $C^{18}O$  and  $N_2^{16}O$  co-feed over MIL-100 and the corresponding mass fragments used for identification.

As shown in Figure D9 for the reaction of C<sup>18</sup>O and N<sub>2</sub><sup>16</sup>O over MIL-100(Fe) (473 K, 2.5 kPa CO (95% C<sup>18</sup>O), 3.1 kPa N<sub>2</sub><sup>16</sup>O), there is a significant increase in the intensity of the signal corresponding to m/z = 46 above the baseline intensity. In order to determine if this increase corresponds to the formation of <sup>12</sup>C<sup>18</sup>O<sup>16</sup>O, <sup>14</sup>N<sub>2</sub><sup>18</sup>O, or both, analysis of the secondary mass fragments associated with <sup>14</sup>N<sub>2</sub><sup>18</sup>O were considered (Table D3). Specifically, <sup>14</sup>N<sup>18</sup>O mass fragments produced with <sup>14</sup>N<sub>2</sub><sup>18</sup>O by MS analysis should result in an increase in the baseline intensity for the m/z = 32 signal. As shown for <sup>14</sup>N<sub>2</sub><sup>16</sup>O in Figure D10, the intensity of the <sup>14</sup>N<sup>16</sup>O fragment (m/z = 30) is approximately 13% of the primary mass fragment, <sup>14</sup>N<sub>2</sub><sup>16</sup>O (m/z = 44). Under the reaction conditions tested, no increase in the m/z = 32 signal was observed above its baseline value (Figure D9),

furthermore, it was assumed that the large increase in the intensity of the m/z = 46 signal could be entirely attributed to the formation of  $C^{18}O^{16}O$ , the molar flow rate at the reactor outlet of which, was determined assuming an identical calibration factor for every  $CO_2$  isotopologue relative to the internal standard, Ar, for quantification by MS.



**Figure D9.** For the reaction of C<sup>18</sup>O and N<sub>2</sub><sup>16</sup>O over MIL-100(Fe), the intensity of the relevant m/z signals analyzed by mass spectroscopy normalized by their baseline signals under reactant flow (473 K, 2.5 kPa CO (95% C<sup>18</sup>O), 3.1 kPa N<sub>2</sub><sup>16</sup>O).

Under conditions tested in this report for both MIL-100(Fe) and MIL-100(Cr),  $C^{16}O^{18}O$  formation rates determined, alone, were not adequate to account for the overall CO<sub>2</sub> formation rate measured by GC analysis (Figure 5.5 and Figure 5.19), in Section 5, suggestive of the formation of other CO<sub>2</sub> isotopologues. As <sup>12</sup>C<sup>18</sup>O<sub>2</sub> was identified as the only species which could give a primary/secondary mass fragment at m/z = 48 (Table D3), it was assumed that any increases in the baseline intensity for this signal could be attributed to <sup>12</sup>C<sup>18</sup>O<sub>2</sub> formation. C<sup>16</sup>O<sub>2</sub> would represent the third CO<sub>2</sub> isotopologue which could form

under reaction conditions, however, the identical main masses of <sup>14</sup>N<sub>2</sub><sup>16</sup>O and <sup>12</sup>C<sup>16</sup>O<sub>2</sub> (m/z = 44) make its discrimination solely from the mass spectra unfeasible. Furthermore, as there is evidence of isotopic scrambling of CO oxygen atoms originating from N<sub>2</sub><sup>16</sup>O based on finite C<sup>18</sup>O<sub>2</sub> and net C<sup>16</sup>O formation rates, it is assumed that C<sup>16</sup>O<sub>2</sub> may also form by the participation of C<sup>16</sup>O (formed in-situ or present as impurity in the 95% C<sup>18</sup>O reactant mixture) in the formation of C<sup>16</sup>O<sub>2</sub>. Furthermore, the formation rate of C<sup>16</sup>O<sub>2</sub> is assumed to correspond to the residual total CO<sub>2</sub> formation rate, which cannot be account for by C<sup>16</sup>O<sup>18</sup>O or C<sup>18</sup>O<sub>2</sub> formation, as given by the following relationship

$$\frac{mol\ CO_2}{(mol\ M^{2+})\cdot s} = \frac{mol\ C^{18}O^{16}O}{(mol\ M^{2+})\cdot s} + \frac{mol\ C^{18}O_2}{(mol\ M^{2+})\cdot s} + \frac{mol\ C^{16}O_2}{(mol\ M^{2+})\cdot s}$$
(D.160)

where the total CO<sub>2</sub> formation rate is measured by GC analysis and the  $C^{18}O^{16}O$  and  $C^{18}O_2$  formation rates are measured directly by MS analysis.



**Figure D10.** Relative intensity of the m/z signals corresponding to  ${}^{14}N_2$  (28),  ${}^{14}N^{16}O$  (30), and  ${}^{14}N_2{}^{16}O$  to the primary mass fragment (m/z = 44) for 2.9 kPa  ${}^{14}N_2O$  with 2.5 kPa Ar in He.

Product	Quantification Method
$N_2$	GC analysis at steady-state reaction
Total CO <sub>2</sub>	GC analysis at steady-state reaction
$^{12}C^{18}O^{16}O$	MS analysis of primary $m/z = 46$
$^{12}C^{18}O_2$	MS analysis of primary $m/z = 48$
$^{12}C^{16}O_2$	Balance of CO <sub>2</sub> all isotopologues (Eq. D.160)
<sup>12</sup> C <sup>16</sup> O	MS analysis of primary $m/z = 28$ (accounting for contributions from N <sub>2</sub> formation rates measured by GC analysis (Eq. D.159)

**Table D4.** Quantification method used to determine the molar flow rate of each product species<br/>formed during the reaction of  $C^{18}O$  and  $N_2^{16}O$  over MIL-100.

### D2.7. Stepped/Sequential N<sub>2</sub>O and CO Reaction over MIL-100(Fe)

Stepped or sequential reaction experiments with N<sub>2</sub>O over MIL-100(Fe) were conducted by first exposing the catalyst to N<sub>2</sub>O in He, purging with He, and then exposing the catalyst to CO in He, all at 473 K. Figure D11 shows the concentration of N<sub>2</sub>O measured at the reactor outlet reaches less than 1% of its initial concentration (62 kPa) after purging with He for approximately 4 minutes and is less than 0.05% of its initial concentration after purging with He for 30 minutes. Figure D12 shows the effect of the He purging time on the stoichiometric quantity of CO<sub>2</sub> formed (per total mol Fe<sup>2+</sup>), where after purging for 3 hours under He flow, there are no reactive surface intermediates remaining for reaction with CO to form CO<sub>2</sub>.



Figure D11. Normalized concentration of  $N_2O$  and Ar as a function of time when switching from a gas stream of (1)  $N_2O$  (62 kPa), Ar (2.5 kPa), and He to (2) pure He (64 mL min<sup>-1</sup>) at 473 K over MIL-100(Fe).



**Figure D12.** Cumulative moles of CO<sub>2</sub> formed (per mol Fe<sup>2+</sup>) at 473 K when MIL-100(Fe) is first exposed to N<sub>2</sub>O (64 kPa) in He, purged under He flow (64 mL min<sup>-1</sup>) for the time designated on the x-axis, and then exposed to CO (32.2 kPa in He).

# D2.8. Additional Analysis of the Reaction of <sup>18</sup>O<sub>2</sub>-N<sub>2</sub><sup>16</sup>O over MIL-100(Fe)

Figure D13 shows the cumulative moles of <sup>18</sup>O<sup>16</sup>O formed (per mol Fe<sup>2+</sup>) formed over MIL-100(Fe) upon exposure to <sup>18</sup>O<sub>2</sub> and N<sub>2</sub><sup>16</sup>O at 473 K. After approximately 700 s of reaction, the rate of <sup>18</sup>O<sup>16</sup>O formation is nearly constant, as indicated by the linear increase in the cumulative moles of <sup>18</sup>O<sup>16</sup>O formed with time at this point. Extrapolation of the linear portion of this profile (from a reaction time of 700 – 1000 s) to a reaction time of 0 seconds provides a y-intercept of approximately 0.99 cumulative moles of <sup>18</sup>O<sup>16</sup>O formed per mol Fe<sup>2+</sup>. Furthermore, this analysis suggests that the initially high rates of <sup>18</sup>O<sup>16</sup>O formation are due primarily to the reaction of <sup>18</sup>O with intermediates formed by the decomposition of N<sub>2</sub><sup>16</sup>O (M + N<sub>2</sub>O<sub>(g)</sub>  $\rightarrow$  M-<sup>16</sup>O + N<sub>2(g)</sub>; <sup>18</sup>O<sub>2(g)</sub> + M-<sup>16</sup>O  $\leftrightarrow$  M-<sup>18</sup>O + <sup>16</sup>O<sub>2(g)</sub>). After this point, residual <sup>18</sup>O<sup>16</sup>O formation rates can be attributed to isotopic exchange between the surface intermediates with <sup>18</sup>O<sub>2</sub> and trace <sup>16</sup>O<sub>2</sub> impurities in the oxygen gas stream (97 mol% <sup>18</sup>O<sub>2</sub>).



Figure D13. Cumulative moles of <sup>18</sup>O<sup>16</sup>O formed (per mol Fe<sup>2+</sup>) as a function of the reaction time when exposed to N<sub>2</sub>O (62 kPa) and O<sub>2</sub> (97% <sup>18</sup>O<sub>2</sub>, 2.3 kPa) at 473 K.

### **D2.9.** Supplementary Results of XAFS Analysis



Figure D.14. Comparison of the XANES spectra of (a) the as-synthesized MIL-100(Fe) sample to  $Fe^{3+}$  reference compounds and (b) the thermally activated MIL-100(Fe) sample to  $Fe^{2+}$  reference compounds.



**Figure D15.** Fe EXAFS fit results for the as-synthesized MIL-100(Fe) sample (a) including only Fe-O (N = 6) and Fe-Fe (N = 2) single scattering paths and (b) adding the Fe-C (N = 4) scattering path. Results summarized in Table D5.

**Table D5.** Fe K edge EXAFS fit results from Figure D15 for the as synthesized MIL-100(Fe) sample (k =  $3.1 - 10.5 \text{ Å}^{-1}$ ),  $\Delta k = 0.1$ ,  $k^{N} N = 1,2,3$  weighting, R = 1.0 - 3.3 Å), simultaneous fit with  $\Delta E_0$  for all scattering paths.

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Sample	Path	Ν	<b>R</b> (A)	$\sigma^2 (x 10^{-3} A^2)$	$\Delta E_0 (eV)$	$S_0^2$	R-factor
As Synthesized	Fe-O	6	$1.992 \pm 0.012$	$7.6 \pm 1.7$	-0.91 ±	$0.79 \pm$	0.018
Fe-C excluded	Fe-Fe	2	$3.303 \pm \ 0.019$	$6.3~\pm~2.1$	1.78	0.11	
As Synthesized	Fe-O	6	$1.997 \pm 0.013$	8.8 ± 1.7	-0.39 ±	0.91 ±	0.009
Fe-C included	Fe-C	4	$2.846 \pm \ 0.049$	$7.4\pm~2.1$	1.99	0.13	
	Fe-Fe	2	$3.305 \pm 0.020$	$5.4 \pm 7.5$			



**Figure D16.** X(k), k<sup>3</sup>-weighted, spectra of MIL-100(Fe) measured of the as synthesized sample at room temperature (RT) and following thermal activation measured at 473 K.



Figure D17. Fe EXAFS fit results for the thermally activated MIL-100(Fe) sample (a) including only the Fe-O single scattering path and (b) adding the Fe-Fe (N = 2) scattering path. Results summarized in Table D6.

**Table D6.** EXAFS fit results from Figure D17 for the thermally activated MIL-100(Fe) sample at 473 K (k =  $3.1 - 10.5 \text{ Å}^{-1}$ ),  $\Delta k = 0.1$ ,  $k^{N} N = 1,2,3$ , R = 1.0 - 2.2 Å without Fe-Fe included, R = 1.0 - 3.3 Å with Fe-Fe included),  $S_0^2$  set to 0.79 provided in Table D5.

Sample	Path	Ν	<b>R</b> (Å)	$\sigma^2 (x 10^{-3} \text{\AA}^2)$	$\Delta E_0 (eV)$	<b>R-factor</b>
Thermally activated (Fe-Fe excluded)	Fe-O	$4.544 \pm 0.629$	1.968 ± 0.012	8.6 ± 1.7	-1.74 ± 2.01	0.002
Thermally activated	Fe-O	$4.480\pm0.627$	$1.966 \pm 0.013$	8.5 ± 1.7	-2.16 ± 2.07	0.013
(Fe-Fe included)	Fe-Fe	2	$3.262 \pm 0.046$	$20.6\pm~5.0$		



**Figure D18.** Fe EXAFS fit results for the thermally activated MIL-100(Fe) sample at 473 K showing (a) the magnitude of X(R) and (b) X(k). Results summarized in Table 5.7.



**Figure D19.** Fe EXAFS fit results for MIL-100(Fe) under reaction conditions ( $N_2O/CO = 3$ ) at 473 K showing (a) the magnitude of X(R) and (b) X(k). Results summarized in Table 5.7.



Figure D20. Fe EXAFS fit results for MIL-100(Fe) under reaction conditions ( $N_2O/CO = 50$ ) at 473 K showing (a) the magnitude of X(R) and (b) X(k). Results summarized in Table 5.7.



**Figure D21.** Fe EXAFS fit results for MIL-100(Fe) under reaction conditions (N<sub>2</sub>O and O<sub>2</sub> cofeed) at 473 K showing (a) the magnitude of X(R) and (b) X(k). Results summarized in Table 5.7.



**Figure D22.** Fe EXAFS fit results for the difference spectra between the thermally activated MIL-100(Fe) sample and the sample measured under N<sub>2</sub>O/O<sub>2</sub> co-feed at 473 K showing (a) the magnitude and real components of X(R) and (b) X(k). Results summarized in Table 5.7.



Figure D23. Comparison of the weighted contribution of the spectra of the as-synthesized MIL-100(Fe) sample to the LCF to (a) the difference in the Fe-O coordination number and the expected fraction of  $Fe^{2+}$  sites oxidized to Fe-O estimated from kinetic measurements.

D2.10. Additional CO Oxidation Kinetic Data over MIL-100(Cr)



**Figure D24.** Effect of product co-feed on the CO oxidation turnover rate at (a) 393 K and (b) 473 K measured over MIL-100(Cr) with CO<sub>2</sub> or N<sub>2</sub> (8.7 kPa N<sub>2</sub>O, 13.2 kPa CO).



**Figure D25.** (a) Molar flow rate of different product and reactant isotopologues when (a) <sup>15</sup>N<sub>2</sub> (2.8 kPa) or (b) 2.8 kPa <sup>13</sup>CO<sub>2</sub> are co-fed during reaction (473 K, 8.7 kPa <sup>14</sup>N<sub>2</sub>O, 13.2 kPa <sup>12</sup>CO).

Condition	CO <sub>2</sub> Formation Rate / x10 <sup>-4</sup> mol (mol Cr) <sup>2+</sup> s <sup>-1</sup>	N2 Formation Rate / x10 <sup>-4</sup> mol (mol Cr) <sup>2+</sup> s <sup>-1</sup>
3.8 kPa O <sub>2</sub>		
3.8 kPa O <sub>2</sub> + 32 kPa CO	1.70	
3.8 kPa O <sub>2</sub> + 32 kPa CO + 2.9 kPa N <sub>2</sub> O	1.72	0.21
$\begin{array}{c} 32 \text{ kPa CO} + 2.9 \text{ kPa} \\ \text{N}_2\text{O} \end{array}$	4.07	3.95

**Table D.7.** Comparison of the CO<sub>2</sub> formation rate under various reaction conditions over MIL-100(Cr) with O<sub>2</sub>, CO, and N<sub>2</sub>O demonstrating that O<sub>2</sub> co-feed inhibits the oxidation of CO with N<sub>2</sub>O, however, results in CO<sub>2</sub> formation in the presence of CO solely.

### **D2.11. CO Kinetic Isotope Effect Calculations**

In this section, an estimation of the kinetic isotope effect is provided following the methodology described by Sullivan and Bhan,<sup>419</sup> for the CO isotopic exchange reaction and oxidation to CO<sub>2</sub> given by the following expressions

$$M^{-n}O + C^{m}O \leftrightarrow M^{-m}O + C^{n}O, \qquad (D.161)$$

and 
$$M-O+CO \rightarrow M + CO_2$$
, (D.162)

respectively, where *n* and *m* correspond to the mass number of the oxygen isotope. Using a simple approximation of the kinetic isotope effect associated with the replacement of  $C^{16}O$  with  $C^{18}O$ , we can describe the reaction rate constant for Eq D.161 or D.162 as

$$k = \frac{k_b T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$$
(D.163)

where k is the rate constant,  $k_b$  is Boltzmann's constant, T is temperature, h is Planck's constant, R is the ideal gas constant, and  $\Delta G^{\ddagger}$  is the difference in free energy between the initial and transition state. Here we make the assumption that  $\Delta G^{\ddagger}$  can be entirely reflected by the vibration frequency of the C-O bond being severed or formed. Furthermore, the kinetic isotope effect (KIE) can be defined as the ratio between the rate constant associated with C-<sup>16</sup>O and C-<sup>18</sup>O bond scission/formation as follows

$$KIE = \frac{k_{C^{16}O}}{k_{C^{18}O}} = e^{\frac{\Delta\Delta G^{\ddagger}}{RT}},$$
 (D.164)

$$\Delta \Delta G^{\ddagger} = \Delta G_{C^{18}O}^{\ddagger} - \Delta G_{C^{16}O}^{\ddagger}, \qquad (D.165)$$

and 
$$\Delta\Delta G^{\ddagger} = \frac{1}{2}h[\nu(C^{-16}O) - \nu(C^{-18}O)]$$
 (D.166)

where  $k_{C^{16}O}$  is the reaction rate constant for C-<sup>16</sup>O bond scission/formation,  $k_{C^{18}O}$  is the reaction rate constant for C-<sup>18</sup>O bond scission/formation, and  $\Delta\Delta G^{\ddagger}$  represents the difference between  $\Delta\Delta G^{\ddagger}$  for C-<sup>18</sup>O and C<sup>16</sup>-O bond scission/formation as defined in Eq

D.165. Moreover,  $\Delta\Delta G^{\ddagger}$  can be estimated as the difference in energy of the C-<sup>16</sup>O and C-<sup>18</sup>O bond, Eq D.166, where  $\nu(C-^{16}O)$  and  $\nu(C-^{18}O)$  are the vibrational frequency of the C-<sup>16</sup>O and C-<sup>18</sup>O bonds, respectively. For C-O bond forming steps, this estimate assumes that the transition state represents a completely formed C-O bond whereas, for C-O bond breaking steps, it is assumed that the transition state represents a completely severed C-O bond. Thus, the calculated KIE will be an upper limit, as the character of the C-O bond in the transition state could fall between completely severed or formed and would reduce the magnitude of  $\Delta\Delta G^{\ddagger}$  and subsequently the KIE.

Typical values of  $\nu(C^{-16}O)$  for free CO are near (2143 cm<sup>-1</sup>)(3x10<sup>8</sup> m s<sup>-1</sup>).<sup>420,421</sup> Estimates for the C-O bond vibrational frequencies ( $\nu(C - O)$ ) can be estimated from a simple harmonic oscillator model as follows

$$\nu(C-0) = \frac{1}{2\pi} \sqrt{\frac{k_s}{\mu_{C-0}}}$$
(D.167)

where  $k_s$  is the spring constant, and  $\mu_{C-O}$  is the reduced mass of the C-O bond and can be calculated by the following

$$\mu_{C-0} = \frac{m_C m_0}{m_C - m_0} \tag{D.168}$$

in which  $m_c$  and  $m_o$  and the molar mass of carbon and oxygen, respectively. Using equations D.167 and D.168, the vibrational frequency of  $\nu(C^{-18}O)$  can be estimated assuming that k<sub>s</sub> is constant for both the C-<sup>18</sup>O and C-<sup>16</sup>O bonds. Rewriting the ratio of  $\nu(C^{-18}O)$  and  $\nu(C^{-16}O)$  thus provides the following equation as

$$\frac{\nu(C^{-18}O)}{\nu(C^{-16}O)} = \frac{\frac{1}{2\pi}\sqrt{\frac{k_s}{\mu_{C^{-18}O}}}}{\frac{1}{2\pi}\sqrt{\frac{k_s}{\mu_{C^{-16}O}}}} = \sqrt{\frac{\mu_{C^{-16}O}}{\mu_{C^{-18}O}}}$$
(D.169)

where  $\mu_{C^{-16}O}$  and  $\mu_{C^{-18}O}$  are the reduced masses for the C-<sup>16</sup>O and C-<sup>18</sup>O bonds, respectively. Lastly the theoretical maximum KIE for C-<sup>16</sup>O versus C-<sup>18</sup>O bond scission/formation at 473 K (reaction temperature used for C<sup>18</sup>O oxidation measurement) can be calculated by combining equation D.164, D.166, D.168, and D.169 as follows:

$$KIE = e^{\frac{h[\nu(C^{-16}O) - \nu(C^{-18}O)]N_A}{2RT}},$$
 (D.170)

$$KIE = e^{\frac{h*\nu(C^{-16}O)*\left(1 - \sqrt{\frac{\mu_{C^{-16}O}}{\mu_{C^{-18}O}}}\right)}{2^{k_bT}}},$$
(D.171)

$$KIE = e^{\frac{(6.626 \times 10^{-34} J \cdot s^{-1})(3.0 \times 10^8 m \cdot s^{-1})(214300 m^{-1})\left(1 - \sqrt{\frac{6.9}{7.2}}\right)}{2(1.38 \times 10^{-23} J \cdot K^{-1})(473 K)}},$$
 (D.172)

and KIE = 1.08.

Furthermore, a KIE of 1.08 can be provided as an upper bound for C-O bond scission or formation reactions at 473 K between  $C^{16}O$  and  $C^{18}O$  isotopologues. Thus, the KIE can be considered sufficiently small in order to neglect its influence on rate constants for CO oxygen isotopic exchange reactions (Eq D.161) and oxidation reactions (Eq D.162) with surface metal-oxo species formed by N<sub>2</sub>O decomposition.

### **D2.12.** Estimating Elementary Rate Constants from C<sup>18</sup>O Oxidation Experiments

The oxidation of C<sup>18</sup>O with N<sub>2</sub><sup>16</sup>O over MIL-100(Fe) and MIL-100(Cr) leads to the formation of three CO<sub>2</sub> isotopologues (C<sup>18</sup>O<sup>16</sup>O, C<sup>18</sup>O<sub>2</sub>, and C<sup>16</sup>O<sub>2</sub>), as well as a net formation rate of C<sup>16</sup>O, which can be interpreted by CO undergoing oxygen isotopic exchange reactions with oxidized surface intermediates (M-O) formed by the decomposition of N<sub>2</sub>O. The proposed elementary steps leading to the formation of each CO<sub>2</sub> isotopologue is given in Figure D26, where Step 6 represents the isotopic mixing reaction in which CO can exchange its oxygen with M-O species. For the replacement of

 $C^{16}O$  with  $C^{18}O$ , the estimated theoretical maximum kinetic isotope effect which could be measured is 1.08 (see Section D2.11), furthermore, we neglect kinetic isotope effects associated with C-O bond breaking/formation steps and assume negligible influence of  $O^{18}/O^{16}$  exchange on M-O bond breaking/formation steps. Furthermore, with the regards to the reaction scheme in Figure D26, it has been assumed that CO adsorption/desorption steps (Step 3, 8, 9 and 11) and CO<sub>2</sub> formation steps (Steps 4, 7, 10, and 12) are controlled by the same set of rate constants ( $k_3/k_{-3}$  and  $k_4$ ) regardless of the identity of CO or CO<sub>2</sub> isotopologue involved. The desorption of CO<sub>2</sub>, and regeneration of the active center (M), has also been represented as a single step (Step 5) assuming that the identity of the isotopologue has negligible influence on the sorption of CO<sub>2</sub>.

$$1 \qquad N_2^{16}O_{(g)} + M \qquad \longleftrightarrow \qquad N_2^{16}O \cdots M \qquad K_1$$

$$2 \qquad N_2^{16}O \cdots M \qquad \longrightarrow \qquad N_{2(g)} + M^{-16}O \qquad k_2$$

$$3 \qquad M^{-16}O + C^{18}O_{(g)} \qquad \longleftrightarrow \qquad M^{-16}O \cdots C^{18}O \qquad k_3, k_3$$

$$4 \qquad M^{-16}O \cdots C^{18}O \qquad \longrightarrow \qquad M^{-16}O^{-16}O^{18}O \qquad k_4$$

$$5 \qquad M^{-16}O \cdots C^{18}O \qquad \bigoplus \qquad M^{-18}O \cdots C^{16}O \qquad k_5$$

$$6 \qquad M^{-16}O \cdots C^{18}O \qquad \bigoplus \qquad M^{-18}O \cdots C^{16}O \qquad k_4$$

$$8 \qquad M^{-18}O \cdots C^{16}O \qquad \bigoplus \qquad M^{-18}O \cdots C^{16}O \qquad k_4$$

$$8 \qquad M^{-18}O \cdots C^{16}O \qquad \bigoplus \qquad M^{-18}O \cdots C^{18}O \qquad k_4$$

$$9 \qquad M^{-18}O + C^{18}O_{(g)} \qquad \bigoplus \qquad M^{-18}O \cdots C^{18}O \qquad k_3, k_3$$

$$10 \qquad M^{-18}O \cdots C^{18}O \qquad \bigoplus \qquad M^{-18}O \cdots C^{18}O \qquad k_4$$

$$11 \qquad M^{-16}O + C^{16}O_{(g)} \qquad \bigoplus \qquad M^{-16}O \cdots C^{16}O \qquad k_3, k_3$$

$$12 \qquad M^{-16}O \cdots C^{16}O \qquad \bigoplus \qquad M^{-16}O \cdots C^{16}O \qquad k_4$$



Without isotopic tracing, the kinetics obtained during oxidation of CO with  $N_2O$  at steady-state over MIL-100 can only provide estimation of the lumped rate constants (k' and k''), described in detail in Section 5.3.3. and given by the following set of equations:

$$r = \frac{k_2 K_1 [N_2 O]}{1 + \frac{k_2 K_1 [N_2 O]}{\overline{k_3} [CO] \left(1 - \frac{\overline{k_3}}{\overline{k_3} + k_4}\right)}},$$
(D.173)

$$k' = k_2 K_1$$
, (D.174)

and 
$$k'' = \overrightarrow{k_3} \left( 1 - \frac{\overleftarrow{k_3}}{\overleftarrow{k_3} + k_4} \right).$$
 (D.175)

The formation of various CO<sub>2</sub> isotopologues and C<sup>16</sup>O during the reaction of C<sup>18</sup>O with N<sub>2</sub><sup>16</sup>O, however, provides an additional level of insight into the catalytic sequence of steps as four distinct product formation rates can be identified which have been presumed to be related to the same set of elementary kinetic parameters (k<sub>3</sub>, k<sub>-3</sub>, k<sub>4</sub>, and k<sub>6</sub>  $\approx$  k<sub>-6</sub>). Furthermore, we propose that the identity of each rate constant described in Figure D26 can be estimated through the methods described, hereafter.

First, assuming that Step 2 ( $N_2O$  decomposition) is irreversible and Step 1 is quasi equilibrated, we can describe the rate of  $N_2/CO_2$  formation as equal to the forward rate of Step 2, as follows

$$r_{N_2} = r_{CO_2} = K_1 \overrightarrow{k_2} [N_2 O] [M]$$
 (D.176)

where [M] is the concentration of vacant active sites and the concentration of  $N_2O$  adsorbed to the active site, [M…N<sub>2</sub>O], is represented by

$$[\mathbf{M}\cdots\mathbf{N}_{2}\mathbf{O}] = K_{1}[\mathbf{N}_{2}\mathbf{O}][\mathbf{M}]. \tag{D.177}$$

The  $N_2/CO_2$  formation rate can also be described as equal to sum of the forward rates for Step 4, 7, 10 and 12, or simply as

$$r_{N_2} = r_{CO_2} = \overline{k_4} [\text{M-O}\cdots\text{CO}]$$
(D.178)

where [M-O···CO] represents the concentration of all isotopic variations of CO adsorbed to the M-O intermediates at steady state, given by the following equation

$$[M-O\cdots CO] = [M-{}^{16}O\cdots C^{18}O] + [M-{}^{18}O\cdots C^{16}O] + [M-{}^{18}O\cdots C^{18}O] + [M-{}^{16}O\cdots C^{16}O].$$
(D.179)

At steady-state, the sum of the net rate of all CO adsorption and desorption steps (Steps 3, 8, 9, and 11) should also be equal to rate of  $N_2/CO_2$  formation, given as

$$r_{N_2} = r_{CO_2} = \overrightarrow{k_3}[\text{M-O}][\text{CO}] - \overleftarrow{k_3}[\text{M-O}\cdots\text{CO}]$$
(D.180)

where, here, [M-O] corresponds to the concentration of all isotopic variations of M-O intermediates, represented as follows

$$[M-O] = [M-{}^{16}O] + [M-{}^{18}O].$$
(D.181)

Applying the pseudo-steady state hypothesis (PSSH) to the concentration of all M-O···CO and M-O intermediates also provides the following two equations, which are equivalent to that derived in Section D2.5, given by

$$[M-O] = \frac{\overline{k_2} K_1[N_2 O]}{\overline{k_3}[CO] \left(1 - \frac{\overline{k_3}}{\overline{k_3} + \overline{k_4}}\right)} [M], \qquad (D.182)$$

and 
$$[M-O\cdots CO] = \frac{\overline{k_2} \kappa_1 [N_2 O]}{\overline{k_4}} [M]$$
 (D.183)

with the balance of all sites, being equal to unity at steady-state, given as

$$1 = [M] + [M \cdots N_2 O] + [M - O] + [M - O \cdots CO] + [M \cdots CO_2]$$
(D.184)

where  $[M \cdots CO_2]$  is the concentration of adsorbed CO<sub>2</sub>. However, under conditions tested over both MIL-100(Fe) and MIL-100(Cr), no rate-dependence on the partial pressure of CO<sub>2</sub> was observed (Figure 5.3c and Figure 5.19,Section 5), furthermore, this term is neglected, and the total site balance can be described as

$$1 = [M] + [M \cdots N_2 O] + [M - O] + [M - O \cdots CO].$$
(D.185)

The formation rate of each  $CO_2$  isotopologue can be further represented individually by the forward rates of Steps 4, 7, 10 and 12, given by the following equations:

$$r_{C^{18}O^{16}O} = k_4([M^{-16}O\cdots C^{18}O] + [M^{-18}O\cdots C^{16}O]),$$
 (D.186)

$$r_{C^{18}O_2} = k_4 [\text{M}^{-18}\text{O}^{\cdots}\text{C}^{18}\text{O}], \qquad (\text{D}.187)$$

and 
$$r_{C^{16}O_2} = k_4 [M^{-16}O \cdots C^{16}O]$$
 (D.188)

where  $C^{18}O^{16}O$  isotopologues can form through both Steps 4 and 7. The PSSH can also be applied to the concentration of both M-<sup>18</sup>O····C<sup>18</sup>O and M-<sup>16</sup>O····C<sup>16</sup>O intermediates to provide the following relationships

$$[M^{-18}O\cdots C^{18}O] = \frac{\overline{k_3} [M^{-18}O][C^{18}O]}{\overline{k_3} + k_4}, \qquad (D.189)$$

and 
$$[M^{-16}O\cdots C^{16}O] = \frac{\overrightarrow{k_3}[M^{-16}O][C^{16}O]}{\overleftarrow{k_3} + k_4}$$
 (D.190)

where  $[C^{18}O]$  and  $[C^{16}O]$  represent the partial pressure (in units of kPa) for  $C^{18}O$  and  $C^{16}O$ in the gas phase. Furthermore, combining equations D.187 – D.190, the formation rate of  $C^{16}O_2$  and  $C^{18}O_2$  can be rewritten as follows

$$r_{C^{18}O_2} = k_4 \frac{\overline{k_3} \left[ M^{-18}O \right] \left[ C^{18}O \right]}{\overline{k_3} + k_4}, \qquad (D.191)$$

and 
$$r_{C^{16}O_2} = k_4 \frac{\overline{k_3} [M^{-16}O][C^{16}O]}{\overline{k_3} + k_4}$$
 (D.192)

where, if we apply the PSSH to the concentration of the M-<sup>18</sup>O surface intermediates, it can be defined by the following equation

$$[M^{-18}O] = \frac{\overleftarrow{k_3}([M^{-18}O\cdots C^{18}O] + [M^{-18}O\cdots C^{16}O])}{\overrightarrow{k_3}[CO]}.$$
 (D.193)

The purity of the CO reactant is approximately 95 mol%  $C^{18}O$  and 5 mol%  $C^{16}O$ . Under the tested conditions, the total CO conversion is less than 1.5% and 10% over MIL-100(Cr)

and MIL-100(Fe), respectively, therefore it may be assumed that the total CO pressure is approximately constant throughout the catalyst bed. As the net  $C^{16}O$  formation rate is small (Table D8 and Table D9) in comparison to the feed rate of  $C^{18}O$  under all conditions, it may also be assumed that the  $C^{18}O$  concentration is approximately constant along the length of the catalyst bed. Although the concentration of  $C^{16}O$  is significantly smaller than that of  $C^{18}O$  in the reactant gas stream, the net formation rates of  $C^{16}O$  are less than 13% and 9% of the  $C^{16}O$  feed rate (Table D8 and Table D9) over MIL-100(Fe) and MIL-100(Cr), respectively, furthermore it is assumed that the  $C^{16}O$  partial pressure in the catalyst bed is approximately constant under the conditions tested.

**Table D8.** For MIL-100(Fe) during reaction CO (95% C<sup>18</sup>O, 5% C<sup>16</sup>O) and N<sub>2</sub><sup>16</sup>O under various conditions at 473 K, the rates of C<sup>18</sup>O/C<sup>16</sup>O fed to the reactor and the net formation rate of C<sup>16</sup>O measured at the reactor outlet. All rates are in units of mol (mol Fe<sup>2+</sup>) s<sup>-1</sup>.

Reaction Conditions	C <sup>18</sup> O Feed Rate	C <sup>16</sup> O Feed Rate	Net C <sup>16</sup> O Formation Rate
2.9 kPa N <sub>2</sub> O 2.5 kPa CO	4.72 x 10 <sup>-2</sup>	2.49 x 10 <sup>-3</sup>	2.20 x 10 <sup>-5</sup>
27.2 kPa N <sub>2</sub> O 3.2 kPa CO	4.72 x 10 <sup>-2</sup>	2.49 x 10 <sup>-3</sup>	1.17 x 10 <sup>-4</sup>
51.6 kPa N <sub>2</sub> O 3.1 kPa CO	4.72 x 10 <sup>-2</sup>	2.49 x 10 <sup>-3</sup>	3.35 x 10 <sup>-4</sup>

Reaction Conditions	C <sup>18</sup> O Feed Rate	C <sup>16</sup> O Feed Rate	Net C <sup>16</sup> O Formation Rate
2.9 kPa N <sub>2</sub> O 2.5 kPa CO	5.29 x 10 <sup>-3</sup>	2.78 x 10 <sup>-4</sup>	1.84 x 10 <sup>-5</sup>
1.5 kPa N <sub>2</sub> O 7.0 kPa CO	1.11 x 10 <sup>-2</sup>	5.83 x 10 <sup>-4</sup>	5.08 x 10 <sup>-5</sup>
1.5 kPa N <sub>2</sub> O 30.7 kPa CO	4.87 x 10 <sup>-2</sup>	2.56 x 10 <sup>-3</sup>	1.08 x 10 <sup>-4</sup>

**Table D9.** For MIL-100(Cr) during reaction CO (95% C<sup>18</sup>O, 5% C<sup>16</sup>O) and N<sub>2</sub><sup>16</sup>O under various conditions at 473 K, the rates of C<sup>18</sup>O/C<sup>16</sup>O fed to the reactor and the net formation rate of C<sup>16</sup>O measured. All rates are reported in units of mol (mol Cr<sup>2+</sup>) s<sup>-1</sup>.

The PSSH can also be applied to the concentration  $M^{-16}O\cdots C^{18}O$  and  $M^{-18}O\cdots C^{16}O$ reaction intermediates, as given by

$$[M^{-16}O\cdots C^{18}O] = \frac{\overrightarrow{k_3}[M^{-16}O][C^{18}O] + k_6[M^{-18}O\cdots C^{16}O]}{\overleftarrow{k_3} + k_4 + k_6},$$
(D.194)

and 
$$[M^{-18}O\cdots C^{16}O] = \frac{\overline{k_3}[M^{-18}O][C^{16}O] + k_6[M^{-16}O\cdots C^{18}O]}{\overline{k_3} + k_4 + k_6},$$
 (D.195)

respectively, where the concentration of both intermediates is dependent on the forward and reverse rates of the oxygen isotopic exchange reaction (Step 6) between CO and the oxidized intermediates (M-O), the rate constants of which can be written equivalently as  $k_6$  under the assumption of no significant kinetic isotope effect.

Lastly, a positive net formation rate of  $C^{16}O$  can be measured under the tested reaction conditions (Table D8 and Table D9) over MIL-100(Fe) and MIL-100(Cr). As described in the reaction scheme in Figure D26, the net  $C^{16}O$  formation rate can be estimated as follows

$$net r_{C^{16}O} = \overleftarrow{k_3}([M^{-18}O\cdots C^{16}O] + [M^{-16}O\cdots C^{16}O]) - \overrightarrow{k_3}[C^{16}O][M^{-}O].$$
(D.196)

Using the equations provided in this section, Table D10 describes for each steady-state surface intermediate, species formation rate, and rate constant, the corresponding equation

used to solve for that parameter or whether it was regressed from the experimental data. Specifically, for each reaction condition tested over MIL-100(Fe) or MIL-100(Cr), we have obtained a measured value for the N<sub>2</sub>, total CO<sub>2</sub>,  $C^{18}O^{16}O$ ,  $C^{18}O_2$ ,  $C^{16}O_2$ , and net  $C^{16}O$  formation rates from which we can compare the estimated rates and solve for the suite of rate constants (K<sub>1</sub>, k<sub>2</sub>, k<sub>3</sub>, k<sub>-3</sub>, and k<sub>4</sub>) and two surface intermediate concentrations ([M-<sup>18</sup>O] and [M-<sup>16</sup>O···C<sup>18</sup>O]) that minimize the sum of the squared residuals (SSR) between the measured and estimated formation rates given by the following expression

$$\sum_{i} w_{i} * (r_{i,measured} - r_{i,estimated})^{2}$$
(D.197)

where  $w_i$  is a weighting factor equal to the inverse of the measured rate for species, *i*, at a given reaction condition.

As a first guess for fitting to the experimental data, the lumped rate constants k' and k'' (Equations D.174 and D.175) are set equivalent to values regressed from steady-state oxidation measurements. After solving for the minimum SSR at this condition, the constraint was removed and the minimum SSR was resolved, providing the values for each rate constant in Table D11. Table D12 and Table D13 describe for MIL-100(Fe) and MIL-100(Cr), respectively, the values of the estimated formation rates describe the experimentally determined values well within an error of approximately 20%. Moreover, the rate constant estimated through this method can be used to accurately describe CO oxidation turnover rates at steady-state over all of the experimental conditions tested in this report (Figure D28).

No.	<b>Estimated Parameter</b>	Equation
1	[M]	$1 = [M] + [M \cdots N_2 O] + [M - O] + [M - O \cdots CO] + [M \cdots CO_2]$
2	$[M \cdots N_2 O]$	$[\mathbf{M}\cdots\mathbf{N}_{2}\mathbf{O}]=K_{1}[\mathbf{N}_{2}\mathbf{O}][\mathbf{M}]$
3	N <sub>2</sub> formation rate	$r_{N_2} = r_{CO_2} = K_1 \overrightarrow{k_2} [N_2 O][M]$
4	total CO <sub>2</sub> formation rate	$r_{CO_2} = \overrightarrow{k_3}[\text{M-O}][\text{CO}] - \overleftarrow{k_3}[\text{M-O} \cdots \text{CO}]$
5	C <sup>18</sup> O <sup>16</sup> O formation rate	$r_{C^{18}O^{16}O} = k_4([M^{-16}O\cdots C^{18}O] + [M^{-18}O\cdots C^{16}O])$
6	C <sup>18</sup> O <sub>2</sub> formation rate	$r_{C^{18}O_2} = k_4 \frac{\overrightarrow{k_3} [M^{-18}O][C^{18}O]}{\overleftarrow{k_3} + k_4}$
7	C <sup>16</sup> O <sub>2</sub> formation rate	$r_{C^{16}O_2} = k_4 \frac{\overrightarrow{k_3} [M - {}^{16}O][C^{16}O]}{\overleftarrow{k_3} + k_4}$
8	net C <sup>16</sup> O formation rate	$net \ r_{C^{16}O} = \overleftarrow{k_3}([M^{-18}O \cdots C^{16}O] + [M^{-16}O \cdots C^{16}O]) - \overrightarrow{k_3}[C^{16}O][M^{-}O]$
9	[M-O]	$[M-O] = \frac{\overrightarrow{k_2}K_1[N_2O]}{\overrightarrow{k_3}[CO]\left(1 - \frac{\overleftarrow{k_3}}{\overrightarrow{k_3} + \overrightarrow{k_4}}\right)} [M]$
10	[M-O···CO]	$[M-O\cdots CO] = \frac{\overrightarrow{k_2}K_1[N_2O]}{\overrightarrow{k_4}}[M]$
11	[M- <sup>16</sup> O]	$[M-O] = [M^{-16}O] + [M^{-18}O]$
12	[M- <sup>18</sup> O]	$[M^{-18}O] = \frac{\overleftarrow{k_3}([M^{-18}O\cdots C^{18}O] + [M^{-18}O\cdots C^{16}O])}{\overrightarrow{k_3}[CO]}$
13	$[M-^{16}O\cdots C^{18}O]$	$[M^{-16}O\cdots C^{18}O] = \frac{\overrightarrow{k_3}[M^{-16}O][C^{18}O] + k_6[M^{-18}O\cdots C^{16}O]}{\overleftarrow{k_3} + k_4 + k_6}$
14	$[M-^{18}O\cdots C^{16}O]$	$[M-O\cdots CO] = [M-{}^{16}O\cdots C^{18}O] + [M-{}^{18}O\cdots C^{16}O] + [M-{}^{18}O\cdots C^{18}O] + [M-{}^{16}O\cdots C^{16}O]$
15	$[\mathrm{M}\text{-}^{18}\mathrm{O}\text{\cdots}\mathrm{C}^{18}\mathrm{O}]$	$r_{C^{18}O_2} = k_4 [\text{M}^{-18}\text{O}\cdots\text{C}^{18}\text{O}]$

**Table D10.** For each surface intermediate and rate constant estimated, indication of the equation used to solve for that parameter or if it was regressed from the experimental data.

Table D10 (continued)

16	$[M-^{16}O\cdots C^{16}O]$	$r_{C^{16}O_2} = k_4 [\text{M}^{-16}\text{O}^{-16}\text{O}]$
17	$K_1$	regressed
18	k2	regressed
19	k <sub>3</sub>	regressed
20	k-3	regressed
21	k4	regressed
22	k <sub>6</sub>	$[M^{-18}O\cdots C^{16}O] = \frac{\overrightarrow{k_3}[M^{-18}O][C^{16}O] + k_6[M^{-16}O\cdots C^{18}O]}{\overleftarrow{k_3} + k_4 + k_6}$

**Table D11.** Estimated parameters describing CO oxidation and oxygen exchange reaction determined from experiments with C<sup>18</sup>O and N<sub>2</sub><sup>16</sup>O at 473 K. (MIL-100(Fe): 2.9 – 51.6 kPa N<sub>2</sub>O, 2.5 – 3.1 kPa CO, MIL-100(Cr): 1.5 – 2.9 kPa N<sub>2</sub>O, 2.5 – 30.7 kPa CO).

Parameter	MIL-100(Fe)	MIL-100(Cr)
$K_1$ / kPa <sup>-1</sup>	1.20 x 10 <sup>-4</sup>	1.99 x 10 <sup>-2</sup>
$k_2 / s^{-1}$	9.23 x 10 <sup>-1</sup>	1.79 x 10 <sup>-2</sup>
$k_2 K_1 / (\text{kPa} \cdot \text{s})^{-1}$	1.10 x 10 <sup>-4</sup>	3.56 x 10 <sup>-4</sup>
$\overrightarrow{k_3}$ / (kPa·s) <sup>-1</sup>	1.30 x 10 <sup>-2</sup>	7.56 x 10 <sup>-5</sup>
$\overleftarrow{k_3}$ / s <sup>-1</sup>	4.93 x 10 <sup>-2</sup>	2.25 x 10 <sup>-2</sup>
$k_4$ / s <sup>-1</sup>	8.90 x 10 <sup>-2</sup>	1.45 x 10 <sup>-2</sup>
$k_6 / s^{-1}$	6.26 x 10 <sup>-2</sup>	1.27 x 10 <sup>-2</sup>

Species	N2 <sup>16</sup> O / kPa	C <sup>18</sup> O / kPa	Measured Rate / mol (mol Fe <sup>2+</sup> ) <sup>-1</sup> s <sup>-1</sup>	Estimated Rate / mol (mol Fe <sup>2+</sup> ) <sup>-1</sup> s <sup>-1</sup>	% Error
$CO_2/N_2$	2.9	2.5	3.15 x 10 <sup>-4</sup>	3.15 x 10 <sup>-4</sup>	0.18%
C <sup>18</sup> O <sup>16</sup> O	2.9	2.5	2.69 x 10 <sup>-4</sup>	2.68 x 10 <sup>-4</sup>	0.49%
$C^{18}O_2$	2.9	2.5	2.98 x 10 <sup>-5</sup>	3.31 x 10 <sup>-5</sup>	10.95%
$C^{16}O_2$	2.9	2.5	1.54 x 10 <sup>-5</sup>	1.40 x 10 <sup>-5</sup>	8.99%
net C <sup>16</sup> O	2.9	2.5	2.20 x 10 <sup>-5</sup>	1.91 x 10 <sup>-5</sup>	13.21%
CO <sub>2</sub> /N <sub>2</sub>	27.1	3.1	2.61 x 10 <sup>-3</sup>	2.61 x 10 <sup>-3</sup>	0.04%
C <sup>18</sup> O <sup>16</sup> O	27.1	3.1	2.23 x 10 <sup>-3</sup>	2.22 x 10 <sup>-3</sup>	0.60%
$C^{18}O_2$	27.1	3.1	2.54 x 10 <sup>-4</sup>	2.74 x 10 <sup>-4</sup>	8.09%
$C^{16}O_2$	27.1	3.1	1.22 x 10 <sup>-4</sup>	1.16 x 10 <sup>-4</sup>	5.01%
net C <sup>16</sup> O	27.1	3.1	1.67 x 10 <sup>-4</sup>	1.58 x 10 <sup>-4</sup>	5.53%
CO <sub>2</sub> /N <sub>2</sub>	51.6	3.1	4.40 x 10 <sup>-3</sup>	4.42 x 10 <sup>-3</sup>	0.41%
C <sup>18</sup> O <sup>16</sup> O	51.6	3.1	3.71 x 10 <sup>-3</sup>	3.76 x 10 <sup>-3</sup>	1.29%
$C^{18}O_2$	51.6	3.1	5.13 x 10 <sup>-4</sup>	4.65 x 10 <sup>-4</sup>	9.51%
$C^{16}O_2$	51.6	3.1	1.78 x 10 <sup>-4</sup>	1.97 x 10 <sup>-4</sup>	10.69%
net C <sup>16</sup> O	51.6	3.1	3.35 x 10 <sup>-4</sup>	2.68 x 10 <sup>-4</sup>	20.07%

**Table D12.** All product formation rates over MIL-100(Fe) at 473 K under three different N<sub>2</sub>O/CO ratios, the corresponding rate estimated from the procedure described in this section, and the percent error between the measured and estimated rate.

Species	N2 <sup>16</sup> O / kPa	C <sup>18</sup> O / kPa	Measured Rate / mol (mol Fe <sup>2+</sup> ) <sup>-1</sup> s <sup>-1</sup>	Estimated Rate / mol (mol Fe <sup>2+</sup> ) <sup>-1</sup> s <sup>-1</sup>	% Error
$CO_2/N_2$	2.9	2.5	6.88 x 10 <sup>-5</sup>	6.85 x 10 <sup>-5</sup>	0.33%
C <sup>18</sup> O <sup>16</sup> O	2.9	2.5	5.01 x 10 <sup>-5</sup>	5.10 x 10 <sup>-5</sup>	1.08%
$C^{18}O_2$	2.9	2.5	1.58 x 10 <sup>-5</sup>	1.48 x 10 <sup>-5</sup>	6.06%
$C^{16}O_2$	2.9	2.5	2.82 x 10 <sup>-6</sup>	2.65 x 10 <sup>-6</sup>	6.18%
net C <sup>16</sup> O	2.9	2.5	1.34 x 10 <sup>-5</sup>	1.22 x 10 <sup>-5</sup>	8.79%
$CO_2/N_2$	1.5	7.0	1.50 x 10 <sup>-4</sup>	1.46 x 10 <sup>-4</sup>	2.61%
C <sup>18</sup> O <sup>16</sup> O	1.5	7.0	1.15 x 10 <sup>-4</sup>	1.09 x 10 <sup>-4</sup>	5.68%
$C^{18}O_2$	1.5	7.0	2.86 x 10 <sup>-5</sup>	3.17 x 10 <sup>-5</sup>	10.59%
$C^{16}O_2$	1.5	7.0	6.02 x 10 <sup>-6</sup>	5.64 x 10 <sup>-6</sup>	6.30%
net C <sup>16</sup> O	1.5	7.0	2.38 x 10 <sup>-5</sup>	2.60 x 10 <sup>-5</sup>	9.13%
$CO_2/N_2$	1.5	30.7	3.18 x 10 <sup>-4</sup>	3.23 x 10 <sup>-4</sup>	1.32%
C <sup>18</sup> O <sup>16</sup> O	1.5	30.7	2.39 x 10 <sup>-4</sup>	2.40 x 10 <sup>-4</sup>	0.76%
$C^{18}O_2$	1.5	30.7	6.60 x 10 <sup>-5</sup>	6.99 x 10 <sup>-5</sup>	5.88%
$C^{16}O_2$	1.5	30.7	1.39 x 10 <sup>-5</sup>	1.25 x 10 <sup>-5</sup>	10.54%
net C <sup>16</sup> O	1.5	30.7	5.08 x 10 <sup>-5</sup>	5.74 x 10 <sup>-5</sup>	12.96%

**Table D13.** List of all product formation rates over MIL-100(Cr) at 473 K under three different<br/> $N_2O/CO$  ratios, the corresponding rate estimated from the procedure described in this<br/>section, and the percent error between the measured and estimated rate.



**Figure D27.** Parity plot comparing the CO<sub>2</sub>/N<sub>2</sub>, C<sup>18</sup>O<sup>16</sup>O, C<sup>18</sup>O<sub>2</sub>, C<sup>16</sup>O<sub>2</sub>, and net C<sup>16</sup>O formation rates measured over (a) MIL-100(Fe) and (b) MIL-100(Cr) at 473 K to the estimated rate for each reaction condition tested (P<sub>N2O</sub>, P<sub>CO</sub>) / kPa.



Figure D28. Comparison of the oxidation turnover rate measured at steady state over (a) MIL-100(Fe) and (b) MIL-100(Cr) to the rate estimated from the rate constants determined from the oxidation of C<sup>18</sup>O with N<sub>2</sub><sup>16</sup>O, described in Table D11.



**Figure 5.25.** Comparison of the oxidation turnover rate measured at steady state over MIL-100(Fe) (473 K, 1.7-62 kPa N<sub>2</sub>O, 1.5 - 5.0 kPa CO) to the rate estimated for a given value of  $k_2K_1$  (k' = 1.10 x 10<sup>-4</sup> (kPa-s)<sup>-1</sup>), however, changing the relative magnitude of K<sub>1</sub> and  $k_2$ , as indicated.

# E. Supporting Information for Section 6

### **E1. Experimental Methods**

### **E2.** Results and Discussion

### **E2.1.** Coordinated Alcohol Exchange Results

The effect of exchanging coordinated water ligands with various alcohols (methanol, ethanol, and isopropanol) was evaluated in the context of CO oxidation with N<sub>2</sub>O over MIL-100(Fe). Details of the procedure for alcohol exchange and quantification are provided in Section 6.2.5. Table E1 summarizes the results for exchanging CH<sub>3</sub>OH, where the density of Fe<sup>2+</sup> open-metal sites was either enumerated through titration with NO or by quantification of the amount of CH<sub>3</sub>OD evolved when the sample was exposed to D<sub>2</sub>O after treatment (Figure E1) using calibration data for CH<sub>3</sub>OD estimated in previous reports.<sup>109,112</sup> As shown, results of the methanol exchange provide nearly reproducible Fe<sup>2+</sup> open-metal site densities, coordinated CH<sub>3</sub>OH to Fe<sub>3</sub>O node molar ratios, and oxidation turnover rates across two independent experiments. Quantification of the Fe<sup>2+</sup> open-metal site density and coordinated R-OH to node ratio for all three alcohols (methanol, ethanol, and isopropanol) is provided in Table E2, showing similar alcohol coverages can be produced through treatment under the same conditions.

**Table E1.** Results of exchanging coordinated water/hydroxide molecules with methanol/<br/>methoxide molecules where the  $Fe^{2+}$  site density is estimated from NO titration (0.5<br/>kPa) or by D<sub>2</sub>O adsorption (1.5 kPa), as indicated. (14.6 kPa N<sub>2</sub>O, 1.5 kPa CO, 423 K).

Trial	Fe <sup>2+</sup> open-metal site density / mol Fe <sup>2+</sup> (mol Fe) <sup>-1</sup>	mol CH3OH (mol Fe3O) <sup>-1</sup>	Oxidation Rate / mol (mol Fe <sup>2+</sup> ) <sup>-1</sup> s <sup>-1</sup>
1	0.19 (NO)	0.53	1.0 x 10 <sup>-4</sup>
2	0.19 (D <sub>2</sub> O) / 0.18 (NO)	0.54	1.1 x 10 <sup>-4</sup>



- Figure E1. Molar flow rate of  $CH_3OH$ ,  $CH_3OD$ , and  $D_2O$  measured at the reactor outlet when  $D_2O$  (1.5 kPa, 423 K) is introduced to MIL-100(Fe) at t = 0 s following methanol treatment.
- **Table E2.** For the three different coordinated alcohols evaluated, the  $Fe^{2+}$  open-metal site density remaining after treatment (estimated from NO titration, 0.5 kPa, 423 K) and the corresponding molar ratio of coordinated alcohol  $Fe_3O$  nodes.

Alcohol	Fe <sup>2+</sup> open-metal site density / mol Fe <sup>2+</sup> (mol Fe) <sup>-1</sup>	mol R-OH (mol Fe3O) <sup>-1</sup>
Methanol	0.18	0.54
Ethanol	0.11	0.48
Isopropanol	0.09	0.51
### E2.2. N<sub>2</sub>O Reaction Orders with Activation Temperature



Figure E2. CO turnover rates (per available  $Fe^{2+}$  active site) as a function of N<sub>2</sub>O partial pressure for MIL-100(Fe) thermally activated at 423 or 523 K under He flow for 12 hours, prior to reaction (CO: 1.5 kPa).

### E2.3. Infrared Spectroscopy Analysis - NO Adsorption under H<sub>2</sub>O Co-feed



**Figure E3.** For MIL-100(Fe) activated at 523 K, the (a) v(NO) portion of the IR spectrum under NO flow (0.5 kPa) and upon introduction of 2  $\mu$ L injections of H<sub>2</sub>O at 423 K. (b) Area of the v(NO-Fe<sup>2+</sup>) band for each spectrum.



**E2.4. NO Temperature-Programmed Desorption Results** 

**Figure E4.** Temperature-programmed desorption of NO under He flow (65 mL min<sup>-1</sup>) following in-situ titration purging during CO oxidation (0.5 kPa NO, 14.6 kPa N<sub>2</sub>O, 1.5 kPa CO) for MIL-100(Fe) catalyst samples thermally treated at (a) 523, (b) 498, (c) 473, (d) 448 , and (e) 423 K.

E2.5. MIL-100(Fe) H<sub>2</sub>O Co-Feed and Titration Results



Figure E5. (a) H<sub>2</sub>O breakthrough adsorption curve when co-fed during the oxidation of CO and N<sub>2</sub>O (0.35 kPa H<sub>2</sub>O). (b) Oxidation rate with time. (c) Introduction of NO (0.5 kPa) with N<sub>2</sub> after reaction to determine the Fe<sup>2+</sup> site density. (423 K, 14.6 kPa N<sub>2</sub>O, 1.5 kPa CO)

### E2.6. Transient In-Situ Titration with H<sub>2</sub>O



Figure E6. Breakthrough adsorption curve for H<sub>2</sub>O in MIL-100(Cr) during the oxidation of CO with N<sub>2</sub>O under two different N<sub>2</sub>O partial pressures (2.9 or 9.0 kPa). Conditions: 31.9 kPa CO, 423 K, sample activated at 523 K under vacuum prior to reaction.



**Figure E7.** Breakthrough adsorption curve for H<sub>2</sub>O in MIL-100(Fe) during the oxidation of CO with N<sub>2</sub>O under two different N<sub>2</sub>O partial pressures (14.7 or 30.5 kPa). Conditions: 1.5 kPa CO, 423 K, sample activated at 523 K under He flow prior to reaction.



**Figure E8.** (a) Normalized oxidation rate over MIL-100(Fe) (a) as a function of time when  $H_2O$  (3.77 x  $10^{-4}$  mol (mol Cr)<sup>-1</sup> s<sup>-1</sup>) is introduced at t = 0 minutes and (b) as a function of the total quantity of  $H_2O$  adsorbed. (2.9 or 9.0 kPa N<sub>2</sub>O, 31.9 kPa CO, 423 K)

# F. Supporting Information for Section 7

## F1. Material Characterization

#### F1.1. MIL-100(Cr) Characterization Results



**Figure F1.** (a) X-ray diffraction pattern, (b) N<sub>2</sub> physisorption (77 K) isotherm, and (c) TGA profile for MIL-100(Cr).

### F1.2. MIL-100(Fe) Characterization Results



**Figure F2.** (a) X-ray diffraction pattern, (b) N<sub>2</sub> physisorption (77 K) isotherm, and (c) TGA profile for MIL-100(Fe).

F1.3. MIL-101(Cr) Characterization Results



**Figure F3.** (a) X-ray diffraction pattern, (b) N<sub>2</sub> physisorption (77 K) isotherm, and (c) TGA profile for MIL-101(Cr).

## F1.4. Cr-oxo Characterization Results



Figure F4. (a) TGA profile and (b) FTIR spectrum of Cr-oxo coordination complex.

### F2. Results and Discussion

### F2.1. Thermodynamic Equilibrium Calculations

The equilibrium constant for the reaction of benzaldehyde and methanol to form benzaldehyde dimethyl acetal (BDA) and water was estimated using condensed phase thermodynamic property values obtained from the NIST Chemistry WebBook (Table F1).<sup>256</sup> Furthermore, this estimation is used to calculate the equilibrium conversion of benzaldehyde expected for the reaction conditions tested in this study (Figure F5).

 

 Table F1. Condensed Phase Thermodynamic Properties (obtained from: NIST Chemistry Web-Book).

Identity	$\Delta H^{\circ}_{f}$ (kJ/mol)	S° (J/mol K)
Benzaldehyde	-87.1	221.2
Methanol	-238.4	127.19
Water	-285.8	69.95
BDA	-308.4	

*Heat of reaction:* 

$$\Delta H_{rxn}^{o} = \Delta H_{f}^{o}(H_{2}O) + \Delta H_{f}^{o}(BDA) - \Delta H_{f}^{o}(Benzaldehyde) - 2 * \Delta H_{f}^{o}(CH_{3}OH) = -30.3 \, kJ/mol$$
(F.1)

## *Estimation for* $\Delta S^{\circ}$ *:*

As the specific entropy of BDA could not be found, it will be assumed that the change is entropy is less than zero as the number of molecules is decreasing through the reaction and there is no change in the state of the molecules.

$$\Delta S^o < 0 \tag{F.2}$$

*Estimation for*  $\Delta G$ *:* 

$$\Delta G = \Delta H_{rxn}^o + \Delta S^o T \tag{F.3}$$

$$\Delta S^o < 0 \tag{F.4}$$
375

$$\Delta G \le \Delta H_{rxn}^o \tag{F.5}$$

$$\Delta G \le -30.3 \, kJ/mol \tag{F.6}$$

*Estimation for K<sub>eq</sub>:* 

$$K_{eq} = e^{-\frac{\Delta G}{RT}} \cong 1 \tag{F.7}$$

Considering a reaction solution containing 1 mL benzaldehyde, 1 mL DMF, and 10 mL of methanol at 298 K, a maximum conversion of approximately 87% can be obtained based on the estimation for  $K_{eq}$ . This value is consistent with results obtained over MIL-100(Cr) at the tested reaction conditions (303 K) as no conversion is measured above this threshold (Figure F5).



**Figure F5.** Conversion of benzaldehyde over MIL-100(Cr) (1 mL benzaldehyde, 1 mL DMF (internal standard), 10 mL methanol, 0.01 g catalyst, 30 °C). The calculated equilibrium conversion (87%) is indicated by the dashed line.

#### F2.2. Accessibility of DTBP in MIL-100

As shown in Figure S6, condensation in the small and large mesoporous cages corresponds to 3.7 and 3.3 mol H<sub>2</sub>O per mol Cr, respectively. As we know the expected volume and surface area of the mesoporous cages based on the topology, we can estimate the surface area fraction in large cages:

$$\frac{V_{ads,L}}{V_{ads,S}} = \frac{3.3 \text{ mol } H_2 0 \ (\text{mol } Cr)^{-1}}{3.7 \text{ mol } H_2 0 \ (\text{mol } Cr)^{-1}} = 0.89,$$
(F.8)

$$V_S = \frac{4}{3}\pi (12 \text{ Å})^3 = 7,238 \text{ Å}^3, \tag{F.9}$$

$$V_L = \frac{4}{3}\pi (14.5 \text{ Å})^3 = 12,770 \text{ Å}^3,$$
 (F.10)

$$A_s = 4\pi (12 \text{ Å})^2 = 1,810 \text{ Å}^2,$$
 (F.11)

$$A_L = 4\pi (14.5 \text{ Å})^2 = 2,642 \text{ Å}^2,$$
 (F.12)

$$\left(\frac{V_{ads,L}}{V_{ads,S}}\right) * \left(\frac{A_L}{V_L}\right) * \left(\frac{V_S}{A_S}\right) = \left(\frac{SA_L}{SA_S}\right) = 0.74,$$
(F.13)

and 
$$\left(\frac{SA_L}{SA_{Total}}\right) = 0.42.$$
 (F.14)

This value (0.42) is the estimated fraction of accessible surface area and subsequently the fraction of active sites in large mesoporous cages.

Papadopoulos and coworkers provided a digitally constructed unit cell of MIL-100(Fe) from powder x-ray diffraction data which contained atoms belonging to 16 small and 8 large mesoporous cages.<sup>158</sup> Consideration of these values provides the surface area fraction within large mesoporous cages to be 0.42:

$$A_S = 4\pi (12 \text{ Å})^2 = 1,810 \text{ Å}^2,$$
 (F.15)

$$A_L = 4\pi (14.5 \text{ Å})^2 = 2,642 \text{ Å}^2,$$
 (F.16)

$$n_L = number \ of \ large \ cages,$$
 (F.17)  
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$$n_S = number \ of \ small \ cages = 2 * n_L,$$
 (F.18)

$$\frac{A_L}{A_{Total}} = \left(\frac{n_L A_L}{(n_L A_L) + (n_S A_S)}\right) = \left(\frac{A_L}{A_L + 2A_S}\right),\tag{F.19}$$

and 
$$\left(\frac{A_L}{A_{Total}}\right) = 0.42.$$
 (F.20)



**Figure F6.** Water adsorption isotherm (303 K) of MIL-100-Cr highlighting the amount of water adsorbed during condensation in the small and large mesoporous cages at lower and higher pressure, respectively.

# S2.3. IR Spectra of Pyridine Adsorption



**Figure F7.** (bottom) IR spectra of MIL-100(Cr) activated at 373 K (top) IR spectra of MIL-100(Cr) following saturation with pyridine through five 2 μL injections into an inert flow at 373 K.