ROLE OF STORAGE MATERIAL IN NOX STORAGE AND REDUCTION (NSR) AND THREE-WAY CATALYSTS (TWC) DURING CYCLING OPERATION

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Abstract

NOx storage and reduction (NSR) is a cyclic catalytic process that eliminates NOx from lean burn vehicles. There is an active debate about the NOx reduction mechanism, particularly at a high temperature and cycle frequency. Three-way catalysts (TWC) are widely applied in stoichiometric combustion vehicles. The invention of novel oxygen storage materials (OSM), such as spinels, requires more advanced understanding of their promotion impacts.

NOx reduction under net lean and near-stoichiometric conditions was carried out on CeO₂, Pt/Al₂O₃, Pt/CeO₂/Al₂O₃ and Pt/BaO/Al₂O₃ washcoated monoliths to compare performance features and identify reaction pathways. The NOx storage functionality is essential for NOx reduction under net lean conditions while the oxygen storage functionality promotes NOx reduction for near-stoichiometric conditions. The improved NOx storage utilization is mainly responsible for NOx conversion enhancement under fast cycling. A ceria redox pathway has only a secondary effect on NOx conversion under excess O₂.

Simultaneous conversion of NO, CO and C₃H₆ under stoichiometric conditions was carried out on catalysts containing OSM-promoted mixed precious group metal (PGM: Pt(95%)/Pd(5%)). The studied OSMs include ceria-zirconia (Ce_{0.3}Zr_{0.7}O₂; CZO) and mixed metal oxide spinel (Mn_{0.5}Fe_{2.5}O₄; MFO). PGM supported directly on the OSM was found to be the best design for CZO while a dual-layer architecture (top PGM layer, bottom MFO layer) outperformed the MFO-supported PGM catalyst. Close coupling between the PGM and CZO is responsible for the activity promotion. Enhancement obtained with the dual-layer PGM-MFO architecture relies on a direct catalytic contribution from the spinel.

A combined experimental and modeling study of dynamic oxygen storage capacity (DOSC) of CZO and MFO spinel using CO and H₂ was conducted. During reduction (or oxidation), either oxide exhibits a transition in rate-controlling regime, from a fast, reaction-controlled process to a much slower diffusion-controlled process. For CZO the classical shrinking-core model is successfully applied to describe the transient DOSC performance. For MFO, with its higher oxygen storage capacity (OSC), reduction is confined to oxygen within the first surface layer of the dispersed spinel crystallites. A progressive model is developed for MFO that is capable of capturing the DOSC performance under both long cycle (60s) and short cycle (1~2s).

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Nomenclature

Latin characters:

a_s :	ratio of surface area to volume in pellet (m ⁻¹)
A_j :	Pre-exponential factor of reaction j
<i>C</i> ₀ :	total concentration in gas phase (mol/m ³)
<i>c_{pf}</i> :	heat capacity of gas (J/kg/K)
<i>c</i> _{<i>pw</i>} :	heat capacity of solid wall (J/kg/K)
d_{pellet} :	diameter of OSM pellet (m)
$D_{e,i}$:	effective diffusivity of species i in pellet or washcoat (m ² /s)
$D_{e,PA,i}$:	effective diffusivity of species i in PGM washcoat (m ² /s)
$D_{e,SA,i}$:	effective diffusivity of species i in Spinel washcoat (m^2/s)
$D_{f,i}$:	diffusivity of specie i in fluid phase (m ² /s)
E_j :	Activation energy of reaction j (J/mol)
h:	heat transfer coefficient (W/m ² /K)
ΔH_j :	enthalpy of reaction j (J/mol)
$k_{c,i}$:	mass transfer coefficient of species i (m/s)
k _{me,i} :	external mass transfer coefficient of species i (m/s)
k_w :	heat conductivity of wall (W/m/K)
L_b :	length of catalyst bed (m)
L_m :	length of monolith (m)
M_i :	molecular weight of species i (kg/m ³)
Nu:	Nusselt number
<i>r</i> :	radial coordinate in pellet (m)
r_s :	radius of pellet (m)
<i>r_{i,j}</i> :	volumetric rate of reaction i in reaction j $(mol/m^3/s)$

<i>R</i> :	Ideal gas constant (J/mol/K)
$R_{\Omega 1}$:	effective transverse diffusion length for flow area (m)
$R_{\Omega w}$:	effective wall thickness (m)
Sh _e :	Sherwood number
$Sh_{e,\infty}$:	Asymptotic external Sherwood number
<i>t</i> :	time (s)
T_f :	gas phase temperature (K)
<i>T_s</i> :	solid phase temperature (K)
u_f :	average superficial velocity (m/s)
$x_{f,i}$:	mole fraction of species i in fluid phase
$x_{PA,i}$:	mole fraction of species i in PGM washcoat layer
$x_{SA,i}$:	mole fraction of species i in Spinel washcoat layer
$x_{s,i}$:	mole fraction of species i in pellets
<i>x_{sur,i}</i> :	mole fraction of species i in pellets or washcoat surface
$x_{wc,i}$:	mole fraction of species i in washcoat
<i>y</i> :	radial coordinate in monolith (m)
<i>z</i> :	axial coordinate (m)

Greek symbols:

ε_b :	void fraction in cat. bed (m^3 void/ m^3 cat. bed)
ε_p :	volume fraction of OSM pellet (m ³ OSM/m ³ cat. bed)
ε_{PA} :	porosity of PGM washcoat layer
\mathcal{E}_{SA} :	porosity of Spinel washcoat layer
$ ho_f$:	density of gas (kg/m ³)
$ ho_w$:	density of solid wall (kg/m ³)
λ:	ratio of fluid phase diffusivity to effective washcoat diffusivity

$v_{i,j}$:	stoichiometry of species i in reaction j
ϑ_k :	mole fraction of species k
	($k = CZO_2$ and $CZO_{1.85}$ or CZO ; $k = MFO_4$, MFO ₃ , MFO _{0.5} for MFO)
Ω_S :	site density of spinel MFO in packed-bed or washcoat (mol/m ³)
Ω_C :	site density of CZO in packed-bed or washcoat (mol/m ³)
τ:	tortuosity of particles
ε:	porosity of particles
δ_{PA} :	thickness of PGM washcoat layer
δ_{SA} :	thickness of Spinel washcoat layer

Abbreviations:

ASC:	Ammonia Slip Catalyst
CARB:	California Air Resources Board
CLC:	Chemical Lopping Combustion
CZO:	Zirconia Stablized Ceria
Di-Air:	Diesel NOx Aftertreatment by Adsorbed Intermediate Reductants
DOSC:	Dynamic Oxygen Storage Capacity
EPF:	Environmental Protection Agency
GHG:	Greenhouse Gas
GPF:	Gasoline Particulate Filter
ICE:	Internal Combustion Engine
LDT:	Light-Duty Truck
LDV:	Light-Duty Vehicles
LNT:	Lean NOx Trap

- MDPV: Medium-Duty Passenger Vechicle
- NMOG: Non-Methane Organic Gases (non-methane oxygenated and non-

oxygenated hydrocarbon)

- NSC: NOx Storage Capacity
- NSM: NOx Storage Material
- NSR: NOx Storage and Reduction
- OC: Oxygen Carrier
- OSC: Oxygen Storage Capacity
- OSCC: Complete Oxygen Storage Capacity
- OSCR: Reductant Limited Oxygen Storage Capacity
- OSM: Oxygen Storage Material
- PC: Passenger Cars
- PM: Particulate Matters
- SCM: Shrinking Core Model
- SCR: Selective Catalytic Reduction
- S_N: Stoichiometric Number
- SR: Steam Reforming
- TPO: Temperature Programmed Oxidation
- TPR: Temperature Programmed Reduction
- TWC: Three-Way Catalyst
- WGS: Water Gas Shift

Chapter 1 Introduction

1.1 Emission Control Technologies

Nowadays, the emission standards for internal combustion engines (ICE) are becoming more and more stringent, for the purpose of environment and health protection. Regulation targeted pollutants include CO, NOx (NO and NO₂), non-methane organic gases (NMOG) and particulate matters (PM). In US, two sets of emission regulations, Tier 3 [1] and LEV III [2], have been issued by Environment Protection Agency (EPA) and California Air Resources Board (CARB) respectively and plan to phase-in from 2015 to 2025. Fig. 1.1 (a) shows the Tier 3 standard of fleet average NMOG + NOx for light-duty vehicles (LDVs), light-duty trucks (LDTs) and medium-duty passenger vehicles (MDPVs) in the federal test procedure (FTP). The fleet average NMOG + NOx standard needs to drop ~ 70% from 2017 (0.086 g/mile for LDV and 0.101 g/mil for MDPV) to 2025 (0.03 g/mile for LDV and MDPV). Emission standard for PM also becomes stricter. LEV III requires the PM limit for passenger cars and LDTs to lower from 3 mg/mile (2017-20201 period) to 1 mg/mile (2025-2028 period). Together with the decrease in pollutant standards, attention have also be paid to lower the greenhouse gas (GHG, e.g., CO₂, CH₄, N₂O etc.) emissions [3]. In 2004, CARB approved GHG regulations from LEV II vehicles beginning with 2009 model year [2]. LEV III exhaust emission standards requires ~ 30% reduction in PC fleet average CO₂ from 2017 to 2025 (Fig. 1.1 (b)).

The more and more stringent regulations motivates the technical advancement for both powertrain and emission aftertreatment systems. Considering future bans of ICE in some countries or areas [3], electrification on vehicles, or adopting batteries or fuel cells as the power source, is growing more and more popular. The immature aspects limiting large-scale adoption of battery electric vehicles (BEVs) include low energy density of batteries, inconvenience of battery recharging and relative high costs. Still, improvements on current technologies and research for other solutions are on the way, such as improvement of combustion efficiency [4], decrease of pollutant generation in powertrain system [5], as well as discovery of advanced catalytic materials [6] and optimization of operation conditions [7] in aftertreatment system.



Figure 1.1 (a) Tier 3 LDV, LDT and MDPV fleet average FTP NMOG + NOx standards;
(b) LEV III PC fleet average CO₂ requirements (PC: passenger cars with a footprint ≤ 41 ft² or > 56 ft² for PC 1 or PC 2)

The dominant deNOx catalytic converter used in aftertreatment system for stoichiometric combustion ICE is Three-Way Catalysts (TWC) [8]. NOx, CO, hydrocarbons (HCs) along with near-stoichiometric O₂ react simultaneously on preciousgroup metal (PGM) based catalysts. Besides TWC, several other converter blocks are also implemented, including hydrocarbon trap [9] and Gasoline Particulate Filter (GPF). Invented as a solution to hydrocarbon removal difficulty during cold-start, the hydrocarbon trap [9] converter is placed upstream of TWC converter. During the first several minutes of engine start-up, the temperature inside converter is too low for reactant activation on TWC. Ideally, hydrocarbon adsorbers first trap exhaust HCs during cold-start and then release HCs for HC conversion on downstream TWC after engine warm-up. The released HCs will be fed into downstream TWC converter for abatement. The GPF converter is used to remove particulate matters through trapping and oxidation.

Compression-ignited lean-burn vehicles are considered as an attractive alternative over spark-ignited stoichiometric gasoline vehicles due to their higher fuel economy and lower CO₂ emission. However, challenge arises in NOx abatement due to the excess O₂ conditions. Currently applied deNOx aftertreatment technologies for lean-burn combustion include Diesel Oxidation Catalyst (DOC) [10], Selective Catalytic Reduction (SCR) [11], NOx Storage and Reduction (NSR) [12] and Passive NOx Adsorber (PNA) [13]. DOC converts unburnt reductants (CO or HCs) and NO to oxidants (CO₂, H₂O and NO₂) and is usually placed upstream of NOx abatement converters (NSR and/or SCR) [10]. The oxidation reactions occurred in DOC provide heat for downstream deNOx converters and NO₂ is comparably easier to be converted to benign products than NO in downstream deNOx blocks. The most widely applied SCR technology is NH₃-SCR [11], which utilizes NH₃ (from thermal decomposition of injected urea) to selectively reduce NOx. The NH₃-SCR technology has been successfully applied for heavy-duty vehicles, especially heavyduty trucks [14]. Additionally, Ammonia Slip Catalyst (ASC) [15] block is added after the SCR block to convert excess NH₃ into benign N₂ through selective oxidation of NH₃. Compared to medium or heavy duty vehicles, the compact design of light-duty small vehicles does not have the space for urea storage and injection blocks. This limits the application of NH₃-SCR in light-duty gasoline vehicles. Served as an option for light-duty vehicles, NSR [12] converter periodically stores and reduces NOx during operation and does not require additional NH₃ injection. The reductants in NSR technology comes from incompletely combusted fuels during fuel-rich operation. Both NSR and SCR can provide satisfactory deNOx performance once catalysts are activated (e.g., > 200 °C). However, the NOx abatement during cold-start or low temperature range (i.e., room temperature ~ 250 °C) still remains a challenge. Accordingly, PNA is proposed and considered as a promising solution for deNOx difficulty during cold-start [13]. Ideally, PNA adsorbs or stores NOx generated at low temperatures (e.g., <200 °C) and releases stored NOx at high temperatures (e.g., > 200 °C) for effective NOx conversion by downstream SCR or NSR. Compared to others, PNA is a relatively new technology and expected more studies will be conducted for material screening, design optimization, performance evaluation and modeling.

1.1.1 NOx Storage and Reduction (NSR)

As a solution for NOx abatement difficulty in excess O₂ environment, Takahashi et al. first introduced the concept of NOx storage and reduction (NSR) in late 1990s [16]. The

key point of this technology is to reduce NOx generated within a long O₂-excess period during a short deliberately created O₂-deficient period, while still maintaining the cycleaveraged fuel-lean environment.



Figure 1.2 Mechanistic illustration: (a) NOx storage and reduction mechanism; (b) hydrocarbon intermediate mechanism; (c) redox pathway.

The NSR catalysts are designed to contain several components [17]: precious group metals (PGM: Pt, Pd, Rh), NOx storage materials (alkane or alkaline oxides: BaO, K₂O etc.) and a support with high surface area (e.g., γ - Al₂O₃). In the NSR technology, the operation conditions are divided into two modes: fuel-lean mode and fuel-rich mode [12]. The duration of rich or lean periods can range from several seconds to several minutes. Fig. 1.2 (a) shows the NSR mechanism during lean/rich cycling. During lean mode, fuels and excess O₂ are fed into ICE and the effluent gas contains NO and excess O₂. In NSR converter, NOx is stored on NOx storage material. During rich mode, excess fuels and limited O₂ are fed into ICE and the effluent gas contains excess reductants. In NSR converter, reductants (H₂, CO or HC) are used to reduce NOx stored on NSR catalysts. The three crucial during NSR operation are listed as follows [12]:

(1) NO oxidation to NO_2 by O_2 on PGM sites.

- (2) NOx (NO and NO₂) adsorption on NOx storage material (NSM).
- (3) Reduction of stored NOx by fed reductants (i.e., CO, H₂ and HCs) to N₂, N₂O and NH₃ on PGM sites.

For real-world application, it's more practical to combine the NSR converter with other NOx abatement blocks (i.e., PNA and NH₃-SCR) for satisfactory deNOx performance. Gandhi et al. [18] invented the NSR + SCR combination design and reported higher NOx reduction efficiency and lower NH₃ emissions [19]. With such design, NH₃ generated from NSR is considered as a useful byproduct for downstream SCR block and there is no need to install a separate urea injection system. Generally, State-of-art NSR and SCR technologies function well between ~200°C to ~400°C [11] [12]. However, the NOx conversion decreases outside that temperature range due to inadequate catalyst activity at lower temperature (< 200 °C) and due to either storage limitations (NOx for NSR; NH₃ for SCR) and/or side reactions (e.g., NH₃ oxidation for SCR) at higher temperatures (> 450 °C).

1.1.2 Di-Air system (diesel NOx aftertreatment by adsorbed intermediate redutants)

Based on the NSR technology, Toyota researchers [20] introduced a new deNOx system, Di-Air (diesel NOx aftertreatment by adsorbed intermediate reductants), which involves fast injection of fuels into exhaust upstream of a NSR converter. Compared to traditional NSR system, the lean/rich cycling frequency in Di-Air system is much faster, i.e., from several seconds or minutes to tens or hundreds of milliseconds. Experimental data suggests that the Di-Air system has superior performance than conventional NSR systems in many aspects [20], such as higher NOx conversion within wider ranges of

temperature and space velocity range, as well as improved thermal and sulfur durability of the catalyst.

Several studies followed after the first report of Di-Air, including mechanism investigation, system design and optimization. Inoue et al. [21] proposed a hydrocarbon intermediate pathway (Fig. 1.2 (b)) based on reactivity and surface spectroscopy data from experiments. Isotopic labelling experiments revealed the existence and consumption of thermally stable hydrocarbon intermediates such as nitrous acid esters and amides on the catalyst surface during fast cycling [21]. They concluded that such intermediates, which survive on the surface long enough during fast cycling at elevated temperatures, are subsequently oxidized by NO and/or O₂ to benign N₂, CO₂, and H₂O. They also claimed that this mechanism was mainly responsible for the enhanced NOx abatement performance in the Di-Air system [21]. The conventional NSR pathway (Fig. 1.2a) with enhanced NOx storage utilization has been proposed and examined in several recent studies [22][23][24]. Reihani et al. [22] compared the dynamic NOx storage capacity (NSC) at low and fast cycling frequencies and concluded that fast cycling results in more efficient NOx storage and reduction and therefore higher NOx conversion. Ting et al. [23][24] confirmed the presence of hydrocarbon intermediate pathway but ascribed the majority of the enhancement by fast cycling to the conventional NSR mechanism through comparison of the overall deNOx performance with H_2 or C_3H_6 as the reductant. Ting et al. [24] also used a non-isothermal 1-D monolith reactor model containing a global kinetic scheme to capture the experimental trends in H_2 case based on the conventional NSR pathway. The cyclic redox of ceria (Fig. 1.2(c)) has been advanced by Makkee and coworkers [25][26]. They used TAP (Temporal Analysis of Products) to show that oxygen vacancies are generated

at high temperatures on reduced ceria which serve as sites for NO decomposition/reduction. Wang et al. [26] showed that carbonaceous species deposited during the pulsing of the reductant (H₂, CO, HC) were converted under the subsequent oxidizing (NO, O₂, CO₂) conditions. While a supported ceria catalyst was effective at high temperatures, the addition of precious metal lowered the temperature needed for the reaction (Pt/CZO and Rh/CZO) [25].

Zheng et al. [27][28] investigated the enhanced deNOx performance over a duallayer LNT+SCR catalyst. Uenishi et al. [29] and Reihani et al. [30] proposed improved designs to minimize axial dispersion upstream of the NSR converter which enabled more intense hydrocarbon pulses. Faster cycling generally has led to higher NOx conversion with hydrocarbons typically outperforming H₂ or CO at high temperature (e.g., >350 °C). Both Reihani et al. [30] and Li et al. [31] pointed out that olefins (e.g., C₃H₆ or C₂H₄) are better reductants than the corresponding alkanes.

1.1.3 Three-Way Catalysts (TWC)

In order to efficiently remove the hazardous gases from ICE (CO, NO and HCs), the concept of so-called Three-Way Catalyst (TWC) was proposed [32]. The working methodology of TWC is that simultaneous remove reductants (CO, HCs) and oxidants (NO) in a near stoichiometric atmosphere.

Such design can be achieved on precious group metal (PGM) sites on PGM/support (i.e., PGM/Al₂O₃, PGM/SiO₂) catalysts with a continuous near stoichiometric feed. However, such design cannot accommodate the feed modulation conditions during real driving sufficiently [33]. The lambda sensor installed ahead of ICE monitors the O₂ concentration and controls air-to-fuel ratio (usually denoted as λ) near 14.6 (the stoichiometric ratio between gasoline and air). Due to the impact control of lambda sensor, the fed λ always fluctuates around 14.6 and hence the exhaust always fluctuates between reductant-rich and oxidant-rich phases. Due to the inherent chemistry, either excess reductants or oxidants results in unsatisfactory pollutant (CO, HCs and NO) abatement performance. With excess oxidants (O₂), CO and HCs can be fully removed through oxidation reactions but NO cannot be removed totally, as NO is a less effective oxidant than O₂. With excess reductants (CO and HCs), NO can be fully reduced but the excess CO and HCs cannot be removed. As a result, the cycle-averaged pollutant conversions under modulation conditions drops compared to those obtained with steady-state feed. As shown in Fig. 1.3 [34], a tighter control of air-fuel ratio provided from more advanced controller can narrow the fluctuation window of pollutant conversions.

The improvement of control technology was not enough to meet the tight stoichiometric constrain in a randomly oscillating dynamic combustion. Further in 1980s, TWC formulation was improved with the addition of the oxygen storage material (OSM) as the promoter. Such material should be capable of fast oxygen uptake and release between gas and its lattice depending the surrounding atmosphere [35]. CeO₂ was first introduced as the OSM by Ford in 1980s [36]. Besides its excellent oxygen buffering performance, the beneficial strong metal-support interaction (SMSI) [37] between ceria and precious group metal (PGM) dramatically eases the activation of lattice oxygen and enhances the oxygen storage capacity (OSC). Till now, CZO is still the dominant OSM in TWC formulation, due to its impressive oxygen buffering feature and many other advantages

(e.g., promotion of CO oxidation, NO reduction, water gas shift reaction and promotion of PGM stabilization) [33][37][38].



Figure 1.3 TWC conversion plot for HC, CO and NOx as a function of air-fuel ratio. Also shown are representative air-fuel ratio vs. time traces for 1986 and 1990 vehicles with control bandwidth mapped onto the catalyst efficiency plot [34].

Recently, CH₄ is considered as a transportation fuel due to the abundant CH₄ stock, mostly from shale gas reserves [39]. Compare to conventional ICE using gasoline or diesel as fuels, CH₄-powered engines, especially stoichiometric CH₄-powered engines, emit CH₄ along with other pollutants (CO, NOx etc.) in exhaust. This poses a challenge to emission control of CH₄-powered vehicles under more stringent GHG regulations [2], as current PGM-based TWC cannot provide satisfactory CH₄ conversion performance at low and medium temperatures (e.g., < 500 °C). On-going studies [40][41] on catalytic converters for near stoichiometric CH₄-powered engines includes material screening, performance evaluation, system optimization and predictive model development.

1.2 Storage Material

In NSR and TWC converters, the storage materials (either NSM or OSM) participate in the overall processes through the paired storage/release half cycles depending on the periodically changed fuel-rich/fuel-lean feeds. Instead, the applied trapping material, or storage materials in PNA or hydrocarbon trap undergoes the storage/release cycles depending on changed temperature conditions. Different design concepts raises different requests for storage material.

1.2.1 NOx Storage Material (NSM)

In NSR technology, applied catalysts are designed to periodically store and release NOx depending on feeds at varied temperatures. Therefore, the desired NSM should be able to store considerable amount of NOx at a wide range of temperatures (e.g., 150 °C ~ 400 °C). Alkali- and alkaline-earth metal oxides are selected as the NSM in NSR technology [12]. During trapping, NOx (NO and NO₂) are stored on these metal oxides in the form of nitrate and/or nitrites [42]. Evidence shows that nitrates are the dominant trapping species, especially at high temperatures (e.g., > 200 °C). Nitrites are mostly detected at low temperatures (e.g., 150 °C ~ 200 °C) [43].

Both experimental results and thermodynamic calculation show that NOx storage capacity is directly related to the basicity of the NSM [16][44]. The metal oxide with a

stronger basicity gives a higher NOx storage capacity. The NOx storage capacity evaluation at 350 °C by Kobayashi et al. [44] gave a list of metal oxides with a decreased NSC order: K > Ba > Sr > Na > Ca > Li > Mg [44]. However, the overall deNOx performance is not singly determined by the NSC. During rich phase, stored NOx can release from NSM due to heat generated by exothermic reaction [45] as well as the rich excursion accomplished by the net rich environment from introduction of rich species [12]. This part of released NOx results in a decrease of cycle-averaged NOx conversion. Generally, Ba is most widely reported NSM for NSC catalysts in literature. Besides alkaliand alkaline-earth metal oxides, ceria has also been reported to possess notable NSC, especially at low temperatures (e.g., < 250 °C) [46].

In PNA technology, the ideal NOx trapping material should have superior NOx trapping efficiency at low temperatures (e.g., < 200 °C) and release the finite amount of trapped NOx at elevated temperature for downstream deNOx converters (i.e., NSR and/or SCR). Literature reported materials are Pd or Pt-based catalysts, including Pt/Pd/Al₂O₃, Pt/Pd/CeO₂ and Pd/zeolites [47]. Pd/zeolites are the most promising candidate among all there materials, due to its excellent resistant to sulfur poisoning [48] and high NOxt-to-PGM trapping ratio [47]. The NOx adsorption process in NSR is usually kinetically controlled at low temperature (e.g., < 300 °C), as NO first needs to be oxidized to NO₂ on PGM sites for effective adsorption. In contrast, experimental results show that the NOx adsorbs on PNA with a small or near zero activation energy [47].

1.2.2 Oxygen Storage Material (OSM)

Some solid oxides are called "oxygen storage material" (OSM) due to their capability of rapid and reversible oxygen storage and release between lattice and surrounding environment [37][49][50]. Such unique feature motives the utilization of OSM in oxygen-related applications, especially those with frequently changed feed conditions, for example, emission control systems of stoichiometric gasoline powered vehicles [8][51] and chemical-looping processes [52][53]. During normal ICE operation, the imperfect feedback control of the stoichiometric air-to-fuel ratio leads to the continuous cycling or modulation of exhaust between net fuel-rich and net fuel-lean conditions [54]. As a solution, OSM is added into emission catalysts to buffer the inherent lean/rich modulation and thus sustain satisfactory abatement performance of CO, NO and hydrocarbons (HCs) [33]. In chemical looping processes, OSM, or the so-called oxygen carrier (OC) is circulated between the oxidation and reduction reactors for the desired separated redox reactions [52][55].

One of the most well-known OSM is ceria or zirconia-stabilized ceria (CZO), which has been successfully added in three-way catalysts (TWC) formulation since its first introduction by Ford [36]. Still, continuous studies are carried out for alternative OSMs to lower catalyst costs and explore more options. During several decades of study, perovskites [55][56] and spinels [57][58] are considered as potential candidates due to their high OSC and low cost. The general formula for perovskites and spinels are ABO₃ and AB₂O₄ (Fig. 1.4) respectively, where A and B denote two cations. The catalytic properties and OSC of perovskites and spinels can be tuned by a bunch of ways, including changing cation types and tuning cation portions. Attempts have also been made to apply perovskites [59] and spinels [60] in chemical-looping processes, such as chemical-looping combustion.



Figure 1.4 Lattice structure of spinel AB₂O₄. (http://www.cdti.com/spinel/).

Recently, researchers from CDTi Inc. have invented a group of spinel and tried to apply spinel into CH₄ related applications [57][58]. Preliminary work in CDTi Inc. and University of Houston show that dual-layer PGM-spinel monolith catalysts dramatically promote CH₄ light-off, especially under lean/rich modulation. Results show that compared to a commercial PGM-CZO monolith catalyst, a dual-layer PGM-Mn_{0.5}Fe_{2.5}O₄ (later referred as MFO) spinel monolith catalyst with lower PGM loading surprisingly gives a lower CH₄ light-off temperature [40]. Experimental results [61] show that MFO spinel exhibits higher OSCC (complete oxygen storage capacity) and DOSC (dynamic oxygen storage capacity, which was evaluated within 2s) than CZO. Despite these promising results, more research is needed to fully understand the spinel functionality and evaluate its performance quantitatively. As an important property parameter for OSM, oxygen storage capacity (OSC) is quantified as the accessible oxygen in oxygen storage material. In TWC-related work, the so-called dynamic oxygen storage capacity (DOSC) [36] is a more reasonable characterization parameter. Due to the inherent fast lean/rich modulation conditions from engine operation (usually in several Hz), it's crucial to evaluate the OSC obtained in short time periods (e.g., in seconds) [36].

1.3 Modeling of Dynamic Oxygen Storage Capacity (DOSC)

Plenty of experimental and modeling work has been conducted for CZO-based OSM. Researchers [62][63][64] highlighted the effects of CZO composition (i.e., Ce/Zr ratio), texture property and PGM-CZO interaction on DSOC performance. Mathematical models, such as simplified control-oriented models [65], global kinetic models [66] and detailed microkinetic models [67], can successfully capture the transient DOSC features resulted from PGM-deposited CZO. In PGM-CZO catalyst, the strong synergetic interaction between PGM and CZO eases the oxygen activation near PGM atoms. For those oxygen atoms far away from PGM, surface oxygens are more easily to be activated compared to bulk oxygens, as bulk oxygen needs to overcome diffusion barrier to reach surface for reduction. Therefore, multiple types of oxygen sites are generally considered in DOSC modeling for PGM-CZO, depending on positions of oxygen (or oxygen vacancy) sites in the catalyst, for example, distance to PGM atoms and distance to CZO lattice surface. Li et al. [68] defined three types of oxygen (or vacancy) sites in the OSC model to capture experimental CO-TPR and long CO reduction results obtained from a commercial TWNSC catalyst. Gong et al. [69] used a dual-site OSC model to simulate the transient reductant (CO, H_2 or CH₄) – O_2 profiles during 60s/60s cycling on a commercial TWC catalyst. Rajbala [67] used a crystallite-scale approach to predict the OSC performance of Pd-CZO catalysts with varied Pd crystallite size and Pd dispersion. However, very few studies have been reported for the redox performance of spinel-containing catalysts and no modeling DOSC work has been reported for spinel-based materials.

1.4 Research Objectives and Outline

The main objective of this work is to study and quantify the impacts of two types of storage material, NOx storage material and oxygen storage material in Di-Air and TWC processes. For the Di-Airy process, the mechanism remains controversy, especially regarding contribution from NOx and oxygen storage material. For TWC process, the impacts from newly developed OSM, such as spinels, remains unclear. In the experimental parts of this study, the catalytic performance is compared for a group of catalyst formulations and architectures over a range of operating conditions including feed temperature, feed concentration, reductant type, feed operation mode (steady-state or modulation). Findings from experiments are interpreted to advance the understanding and application of fast cycling NSR and TWC. In the modeling part, the reaction kinetics and kinetic parameters are first determined and then tested the validity with experimental results.

The specific objectives of this study are as follows:

- 1. Determine the role of CeO₂ in the Di-Air, or fast cycling NSR system.
- Compare the deNOx contribution from NOx and oxygen storage materials (e.g., BaO and CeO₂) in Di-Air system

- Investigate the role of MFO spinel in TWC performance, especially under modeling conditions
- 4. Evaluate and compare the DOSC performance of CZO and MFO spinel
- 5. Develop a predicative model that applicable for spinel-based catalysts under feed modulation conditions

The dissertation is organized as follows:

Chapter 2 describes the experimental conditions and mathematical models. Contents in experimental conditions include illustration of reactor setups, list of applied catalysts, as well as description of experiments and characterization tests. The model part include the heterogeneous model for fixed-bed reactor and the 1+1D model for monolith reactor. The governing equations, boundary conditions and initial conditions are included.

Chapter 3 presents the NO abatement performance on ceria under cycling conditions. The experimental results illustrates the reaction pathways of NO reduction on ceria. The impact of O₂ and cycling frequency are discussed. Based on experimental results, the contribution from ceria on deNOx performance in Di-Air system is determined.

Chapter 4 presents the impact of oxygen and NOx storage materials (CeO₂, BaO) on NOx conversion during fast lean-rich switching. The deNOx performance with three catalysts, Pt/Al₂O₃, Pt/CeO₂/Al₂O₃, Pt/BaO/Al₂O₃, is systematically compared over a range of operating conditions. Based on experimental results, the role of oxygen and NOx storage materials in Di-Air system is determined.

Chapter 5 discusses the impacts of two types of OSM (CZO and MFO spinel) on TWC performance. The catalytic performance is compared for a group of catalyst formulations and architectures over a range of operating conditions. Catalyst characterization and DOSC measurements provide mechanistic insight into the functionality and contribution of the OSM. The findings advance the understanding and identify new catalysts that may have utility in TWC and related applications.

Chapter 6 presents the experimental and modeling results of DOSC behavior of the two model OSMs, CZO and MFO spinel. The reduction/oxidation kinetics of two CZO and MFO spinel are first discussed based on experimental OSC results from the fixed-bed reactor. Modeling results using the determined kinetics and the heterogeneous reactor model are validated with experimental results. Lastly, experimental and modeling results on a PGM-MFO dual-layer monolith are compared.

Chapter 7 summarizes the main conclusions of this work and proposes some recommendations for future work.
Chapter 2 Experimental System and Mathematical Models

2.1 Reactor Systems

2.1.1 Flow reactor for monolith tests

Fig. 2.1 [70][71] shows a schematic of the reactor. Since the experimental conditions requires periodic changes of certain gases and continuous feed of other gases, the flow reactor was designed to have three different feed lines: a main line, a rich line and a lean line. The main line contained all of the continuously fed gases (e.g., NO, CO, H₂, $C_{3}H_{6}$, CO₂, H₂O, and Ar for experiments discussed in Chapter 4 and 5). The lean line and the rich line delivered the modulated feed. The lean line contained the "fuel-lean" feeds, which were usually NO and O₂. In contrast, the rich line contained the "fuel-rich" feeds, which were usually reductants (CO, H₂ etc.). During experiments, the main line was mixed with either the lean or the rich lines before fed into the reactor. A solenoid-actuated, fourway valve (Valco Inc., Micro-electric two position valve) enabled the switching between lean and rich streams at a desired switching frequency. The switching valve was placed ~ 2 ft ahead of monolith to minimize the axial dispersion of pulsed feed. In addition, a syringe pump (Teledyne Isco model 100DX) and vaporization system generated a stable feed of gaseous H₂O.

The reactor system was composed of a quartz tube (OD = 0.75 in, ID = 0.63 in), a ThermocraftTM furnace, monolith catalyst and three thermocouples. Before inserting inside the quartz tube, the monolithic samples were wrapped with Fiberfrax® ceramic paper to minimize bypassing. Three K-type stainless steel, sheathed thermocouples (Omega Engineering Inc.) was placed ~1 cm upstream, in the middle, ~ 1 cm downstream of the monolith sample to measure the feed, monolith and effluent temperatures respectively. A

FTIR (Thermo Scientific, Nicolet 6700) was used to measure the concentrations of NO, NO₂, N₂O, NH₃, CO, CO₂, C₃H₆ and H₂O. A quadrupole mass spectrometer (QMS; Hiden Analytical, HPR20) was used to measure the H₂ (m/Q = 2), N₂ (m/Q = 28) and O₂ (m/Q = 32) concentration in selected experiments. When H₂ was used as the reductant and CO₂ was absent in the feed, the N balance was closed within 5%. Otherwise, the amount of N₂ generated was calculated from the overall nitrogen balance because of the overlap of m/e = 28 signal from CO and CO₂ in the mass spectrometer. When CO or C₃H₆ was used as the reductant experiments, H balance and O balance cannot be calculated, as H₂O signal monitored by FTIR is not accurate enough for quantitative evaluation.

During experiments, MFCs and the switching valve was controlled by the LabView program. For accurate measurement, the FTIR and the mass spectrometer was calibrated daily and the MFC controllers were calibrated every 6 months.



Figure 2.1 Schematic of the flow reactor for monolith tests.

2.1.2 Fixed-bed reactor for powder tests

A home-built fixed-bed reactor was used to evaluate performance of powder catalysts in several tests (i.e., TPR tests and DOSC tests). Fig. 2.2 [61] shows the schematic of the fixed-bed reactor. Fed gases were supplied by gas cylinders (Matheson Tri-Gas; Praxair, Inc.) and controlled by a group of mass flow controllers (MKS Inc.) before fed into the reactor. The fixed-bed reactor was designed that for experiments with either continuous feed (e.g., for temperature-ramped tests) or time-varied feeds (e.g., for DOSC tests with periodic changes between reductants and O₂). In the continuous feed line, desired gas mixture was premixed in a 1/8" stainless steel tube upstream of the reactor. In the pulsing line, two in-series, 2-position, 6-port solenoid-actuated switching valves (Valco Inc.) were installed before the reactor [36][72]. Each 6-port switching valve has a sampling loop with calibrated volume. The probe gas inside the sampling loop was injected by carry gas (e.g., Ar) into the reactor during pulsing. The ideal pulse time can be determined by the flowrate and sampling volume accordingly.

The reactor system was composed of a quartz tube, a furnace (Thermo Fisher Scientific), catalyst bed, and two thermocouples. The powder catalysts with 40 - 60 mesh particle size were mixed with inert diluents (also with 40 - 60 mesh particle size) placed inside the quartz tube (OD = 6.35 mm). The weight ratio of catalysts to diluents was selected as 1:10. Quartz wool was used to mount the particles. Two K-type stainless steel, sheathed thermocouple (Omega Engineering Inc.) was placed ~0.5 cm upstream and downstream of the catalyst bed to monitor the feed and effluent temperatures respectively. The effluent concentrations of species were monitored by a mass spectrometer (Hiden Analytical, HPR20). Monitored gases included H₂ (m/Q = 2), CO (m/Q = 28), O₂ (m/Q =

32), C_3H_6 (m/Q = 42) and CO_2 (m/Q = 44). A separate calibration was conducted to exclude the contribution from peak overlap. For example, both CO and CO₂ shows peaks at both m/Q = 28. As the solution, the concentration calibration of CO₂ was conducted at both m/Q = 28 and m/Q = 44. Before the CO signal (m/Q = 28) acquired from the mass spectrometer was converted to concentration, the contribution from CO₂ was subtracted by applying the CO₂ calibration relationship at m/Q = 28. A similar approach was applied to C₃H₆. For accurate calibration, the mass spectrometer was calibrated daily and the MFC controllers were calibrated every 6 months.



Figure 2.2 Schematic of DOSC fixed-bed reactor.

2.2 Catalysts

2.2.1 Powder Catalysts

Powder catalysts were used in performance (e.g., DOSC tests) tests, characterization tests (e.g., TPR, SEM and physi- or chemi-sorption) as well as preparation of washocoat-deposited monoliths. The preparation methods, compositions and notations are described as follows.

- Ceria powders were prepared bycalcination of cerium (III) nitrate hexahydrate (Sigma-Aldrich) under static air at 650°C for 4 hours.
- (2) A group of Pt/Al₂O₃ based powders with different storage material, Pt/Al₂O₃ (hereafter denoted as "PtA"), Pt/CeO₂/Al₂O₃ ("PCA") and Pt/BaO/Al₂O₃ ("PBA") were prepared by step-wise incipient wetness impregnation. All three catalyst contained ~1 wt. % Pt (washcoat) while the PCA and PBA contained 11 wt. % CeO₂ and BaO, respectively. The γ-Al₂O₃ (Sasol Inc.) support was calcined in static air at 550 °C for 2 hours before impregnation. For PCA or PBA, the γ-Al₂O₃ powder was impregnated with aqueous solution of cerium (III) nitrate hexahydrate (Sigma-Aldrich) or barium nitrate (Sigma-Aldrich), respectively. The powders impregnated with Ce or Ba precursors were dried overnight at 120 °C and calcined in static air at 550 °C for 2 hours. The Pt impregnation was achieved by impregnating CeO₂/Al₂O₃, BaO/Al₂O₃ and γ-Al₂O₃ powders with aqueous solution of tetraammineplatinum (III) nitrate hydrate (Sigma-Aldrich). The powders impregnated with Pt precursor were dried overnight at 120 °C and calcined in static air at 550 °C for 2 hours.
- (3) A group of OSM powders were provided by CDTi Inc.). Two types of OSMs, Ce_{0.3}Zr_{0.7}O₂ (CZO) and Mn_{0.5}Fe_{2.5}O₄ (MFO) are used in this study. The former served as the model OSM while the latter as the model spinel OSM. The MFO was coated onto an alumina support giving a 25 wt.% MFO/Al₂O₃ washcoat or powder. Unless otherwise stated, results for MFO will be on the alumina-supported material. The performance of ceria-zirconia depends on many factors, such as textural properties and Ce/Zr ratio [73]. Thus, the performance of the specific material used

 $(Ce_{0.3}Zr_{0.7}O_2)$ may not be generalized for all Ce/Zr ratios just as the selected spinel $(Mn_{0.5}Fe_{2.5}O_4)$ cannot be generalized for the even broader class of mixed metal oxide spinels. That said, the intent is to compare the MFO spinel to the conventional CZO for the TWC application. Three PGM-free samples, "A" (pure Al₂O₃), "CZO" and "SA" (alumina-supported spinel) were included to study any catalytic contribution of the support and OSM promoters. The other three PGM-containing samples were supported on alumina (A), CZO, and SA; these are denoted by "PA", "PC" and "PS", respectively. Each has the same PGM loading of 1 wt. %. The PGM elemental ratio was Pt:Pd = 19:1 (mass basis).

The compositions and notations of studies catalysts are summarized in Table 2.1.

Table 2.11 Owder Catalysis Oscu in Tills Study				
Powder Catalysts	Component	Source		
CeO ₂	CeO ₂	Homemade		
PtA	1 wt% Pt/Al ₂ O ₃	Homemade		
PBA	1 wt% Pt/11 wt% BaO/Al ₂ O ₃	Homemade		
PCA	1 wt% Pt/11 wt% CeO ₂ /Al ₂ O ₃	Homemade		
CZO	Ce _{0.3} Zr _{0.7} O ₂ (CZO)	CDTi		
SA	25 wt% (MFO)/75 wt% Al ₂ O ₃ (Spinel)	CDTi		
PA	1wt% PGM (Pt:Pd = 19:1)/Al ₂ O ₃	CDTi		

Table 2.1 Powder Catalysts Used in This Study

2.2.2 Monolith Catalysts

Monolithic catalysts are widely used in converters in aftertreatment systems due to the resilience to vibration, low pressure drop and high catalyst contacting area per unit volume. Therefore, some monolith catalysts were prepared by coating powder catalysts onto monolith substrates.

Before coating powder catalysts onto monolith substrates, blank cordierite monoliths (Mitsubishi, 400 channels per square inch, 1 inch diameter, 2.5 inch in length) were cut into small pieces of certain dimensions, for example, 0.42 inch diameter and 1

inch length with ~56 channels for PtA monolith. The desired catalyst powders were ballbilled in a slurry with boehmite (hydro alumina AlOOH, from Nyacol Nano Technology Inc.) and deionized water for 20 hours to prepare a catalyst-alumina slurry. The slurry contained 10 wt% of solids components, 90% of which was catalyst and 10% was γ alumina from boehmite. The monolith piece was immersed from both ends into the Pt/Al₂O₃ slurry for 30s. Air was then blown for 15s from both ends of the monolith to remove excess slurry and get a uniform coating. After each round of dip-coating, the monolith was dried at 120°C for 2 hour. Successive dip-coating was applied until the desired washcoat loading was achieved (4.6g/in³). The dip-coated monolith pieces were calcined at 550°C for 2 hours. Additionally, PtA, PBA and PCA monolithic catalysts were aged before reaction evaluation in static air at 700 °C for 33 hours for stable catalytic performance.

Monolith Catalysts	Component	Washcoat Loading	Source			
CeO ₂	90 wt% CeO ₂ /10 wt% Al ₂ O ₃	280 g/L	Homemade			
PtA	1 wt% Pt/Al ₂ O ₃	280 g/L	Homemade			
PBA	1 wt% Pt/11 wt% BaO/Al ₂ O ₃	280 g/L	Homemade			
PCA	1 wt% Pt/11 wt% CeO ₂ /Al ₂ O ₃	280 g/L	Homemade			
PA	1wt% PGM (Pt:Pd = 19:1)/Al ₂ O ₃	100 g/L	CDTi			
CZO	Ce _{0.3} Zr _{0.7} O ₂ (CZO)	100 g/L	CDTi			
SA	25 wt% MFO/75 wt% Al ₂ O ₃ (Spinel)	100 g/L	CDTi			
PC	1wt% PGM (Pt:Pd = 19:1)/CZO	100 g/L	CDTi			
PAC_DL	1wt% PGM (Pt:Pd = 19:1)/Al ₂ O ₃ &	200 g/L	CDTi			
	CZO	-				
PS	1wt% PGM (Pt:Pd = 19:1)/Spinel	100 g/L	CDTi			
PAS_DL	1wt% PGM (Pt:Pd = 19:1)/Al ₂ O ₃ &	200 g/L	CDTi			
	Spinel					
PAS_DL_Mod	$1 wt\% PGM (Pt:Pd = 19:1)/Al_2O_3 \&$	200 g/L	CDTi			
	Spinel					

 Table 2.2 Compositions of Used Monolith Catalysts

A group of CZO or spinel containing monolith catalysts were provided by CDTi. Inc. to study the impact of OSM on TWC activity and DOSC during modulation. Two types of architectures were considered. The first was a single-layer washcoat with PGM directly deposited on the OSM, while the second was a dual-layer washcoat comprising a bottom OSM layer and top PGM/Al₂O₃ layer. The PGM elemental ratio was Pt:Pd = 19:1 (mass basis) with a total monolith loading of 30 g/ft³. Each OSM-containing monolith catalyst had a loading of 100 g/dm³. For the spinel-containing monolith catalysts, the loading of MFO was 25 g/dm³, and thus the oxide mixture was 75% Al₂O₃ (by mass). The monolith cores catalysts were cut into smaller pieces having ~60 channels and ~1 cm length for the evaluations. All powder and monolith samples were degreened in static air at 700 °C for 33 hours to enable relative stable catalyst performance.

Table 2.5 Architecture and Dimensions of Osed Wononth							
Monolith Catalysts	Architecture	Cell Density (cpsi, cell/in ²)	# of Channels	Length			
CeO ₂	Single layer	400	56	4.0 cm			
PtA	Single layer	400	56	2.54 cm			
PBA	Single layer	400	56	2.54 cm			
PCA	Single layer	400	56	2.54 cm			
PA	Single layer	600	60	2.0 cm			
CZO	Single layer	400	40	2.0 cm			
SA	Single layer	600	40	2.0 cm			
PC	Single layer	600	60	2.0 cm			
PAC_DL	Dual layer (top PGM and bottom CZO)	600	60	2.0 cm			
PS	Single layer	600	60	2.0 cm			
PAS_DL	Dual layer (top PGM and bottom MFO)	600	60	2.0 cm			
PAS_DL_Mod	Dual layer (top PGM and bottom MFO)	600	600	2.1 cm			

Table 2.3 Architecture and Dimensions of Used Monolith

Table 2.2 and Table 2.3 summarize the composition details and architecture details of used monolithic catalysts respectively. PAS_DL and PAS_DL_Mod has the same architecture and composition but different size. The sample PAS_DL_Mod was only used in the modeling study.

2.3 Catalyst Characterization and Performance Tests

Several characterization and catalytic performance tests were performed to determine the texture properties and reactivity of catalysts. The conditions for characterization tests are listed as follows while the results are included in the following chapters.

2.3.1 Sorption Tests

N₂ physisorption and CO chemisorption tests were conducted to determine the surface area and Pt dispersion for the three samples using a Micromeritics 3 Flex instrument. Catalyst washcoat was scraped from monolith samples for characterization. Physisorption for surface area was carried out using N₂ at 77 K. Chemisorption for Pt dispersion was determined using CO at 35 °C.

2.3.2 SEM Tests

SEM tests were carried out to determine the particle size as well as thickness of washcoat layer. The thickness of washcoat varied peripherally with a thicker thickness in the corner and a thinner thickness on the wall. The thickness of washcoat then be determined as the peripherally-averaged thickness for monolith samples.

2.3.3 Temperature-Programmed Reduction and Desorption

Several of transient experiments, including temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) were conducted over the OSMcontaining catalyst powders (CZO, SA, PC, PS) as well as PA powders to probe the reactivity of oxides. In each temperature-programmed experiment, ~ 60 mg catalyst was used with the temperature increased from 50 °C to 700 °C at a ramp rate of 10 °C/min. 10% CO/Ar or 10% H₂/Ar mixtures flowrates of 60 cm³/min were used in the CO- and H₂-TPR experiments, respectively, for all powder catalysts except PA. In the H₂-TPR experiment for PA, the H₂ concentration was lowered to 4000 ppm, to ensure a QMS-detectable H₂ consumption peak. In the O₂-TPD experiment, pure Ar was used as the catalyst was heated from 50 °C to 700 °C at 10 °C/min. Before any temperature-programmed experiment, the powder catalyst was pretreated at 700 °C for 30 min under 10% O₂/Ar and then cooled to 50 °C in 10% O₂/Ar to ensure that the catalyst is in its fully oxidized state initially. The selection of parameters, including the mass of catalyst, ramp rate and flow rate, were based on the criterion proposed by Monti et al. [74] and Malet et al. [75].

2.3.4 Temperature-Programmed Oxidation

A set of temperature-programmed oxidation (TPO) experiments were conducted to quantify the catalytic oxidation of selected reductants (e.g., CO and C_3H_6) on selected catalyst samples. Stoichiometric feeds were used in the TPO experiments. The ramp rate was 10 °C/min. Before each set of experiments, the catalyst was pretreated by 5% O₂ at 550 °C for 15 min, and then cooled in 5% O₂ atmosphere to room temperature.

2.3.5 Evaluation of NOx Storage Capacity (NSC)

The NOx storage capacities of each of the three samples (PA, PCA and PBA) were measured under a continuous feed of 300 ppm NO and 5% O₂. Prior to each NOx storage experiment, the catalyst was fully regenerated by applying the pretreatment procedure described above. The NOx storage capacity, C_{NO_x} , is calculated from

$$C_{NO_{\chi}} = \frac{F_{NO_{\chi}}t^* - \int_0^{t^*} F_{NO_{\chi}}(t)dt}{m_{wc}},$$
(2.1)

where t^* is the duration and m_{wc} the washcoat mass.

2.3.6 Evaluation of Dynamic Oxygen Storage Capacity (DOSC)

The transient oxygen storage capacity measurements are designed to quantify kinetic parameters in the separated reduction/oxidation steps. To avoid the interference from direct CO oxidation caused by pulse overlap, we conducted measurements in the fixed-bed reactor with deliberately separated reductant/oxidant pulses. For those experiments, 15 mg OSM (CZO or SA) of 40 – 60 mesh along with 150 mg inert quartz diluents (also of 40 - 60 mesh) were used. Each catalyst sample was evaluated at 9 temperatures from 200 °C to 600 °C in 50 °C increments. The pretreatment procedure before every experiment is identical to what reported before [19]. CO, H₂ and C₃H₆ served as the model reductant probes while O₂ served as the oxidant. The kinetics were measured for several reductant concentrations (0.5%, 1.0% and 1.8%) and pulse times. The oxidant (O₂) concentration is fixed at 0.9% and corresponds to a stoichiometric neutral feed for 1.8% CO or H₂. The total flowrate was controlled as 150 cm³/min. Both long cycles (60s) and short cycles (2s or 0.8s) were applied to test the validity of kinetic parameters. The ideal pulse duration 0.8s or 2s were provided by sample loops with size of 2 mL or 5 mL. For

every experiment, the reductant and oxidant pulses were separated by a \sim 36 s Ar purge to ensure no overlap between pulses.

The reported DOSC was calculated as the average of least 5 cycles once cyclic steady-state was reached. The reported DOSC values were calculated based on consumption of reductants, with corresponding equations shown as follows:

$$DOSC (CO) = \frac{N_O}{N_{OSM}} = \frac{N_{CO, cons.}}{N_{OSM}},$$
(2.2)

DOSC (H₂) =
$$\frac{N_0}{N_{OSM}} = \frac{N_{H_2,cons.}}{N_{OSM}}$$
 (2.3)

and DOSC
$$(C_3H_6) = \frac{N_0}{N_{OSM}} = \frac{9 \times N_{C_3H_6,cons.} - N_{CO,gen.} - N_{H_2,gen.}}{N_{OSM}}.$$
 (2.4)

2.3.7 Cyclic Experiments

A set of steady-state and lean-rich cycling experiments were conducted over monolithic catalysts to determine the catalytic performance under cycling conditions (e.g., deNOx performance during lean/rich cycling or simultaneous removal of NO, CO and C_3H_6 during modulation). The feed stoichiometry is characterized using the stoichiometric number defined by

$$S_{N} = \frac{[NO] + 2[O_{2}]}{[CO] + [H_{2}] + 9[C_{3}H_{6}]}.$$
(2.5)

For NSR related experiments, the lean to rich time ratio was 6 to 1 (14.3% rich duty cycle). The fixed duty cycle set the fuel to oxidant ratio. The lean/rich frequencies used in the study spanned 90s/15s, 60s/10s, 30s/5s and 6s/1s. In some experiments the O₂ concentration was varied to study its impact on the deNOx performance. CO, H₂ and C₃H₆ were selected as the model reductants. In most experiments, CO₂ and H₂O were excluded to minimize the impact from side reactions. CO₂ and H₂O were added in several

experiments to study the impact of CO₂ and H₂O. In the current study the experimental approach was to turn off the O₂ during the rich injection in order to avoid the steep exotherm [24][76]. For example, Ting et al. [24] reported temperature rise of up to 300 °C during propylene injection into an O₂-containing feed, under net rich conditions. This approach enables a clearer performance comparison of the Pt/BaO/Al₂O₃ and Pt/CeO₂/Al₂O₃ catalysts, which is the main objective of this study. The cyclic experiments were carried out at feed temperatures ranging from 150°C to 600°C with 50°C temperature increments. Before each set of experiments, the catalyst was pretreated in 2% H₂ until NH₃ was not detected in the effluent, then by 2% O₂ for 10 min, and finally by a 10 min Ar purge. This procedure ensured that no stored NOx accumulated and that the catalysts were fully oxidized.

For TWC related experiments, a cycle-averaged stoichiometric neutral feed ($S_N = 1$) was used to simulate the exhaust from gasoline engines. The O₂ concentration was varied between 0.3% and 0.7% with 4 s/4 s timing while other components remained at the same concentration (0.17% H₂, 0.52% CO, 400 ppm C₃H₆, 500 ppm NO, 0.5% O₂, 7% H₂O, 7% CO₂ and balance Ar). The feed conditions were chosen based on the protocol proposed by CLEERS [77]. Before each set of experiments, the catalyst was pretreated by 5% O₂ for 15 min, and then by a 10 min Ar purge.

The cyclic experiments were carried out at feed temperature ranging from 150°C to 500°C. The temperature increment was 50 °C in most cases except the light-off region. Before light-off, the temperature increment was decreased to 25 °C or 15 °C for accurate measurement. Before each set of experiments, the catalyst was pretreated by 5% O₂ for 15 min, and then by a 10 min Ar purge. Once a cyclic stationary-state was reached, results

from up to 10 cycles were averaged to determine the cycle-averaged reactant (NOx, CO and C₃H₆) conversion and product (N₂O and NH₃) yield. The cycle-averaged reactant conversions (X_{NO_x} , X_{CO} , $X_{C_3H_6}$) and NH₃ and N₂O yields (Y_{NH_3} , Y_{N_2O}) were calculated by standard expressions (Eqns. 2.6, 2.7 and 2.8).

$$X_{i}(\%) = \frac{\int_{0}^{t} ([i]_{0} - [i])dt}{\int_{0}^{t} [i]_{0}dt} \times 100\%, \text{ here } i = NOx, CO, C_{3}H_{6},$$
(2.6)

$$Y_{\rm NH_3} = \frac{\int_0^t [\rm NH_3] dt}{\int_0^t [\rm NO]_0 dt} \times 100\%, \tag{2.7}$$

and
$$Y_{N_2O} = \frac{\int_0^t 2 \times [N_2O]dt}{\int_0^t [NO]_0 dt} \times 100\%.$$
 (2.8)

2.3.8 Steady-State Experiments

A set of steady-state experiments were conducted over monolithic catalysts to determine the catalytic performance for certain reactions (e.g., water gas shift reaction, C₃H₆ steam reforming and NOx reduction under lean or near stoichiometric conditions).

2.4 Reactor Model

2.4.1 Fixed-bed Reactor Model

The conventional two-phase heterogeneous model is used to model fixed-bed DOSC results. The assumptions are listed as follows: (1) Isothermal condition is assumed along the reactor; (2) The concentration gradients along radial direction were ignored; (3) Axial dispersion was neglected in the gas phase, given the large Peclet number (~1000). (4) Physical properties remain constant. (5) Pellets are spherical, uniform and identical. (6) Gases are approximated as ideal gas. (7) Diluents (silica pellets) are inert to reaction and diffusion. Fig. 2.3 shows the schematics of the fixed-bed reactor and the OSM particle.



Figure 2.3 Schematic of packed bed and OSM particles.

The isothermal conditions preclude the need for energy balance. The mass balances of species i in gas phase is given by

$$\frac{\partial x_{f,i}}{\partial t} = -\frac{u_f}{\varepsilon_b} \frac{\partial x_{f,i}}{\partial z} - k_{c,i} a_s \frac{\varepsilon_p}{\varepsilon_b} (x_{f,i} - x_{sur,i}), \qquad (2.9)$$

where $x_{f,i}$, $x_{sur,i}$ are concentration of species i in gas phase and solid surface, u_f is average fluid velocity, $k_{c,i}$ is the external mass transfer coefficient of specie i, a_s is the aspect ratio of pellet (ratio of surface area to volume, calculated as $6/d_{pellet}$ and d_{pellet} is the diameter of spinel pellet), ε_p and ε_b are the volume fraction of pellets and void fraction inside the catalyst bed. The external mass transfer coefficient $k_{c,i}$ is calculated based on Frossling correlation [78] by

$$Sh_e = 2 + 0.6Re^{\frac{1}{2}}Sc^{\frac{1}{3}}.$$
 (2.10)

The mass balances of species i in solid phase is given by

$$\frac{\partial x_{s,i}}{\partial t} = D_{e,i} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial x_{s,i}}{\partial r} \right) + \frac{1}{c_0} \sum_{j=1}^r v_{i,j} r_{i,j}, \qquad (2.11)$$

where $D_{e,i}$, $v_{i,j}$ and $r_{i,j}$ are effective diffusivity of species i in pellet, stoichiometry of species i in reaction j and the rate of species i in reaction j, respectively.

The effective diffusivity D_e inside pellet is calculated based on molecular diffusivity and is given by

$$D_{ei} = \frac{D_{f,i}}{\lambda},\tag{2.12}$$

where $D_{e,i}$ and $D_{f,i}$ are effective diffusivity in pellet and molecular diffusivity in fluid respectively.

The molecular diffusivity of species i in excess diluent Ar is calculated by the Hirschfelder relation. The λ is defined by

$$\lambda = \frac{\tau}{\varepsilon} \tag{2.13}$$

where τ and ε are the tortuosity and porosity of particles respectively. Here λ is chosen as 30, similar to the values reported in previous literature [68] for alumina-supported washcoats.

The reduction/oxidation step of CZO occurs between $Ce_{0.3}Zr_{0.7}O_2CeO_2$ (CZO₂) and $Ce_{0.3}Zr_{0.7}O_{1.85}$ (CZO_{1.85}). The site balance is given by

$$\Omega_C \frac{\partial \vartheta_{CZO_2}}{\partial t} = \sum_{j=1}^2 \upsilon_{CZO_2,j} r_{CZO_2,j}$$
(2.14)

and
$$\vartheta_{CZO_2} + \vartheta_{CZO_{1.85}} = 1,$$
 (2.15)

where Ω_C is the density of CZO, ϑ_{CZO_2} and $\vartheta_{CZO_{1.85}}$ are the molar fractions of CZO₂ and CZO_{1.85}. Rate expressions of CZO (CZO₂ and CZO_{1.85}) – involved reactions are shown in later sections as Eqns. 6.11 and 6.12.

The reduction/oxidation of the dispersed MFO spinel involves multiple steps, which are discussed in section 3.2.1. The site balance in the MFO spinel is given as follows:

$$\Omega_S \frac{\partial \vartheta_{MFO_4}}{\partial t} = \sum_{j=1}^2 \upsilon_{MFO_4,j} r_{MFO_4,j}, \qquad (2.16)$$

$$\Omega_S \frac{\partial \vartheta_{MFO_3}}{\partial t} = \sum_{j=1}^4 \upsilon_{MFO_3,j} r_{MFO_3,j}, \qquad (2.17)$$

and
$$\vartheta_{MFO_4} + \vartheta_{MFO_3} + \vartheta_{MFO_{0.5}} = 1,$$
 (2.18)

where Ω_S is the density of spinel MFO, ϑ_{MFO_4} , ϑ_{MFO_3} , $\vartheta_{MFO_{0.5}}$ are molar fractions of site MFO₄, MFO₃ and MFO_{0.5} respectively. In CO case, rate expressions of MFO (MFO₄, MFO₃ and MFO_{0.5}) – involved reactions are shown in latter section as Eqns. 6.2 ~ 6.7.

The initial and boundary conditions are listed as follows:

$$x_{f,i}(z=0,t) = x_{f,i}^{in}(t), \qquad (2.19)$$

$$x_{f,i}(z=0,t) = x_{f,i}^{in}(t), \qquad (2.20)$$

$$k_{c,i}a_s(c_{f,i}-c_{s,i}) = D_{e,i}\frac{\partial x_{s,i}}{\partial r}\Big|_{r=r_s},$$
(2.21)

and
$$\vartheta_k(r = r_s, t = 0) = \vartheta_{k,0}(z)$$
; (for CZO, $k = CZO_2$ and $CZO_{1.85}$, for MFO, $k = 0$

$$MFO_4, MFO_3 \text{ and } MFO_{0.5}$$
). (2.22)

2.4.2 Dual-Layer Monolith Reactor Model

The non-isothermal 1+1D reactor model is used to model CO modulation results collected in flow experiments. The model comprises full convection-diffusion-reaction model formulation for species balance and reduced two-phase model formulation for energy balance. As pointed out by previous literature [79], the transverse temperature gradient in solid (washcoat and monolith substrate) are negligible, hence it is reasonable to apply the standard two-phase model with lumped capacitance for energy balance. Fig. 2.4 shows the schematics of the PGM-Spinel dual-layer monolith.

The species i fluid phase balance is given by

$$\frac{\partial x_{f,i}}{\partial t} = -u_f \frac{\partial x_{f,i}}{\partial z} - \frac{k_{me,i}}{R_{\Omega 1}} \left(x_{f,i} - x_{wc,i} \right), \tag{2.23}$$

where $x_{f,i}$, $x_{wc,i}$, u_f , $k_{me,i}$ and $R_{\Omega 1}$ are concentration of species i in gas phase and washcoat surface, average fluid velocity, external mass transfer coefficient of specie i and the effective transverse diffusion length for flow area, respectively. The external mass transfer coefficient is given by

$$k_{me,i} = \frac{D_{f,i}Sh_{e,\infty}}{4R_{\Omega 1}},\tag{2.24}$$

where $D_{f,i}$ is the temperature dependent gas phase diffusivity of species i estimated from Lennard-Jones expression and $Sh_{e,\infty} = 3.608$ for round square channel.



Figure 2.4 Schematic of dual-layer monolith catalyst.

The washcoat species balance in PGM and spinel layers are given by the following two equations respectively:

$$\varepsilon_{PA} \frac{\partial x_{PA,i}}{\partial t} = D_{e,PA} \frac{\partial^2 x_{PA,i}}{\partial y^2} + \frac{1}{c_0} \sum_{j=1}^r v_{PA,i,j} r_{PA,i,j}$$
(2.25)

and
$$\varepsilon_{SA} \frac{\partial x_{SA,i}}{\partial t} = D_{e,PA} \frac{\partial^2 x_{SA,i}}{\partial y^2} + \frac{1}{c_0} \sum_{j=1}^r v_{SA,i,j} r_{SA,ij},$$
 (2.26)

where ε_{PA} and ε_{SA} are porosity of PGM and spinel layers, $D_{e,PA}$ and $D_{e,SA}$ are effective diffusivity in PGM and spinel layers, $x_{PA,i}$ and $x_{SA,i}$ are concentration of species j in PGM and spinel layers, v_j and r_j are stoichiometry of species i in reaction j and the rate of reaction j, respectively. The effective diffusivity is estimated by the expression as

$$D_{e,i} = \frac{D_{f,i}}{\lambda}.$$
(2.27)

Here λ is chosen as 30, similar to the values reported in previous literature [68].

The site balance of MFO in monolith samples is also given by Eqns. (2.16 ~ 2.18). The energy balance in fluid is given by

$$\frac{\partial T_f}{\partial t} = -u_f \frac{\partial x_f}{\partial z} - \frac{1}{R_{\Omega 1}} \frac{h}{\rho_f C_{pf}} (T_f - T_s), \qquad (2.28)$$

where ρ_f , C_{pf} , h, T_f and T_s are fluid density, heat capacity of fluid, heat transfer coefficient between fluid and washcoat phase, fluid temperature and solid (washcoat and support) temperature respectively.

The energy balance in solid is given by

$$R_{\Omega w}\rho_{w}C_{pw}\frac{\partial T_{s}}{\partial t} = R_{\Omega w}k_{w}\frac{\partial^{2}T_{s}}{\partial z^{2}} + h(T_{f} - T_{s}) + \int_{0}^{\delta_{PA}} \left(\sum_{j=1}^{r} r_{j}(-\Delta H_{j})\right)dy + \int_{\delta_{PA}}^{\delta_{wc}} \left(\sum_{j=1}^{r} r_{j}(-\Delta H_{j})\right)dy,$$

$$(2.29)$$

where $R_{\Omega w}$, ρ_w , C_{pw} , k_w , h, ΔH_j are effective wall thickness, wall density, heat capacity of the wall, heat conductivity of wall, heat transfer coefficient and enthalpy of reaction j, respectively. The effective wall heat capacity and thermal conductivity [80] are calculated by $R_{\Omega w}\rho_w c_{pw} = R_{\Omega c}\rho_c c_{pc} + R_{\Omega s}\rho_s c_{ps}$ and $R_{\Omega w}k_w = R_{\Omega c}k_c + R_{\Omega s}k_s$. Here the subscripts c and s refer to catalyst (washcoat) and support respectively.

The initial, inlet and boundary conditions for species balance are given as follows:

$$x_{f,i}(z=0) = x_{f,in}(t), \qquad (2.30)$$

$$x_{PA,i}(t=0) = x_{PA,0}(z), (2.31)$$

$$x_{SA,i}(t=0) = x_{SAA,0}(z),$$
 (2.32)

$$\vartheta_k(r = r_s, t = 0) = \vartheta_{k,0}(z), \text{ here } k = MFO_4, MFO_3 \text{ and } MFO_{0.5},$$
 (2.33)

$$-D_{e,PA,i} \frac{\partial x_{PA,i}}{\partial y}\Big|_{y=0} = k_{me,i} (x_{f,i} - x_{s,i}), \qquad (2.34)$$

$$x_{PA,i}(y = \delta_{PA}) = x_{SA,i}(y = \delta_{PA}),$$
 (2.35)

$$-D_{e,PA,i} \frac{\partial x_{PA,i}}{\partial y}\Big|_{\delta_{PA}} = -D_{e,SA,i} \frac{\partial x_{SA,i}}{\partial y}\Big|_{\delta_{SA}},$$
(2.36)

and
$$\frac{\partial x_{SA,i}}{\partial y}\Big|_{y=\delta_{PA}+\delta_{SA}} = 0.$$
 (2.37)

The initial, inlet and boundary conditions for species balance are given as follows:

$$T_{f,i}(z=0) = T_{f,in}(t),$$
 (2.38)

$$T_{f,i}(t=0) = x_{f,0}(t),$$
 (2.39)

$$T_{s,i}(t=0) = x_{f,0}(t),$$
 (2.40)

and
$$\frac{\partial T_s}{\partial y}\Big|_{0,L} = 0.$$
 (2.41)

2.5 Other Reactor Model Blocks

2.5.1 Axial mixing before the monolith

The axial mixing upstream of the monolith will cause the overlap of lean/rich pulses. Such mixing will cause additional reactions, for example direct CO oxidation between CO and O_2 pulses. To account the upstream mixing impacts into the modeling study, the modulated feed conditions under axial dispersion is first determined.

For fixed bed reactor modeling, the feed profile with axial dispersion upstream of the monolith is determined by solving the following equation as

$$D^* \frac{\partial^2 x}{\partial z^2} - u \frac{\partial x}{\partial z} = \frac{\partial x}{\partial t},$$
(2.42)

where D^* is the effective dispersion coefficient and u is the superficial velocity. Since the flow in the fixed-bed reactor is laminar (Re ~ 60), the effective dispersion coefficient is determined by the Aris-Taylor dispersion coefficient (Eqn. 2.43) as

$$D^* = D_f + \frac{u^2 r^2}{48D_f},\tag{2.43}$$

where u is the fluid velocity, r is the radius of tube and D_f is the binary diffusion coefficient.

For monolithic reactor modeling, the impact of axial dispersion is accounted using the method applied by Ting and his coworkers [24]. In the method, a smooth curve replaces the ideal step change of feed concentrations. A finite sine wave with calculated dispersion time is used to represent the unbounded Gaussian distribution. In this study, the dispersion time is determined as 0.3 s.

2.5.2 Axial mixing in the FTIR gas cell

In flow experiments of dual-layer PGM/Spinel monolith, FTIR is used for signal measurement. Such mixing in FTIR gas cell will impact the experimental measurement and data analysis [24][70]. The gas cell has a volume of 200 mL and an average holdup time is ~ 1.67s with a total flowrate of 7.2 L/min. By assuming ideal CSTR mixing, the CSTR model equation is implemented in model blocks as

$$\frac{dC_{mix}(t)}{dt} = \frac{C_{eff}(t) - C_{mix}(t)}{\tau_{cell}}, \qquad (2.44)$$

where τ_{cell} is the holdup time in FTIR gas cell, $C_{eff}(t)$ and $C_{mix}(t)$ are effluent concentration before and after gas cell respectively.

Chapter 3 Impact of Cycling on NO Reduction on Ceria

In this chapter, the impacts of cycling frequency on NO reduction on ceria are discussed. The findings are interpreted to advance the understanding for the working mechanism of the Di-Air (Diesel NOx Aftertreatment by Adsorbed Intermediate Reductants) system.

3.1 Impact of Reductant Type and Cycle Frequency in Absence of O₂

Results with each of the three reductants (CO, H₂ and C₃H₆) were first conducted to quantify their differences. (Selected experiments described later include CO_2 and/or H₂O.) Fig. 3.1 (a) shows the cycle-averaged NO conversion as a function of feed temperature obtained with CO as reductant for cycle times of 90/15s and 6/1s at a fixed rich duty cycle of 14.3%. Nearly identical results were obtained for each cycle time with a high temperature of at least ~450 °C for ceria to get a conversion above 30%. NO conversion increased monotonically with feed temperature, and complete conversion was achieved at ~ 600 °C. The conversion under the fastest cycling (6/1) was only slightly higher (\sim 5%) than for the 90/15 cycle. For both cycle times the NO was mainly converted to N₂ with only trace amounts of NO₂ and N₂O detected. In comparison, a ~1wt.% Pt/CeO₂ monolith with similar ceria and washcoat loading leads to complete conversion by ~250 ^oC for similar conditions (results in Chapter 4). In the absence of H₂O, N₂ and N₂O are the only NO reduction products. Fig. 3.1 (f) shows the corresponding CO conversion as a function of feed temperature. Similar to the NO conversion, the CO conversion increased monotonically with feed temperature with little difference between the two cycle times.



Figure 3.1 Cycle-averaged NO and reductant conversions and NH₃ selectivity as a function of feed temperature with (a) CO, (b) H₂, and (c) C₃H₆ as reductant. [Lean feed: 500 ppm NO; Rich feed: 500 ppm NO, 2.5% CO or 2.5% H₂ or 2778 ppm C₃H₆].

Figs. 3.1 (b) and 3.1 (c) show the NO conversion, respectively using H₂ or C₃H₆ as the sole reductant, for cycle times from 90/15s to 6/1s. As for CO (Fig. 3.1 (a)), the NO conversion increases with feed temperature and lean/rich switching frequency although the cycle time impact is much more pronounced. As the cycle timing is varied from 90/15 to 6/1s the NO conversion increases by ~20% (absolute) for H₂ and ~35% for C₃H₆ over the entire range of feed temperatures. Figs. 3.1 (d) and 3.1 (e) show the corresponding NH₃ selectivity (for H₂ or C₃H₆). NH₃ and N₂ are major products with only trace amounts of NO₂ and N₂O detected. The NH₃ selectivity is sensitive to cycle timing above 600 °C with the selectivity increasing with decreasing cycle time. For H₂ the dependence of NH₃ selectivity exhibits a maximum versus temperature for all cycle timing except 6/1. The H_2 results are consistent with previously proposed [81][82] pathway which involves the dissociative adsorption of H_2 on ceria and formation of H_2O :

$$H_2 + 2O \rightleftharpoons 2HO$$
 (R3.1)

and
$$2\text{HO} \rightleftharpoons \text{H}_2\text{O} + \text{O} + \square$$
. (R3.2)

Here O· represents the basic anionic O²⁻ site and \Box · represents a vacancy site. From DFT calculations, Chen et al. [83] and Watkins et al. [84] showed that the dissociative adsorption of H₂ on ceria (R3.1) is an exothermic reaction while the formation of H₂O (R3.2) is endothermic. With H₂ as the reductant, NO can either react with adsorbed H to form NH₃ or decompose to N₂ with the product oxygen adatoms filling vacancies:

$$NO + * \rightleftarrows NO^*, \tag{R3.3}$$

$$2NO^* + \Box \cdot \rightleftharpoons N_2 + O \cdot + 2^*, \tag{R3.4}$$

and NO* + 3HO·
$$\rightleftharpoons$$
 NH₃ + 3O· + *. (R3.5)

where * represents an acidic cationic Ce⁴⁺ site. At low temperatures, the reduction of ceria is mainly confined to the surface with the generation of surface vacancies and surface hydroxyls HO·. In contrast, at high temperatures, the reduction of ceria first starts with surface reduction and then continues with consumption of bulk oxygen. While HO· is available for NO reduction at all temperatures, more vacancy sites are available at high temperatures. Moreover, the rate of hydrogen desorption through the reverse of (R3.1) increases with temperature. Thus, at high temperatures, NO has a higher probability to decompose on vacancy sites to form N₂ than to react with HO· to form NH₃. Therefore, NH₃ selectivity decreases with feed temperatures in the high temperature range (i.e., >600C). The fastest cycling frequency (6/1s) gives the highest NH₃ selectivity. As ceria reduction consists of two steps (R3.1 and R3.2), there is less time for the HOdesorption enabling more NO to form NH_3 via (R3.5).

Fig. 3.1 (g) shows the $C_{3}H_{6}$ conversion as a function of feed temperature for all four cycle times. Similar to NO conversion (Fig. 3.1 (c)), C₃H₆ conversion increases with both feed temperature and cycle timing. The different dependence of NH₃ selectivity on temperature compared to H_2 is explained by the different reactivities of H_2 and C_3H_6 on ceria. Wang et al. [26] used a TAP reactor to study the reduction of ceria by different reductants (CO, H_2 and C_3H_6). They pointed out that C_3H_6 is a better reductant than H_2 . $C_{3}H_{6}$ produces carbonaceous surface deposits which react with oxygen from the ceria lattice. Indeed, Figs. 3.1 (b) and 3.1 (c) show that at the same temperature and cycling frequency, NO conversion obtained with C₃H₆ exceeds that obtained with H₂. As discussed in previous studies [26][85], ceria reduction by C₃H₆ involves a series of steps. In the first step H is extracted leading to the formation of HO \cdot as in the case of H₂ (step R3.2 above). Also, as for H₂, enhancement of NH₃ selectivity by fast cycling increases with feed temperature. The higher reactivity of C₃H₆ on ceria results in a lower temperature for bulk oxygen reduction compared to H₂. As a result, the dependence of NH₃ selectivity on cycling frequency with C₃H₆ is sensitive before 600°C, when NH₃ selectivity in H₂ case starts to show dependence of cycling frequency.

Detailed transient effluent composition data provide more insights than cycleaveraged data. Figs. 3.2 (a), 3.2 (b) and 3.2 (c) show the effluent concentrations of NO, CO, CO₂, NH₃ and C₃H₆ for the 90/15s cycling using CO, H₂ or C₃H₆ as a sole reductant at 500 °C, 600 °C and 625 °C respectively. Results at different temperatures are shown to emphasize various points. For example, Fig. 3.2 (a) shows transient behavior with CO as reductant at 550°C because NO conversion is ~100% at 600°C or higher. Moreover, since the impact of fast cycling on NO conversion and NH₃ selectivity are amplified at higher temperatures (i.e., 650° C). Fig. 3.2 (a) shows that the intermittent feed of CO is effective in reducing the NO continuously-fed throughout the entire cycle. During the rich feed, the NO is quickly reduced to an undetectable level within ~7s. The protracted NO "tail" is attributed to the mixing in the FTIR gas cell. The FTIR cell mixing resulted in a ~ 20s tail. During the lean phase NO breakthrough occurred ~30s into the lean feed. Oxidation product CO₂ reached a maximum during the first part of the rich feed and approached zero during the early lean feed. Its breakthrough ~30s into the lean feed coincided with the appearance of the aforementioned NO.

The presence of CO and CO₂ leads to a complex chemistry on ceria. Trovarelli [38] showed that CO adsorption on ceria leads to oxygen vacancies, linearly adsorbed CO and surface carbonites [Ce(CO₂)₂]. CO₂ adsorption can lead to surface carbonates [Ce(CO₃)₂]. Thus, NO fed during the lean part of the cycle can react with both vacancies and adsorbed CO leading to N₂ and CO₂ formation. Indeed, Fig. 3.2 (a) shows long tails of CO and CO₂ when the feed was switched from rich to lean. There are at least four possible explanations for the protracted, declining of CO and CO₂ concentrations.

The first reason concerns mixing of product in the FTIR gas cell which has a residence time of ~4s. The mixing attenuates and broadens the peaks.

(R3.3) together with (R3.6) and (R3.7):

$$CO + * \rightleftharpoons CO^*$$
 (R3.6)

and NO* + CO*
$$\neq \frac{1}{2} N_2 + CO_2 + 2^*$$
. (R3.7)

That Fig. 3.2 (a) shows neither NO nor CO_2 present at the start of the lean feed (i.e., 30 - 45s) suggests that NO is efficiently converted on the reduced ceria by decomposition on surface vacancies (reaction (R3.4)) rather than by reaction with adsorbed CO.



Figure 3.2 Effluent concentration profiles for a set of cycling experiments with different reductants: (a) CO, (b) H₂, (c) C₃H₆). [Lean feed: 500 ppm NO; Rich feed: 500 ppm NO and (a) 2.5% CO, (b) 2.5% H₂ or (c) 2778 ppm C₃H₆]

A third possible reason for the sustained appearance of CO and CO₂ during the lean involves competitive adsorption between NO, CO and CO₂.Binet et al. [86] and Lavalley et al. [87] studied the surface properties of ceria in both reduced and oxidized states using several probe gases. Components CO, NO and O₂ [88], act as electron donors and adsorb on acidic cationic centers (Ce⁴⁺). CO₂ can serve as both a Lewis acid and an σ electron donor and be adsorbed on both basic anionic centers (O²⁻) and Ce⁴⁺. Hence, CO₂ adsorption results in several surface species, including linear adsorbed CO₂ on cationic sites, weakly bound, bridged carbonates (CO₃²⁻) and strongly bound, polydentate carbonates on anionic sites, the last of which becomes predominant through bulk-like carbonate species formation upon heating. To this end, adsorption occurs on the cationic Ce⁴⁺ sites (*) by NO (R3.3), CO (R3.6) and CO₂ (R3.8), along with CO₂ adsorption on the basic anionic O²⁻ site (R3.9):

$$\text{CO}_2 + * \rightleftarrows \text{CO}_2 *$$
 (R3.8)

and
$$\operatorname{CO}_2 + \operatorname{O}_2 \rightleftharpoons \operatorname{CO}_3$$
. (R3.9)

Thus, when the feed is switched from rich to lean, NO competes with both CO and CO₂ for adsorption sites, which can lead to some desorption of CO and CO₂.

The fourth possible reason for the sustained generation of CO_2 during the lean feed may be attributed to the decomposition of bulk cerium carbonates formed during exposure of CO to the ceria in the preceding rich period. Previous studies[89][90] show that cerium carbonates can decompose to CeO₂ and CO₂ in an oxidizing environment below 600 °C. This suggests that cerium carbonate has a lower thermal stability than ceria. Padeste et al. [89] reported that compared to a reducing or inert environment, an oxidizing environment is favorable to the decomposition of cerium carbonates, with the temperatures for total decomposition as ~300 °C in the oxidizing environment and ~550 °C in the reducing or inert environment. Binet et al. [86] reported that the adsorption of CO_2 on reduced ceria resulted in formation of bulk-like carbonate species. Results show that after the feed was switched from lean to rich, vacancies were consumed and filled by O, cerium carbonates were decomposed, forming CO_2 . This is confirmed by the coincident slip of NO and CO_2 during the lean phase.

As seen in Figs. 3.2 (b) and 3.2 (c), NO is also converted throughout the cycle when H_2 or C_3H_6 is the sole reductant. NH₃ is detected as a major product for H_2 due to the overall rich conditions throughout the cycle. For both reductants, NH₃ is generated continuously. However, for H_2 , the NH₃ reaches a maximum by the end of the rich phase, while for C_3H_6 NH₃ reaches a maximum during the rich phase (~20s in total cycle and ~5s in lean phase). Other detected species include CO, CO₂ and C₃H₆. Unreacted C₃H₆ is mostly detected during the rich phase. CO is detected in the propylene experiments, indicating that partial oxidation of C₃H₆ occurs as CO is only observed during the rich feed. In contrast, CO₂ is observed throughout the entire cycle, with a maximum at the beginning of the rich phase and continuous generation at a lower concentration during the lean feed. Since H₂ or C₃H₆ are only fed during the rich part of the cycle, continuous generation of NH₃ and CO₂ during the lean phase (Figs. 3.2 (b) and 3.2 (c)) suggests that H₂ and C₃H₆ generate reactive intermediates, which are adsorbed on reduced ceria and further utilized to reduce NO during the lean feed.

Figs. 3.3 (a) -3.3 (f) show transient results with H₂ as the sole reductant at 650°C. The impact of cycle time with H₂ as the reductant is determined by comparing the long cycle (90/15) (Fig. 3.3 (a)) with the shorter cycles in Figs. 3.3 (b) (60/10) and 3.3 (c) (30/5).



Figure 3.3. Effluent concentrations in cases with H₂ as reductant but with different lean/rich switching frequencies. [Conditions: switching frequencies: 90/15s, 60/10s and 30/5s; lean feed: 500 ppm NO; rich feed: 500 ppm NO, 2.5% H₂].

While a longer rich feed leads to a longer period of complete NO conversion, a long lean feed leads to a large breakthrough of NO. Fig. 3.3 column (II) shows that faster cycling results in a later NO breakthrough in the scale of normalized time (t/τ_{total}) where τ_{total} is the total time of a lean/rich cycle. As the reduction of ceria first starts with surface oxygen consumption and then proceeds with bulk oxygen consumption, a longer rich phase results in consumption of more lattice oxygen. Since the consumption rate of bulk oxygen is slower than that of surface oxygen due to solid state diffusion limitations, the overall oxygen consumption efficiency (i.e., total amount of consumed oxygen/rich time) from a longer rich phase is inferior to that of a shorter rich feed. Therefore, NO slips later with faster cycling in the normalized time scale and overall NO decomposition efficiency increases with faster cycling. To state it in another way, shorter cycles have a net beneficial impact on NO conversion due to the more efficient utilization of the reduced ceria surface sites. The data also show that the NH₃ concentration peaks at the end of the rich feed and slowly declines during the lean feed. This suggests a rather slow release of hydrogen from the ceria enabling a sustained generation of ammonia throughout the lean period.

The schematics Figs. 3.4 (a) - 3.4 (c) depict pathways for cyclic NO reduction over ceria with CO, H₂, or C₃H₆ as the sole reductant in the absence of feed O₂., CO reacts with oxygen on the ceria during the rich feed, generating surface vacancies. A combination of adsorption and reaction steps involving adsorbed CO and NO generate NO reduction product N₂ and CO oxidation product CO₂; the steps include adsorbed NO dissociation at the aforementioned vacancies to N₂ and O adatoms, followed by N adatom recombination to N₂ and CO oxidation by O to CO₂, along with direct reaction between adsorbed CO and NO, generating additional N₂ and CO₂. This follows from earlier studies. For example, Breysse et al. [91] proposed a two-step mechanism of ceria reduction by CO, which includes the adsorption of CO and generation of oxygen vacancies. As discussed earlier, Trovarelli [38] showed that on fully oxidized ceria, CO adsorption results in formation of linear CO, carbonate and carboxylate. In contrast, on partially reduced ceria, the primary adsorbates are linear CO and carbonite while formation of carbonate and carboxylate is strongly inhibited due to lack of surface oxygens.



Figure 3.4 Working mechanism of NO reduction over ceria with (a) CO, (b) H₂ or (c) C₃H₆ as reductant and without O₂ in lean stream; (d) The reduction process of a ceria particle by CO.

During lean/rich cycling with H₂ as reductant (Fig. 3.4 (b)), the rich phase H₂ adsorbs on and reacts with ceria, generating oxygen vacancies and adsorbed hydrogen. This follows the study of El Fallah et al. [81] who proposed a ceria reduction pathway with H₂, which includes adsorption of H₂, formation of hydroxyl groups, and generation of oxygen vacancies. Binet et al. [86] reported the formation of different types of hydroxyl species on H₂-reduced ceria. As in the case of CO, NO in the feed replenishes oxygen vacancies through its decomposition. The resulting N and H adatoms react, forming N₂ and NH₃. Direct reaction between H and NO certainly cannot be ruled out

With C₃H₆ as the sole reductant (Fig. 3.4 (c)), similar but more complex chemistry occurs than with H₂. Wang et al. [26] discussed C₃H₆ activation steps on ceria, which include formation of hydrocarbon fragments, hydrogen atoms and oxygen-containing hydrocarbon intermediates. It is of interest to determine how this chemistry is manifested over a range of cycle times and feed temperatures. Exposure of oxidized ceria with C₃H₆ results in a series of adsorption and reaction steps involving hydrocarbon intermediates from C₃H₆ activation, forming CO, CO₂, H₂O and oxygen vacancies. In the presence of NO, N₂ production occurs through NO dissociation on reduced ceria sites and N adatom recombination, along with reaction between adsorbed NO and CO and hydrocarbon intermediates. NH₃ is produced by reaction of adsorbed N and NO with H. Meanwhile, CO, CO₂ and H₂O are generated during the rich phase while only CO₂ and H₂O are generated during the rich phase while only CO₂ and H₂O are generated during the lean phase.

For each reductant, oxygen vacancies and surface intermediates, such as CO and hydrocarbon fragments are generated via reduction of ceria. By the end of the rich feed, oxygen vacancies are available to react with NO fed during the ensuing lean feed. This generates N₂ through NO dissociation while NH₃ is produced through reaction of NO and residual hydrogen-containing intermediates. The anaerobic conditions are not favorable for N₂O production. Later the impact of O₂ on this mechanism is examined.

An increase in cycle frequency (decrease in cycle time) increases the cycleaveraged NO conversion for each reductants (Figs. 3.1 (a) – 3.1 (c)). The increasing NO concentration during the lean feed for each case (Figs. 3.2 (a) – 3.2 (c)) suggests that the rate of NO conversion declines as the ceria is oxidized. As described above, NO adsorption and dissociation occur at reduced ceria sites. As the surface vacancies are depleted, subsurface vacancies must be utilized. However the proximity of oxygen adatoms to the subsurface sites requires an additional diffusion step. Previous studies showed that two peaks existed during temperature-programmed reduction experiments on ceria with CO [36] and H₂ [38]. The two peaks are attributed to surface and lattice oxygen, respectively. The reduction of ceria occurs only on the surface and the bulk oxygen is extracted by diffusion from the lattice to the surface [33][92]. This process, depicted schematically in Fig. 3.4 (d), leads to a slower NO decomposition which in turn leads to an earlier NO breakthrough during the lean part of the cycle. In fast cycling, the process relies less on the lattice diffusion process. Under fast lean/rich switching frequency, surface oxygen vacancies and adsorbed intermediates are generated more efficiently by the reductant and thus utilize more efficiently by NO. This is similar to the improved utilization of NOx storage sites during fast lean-rich cycling in a lean NOx trap [24].

Faster cycling also leads to higher NH₃ selectivity when using H₂ or C₃H₆ as the sole reductant (Figs. 3.1 (d) and 3.1 (e)). This trend suggests that the surface becomes more favorable for the sequential reactions N + H, NH + H, and so on. With a longer cycle, the availability of both N and H decreases as a result of H₂ desorption. Accordingly, NH₃ selectivity increases with faster lean/rich switching frequency and N₂ selectivity decreases.

3.2 Impact of reductant type and cycle frequency in presence of O₂

Exhaust feed always contains O₂.during cyclic operation. Impact of O₂ on NOx reduction are examined over a range of cycle times and feed temperatures.



Figure 3.5 Cycle-averaged NO and CO conversion in cases with CO as reductant and O₂ in lean stream. [Conditions: 6s lean/1s rich; lean: 500 ppm NO, varied concentration of O₂, balance Ar; rich: 500 ppm NO, 2.5% CO, balance Ar].

Figs. 3.5 (a) and 3.5 (b) show the cycle-averaged NO and CO conversion, respectively, as a function of feed temperature for a fixed cycle time of 6/1s with CO as sole reductant and a varied concentration of O₂ during the lean feed. The S_N =0.14, O₂-devoid feed gives an upper bound for the NO conversion and lower bound for the CO conversion over the entire temperature range. For each O₂ concentration (fixed S_N value) the NO conversion increases monotonically with feed temperature while for a fixed temperature the NO conversion decreases monotonically with increasing S_N. The latter decrease is rather sharp, such that for S_N = 1.87 the NO conversion does not exceed 25% at any temperature. Overall, the impact of O₂ is detrimental to NO conversion, especially

at low feed temperatures. On the other hand, the NO conversion in the stoichiometric case $(S_N=1)$ and slightly lean case $(S_N=1.15)$ exceeds 25% when the feed temperature is higher than 550°C. This suggests that NO can be efficiently reduced by CO in a slight stoichiometric excess of O₂ at high temperatures. A similar dependence of NO conversion trends on temperature and S_N are observed for cases with lean/rich switching frequencies of 90/15s, 60/10s and 30/5s. That is the NO conversion decreases with both decreasing temperature and increasing S_N.

For each O₂ concentration (S_N) the CO conversion increases monotonically with feed temperature (Fig. 3.5 (b)), while for a fixed temperature it decreases monotonically with increasing S_N . The latter S_N trend is attributed to two factors; namely, consumption of surface oxygen sites and axial dispersion. Breysse et al. [91] pointed out that for CO oxidation on pure ceria, with an O2 abundant feed, the partial order with respect to oxygen is zero. Sayle et al. [93] did computational studies and concluded that in the process of CO oxidation via ceria, the usage of surface oxygen is more favored than that of bulk oxygen. With a cycle-averaged rich feed (i.e., $S_N = 0.14$), ceria reduced by excess CO fed in rich cannot be fully reoxidized by oxidants (NO and O₂). The reduced ceria surface lacks surface oxygens and thus hinders CO oxidation. In contrast, with a cycle-averaged lean feed (i.e., $S_N = 1.15$ or 1.87), ceria reduced by insufficient CO fed in rich can be fully reoxidized by oxidants (NO and O_2). The abundance of surface oxygen enables high CO oxidation activity and high CO conversion. In cases with excess reductants and limited oxidants, with higher $S_N(O_2)$ surface vacancies are more easily replenished during the lean period enabling a more efficient CO oxidation during the rich period. Meanwhile, CO oxidation is more effective with increased mixing of the rich and lean feeds during the
faster cycling. This is evident from the sharp increase in CO conversion as S_N is increased from 0.14 to 0.81. The increased contacting of CO and O₂ at the leading and trailing transitions between the rich and lean feeds has a large impact for the overall rich feed. The slight increase of CO conversion from $S_N = 1.00$ to 1.87 may result from the additional reductant consumption from axial dispersion. These results are consistent with earlier results that showed CO reacts readily with oxidized ceria. For a lean feed, CO is the limiting reactant which leads to incomplete reduction of ceria, resulting in a decrease in NO conversion. At this point, it is instructive to examine the competitive reactivity of NO and O₂ in a mixed feed situation.



Figure 3.6 Effluent profile of NO in cases with CO as reductant and O₂ in lean stream at 500°C. [Conditions: 90s lean/15s rich; lean: 500 ppm NO, varied concentration of O₂, balance Ar; rich: 500 ppm NO, 2.5% CO, balance Ar].

Fig. 3.6 shows the effluent NO profiles for varied S_N , fixed lean/rich switching frequency of 90/15s, CO as reductant, and feed temperature of 500 °C. For a lean feed devoid of O₂ (S_N =0.14), NO decreases to a negligible level from its maximum of ~280 ppm before the end of the rich feed. It reappears about 10 seconds after the start of the lean feed,

increasing to its maximum by the end of the lean period. This trend suggests that NO is reduced completely during the rich feed and partly throughout the lean feed. However, as O_2 is added to the lean feed with increasing concentration, there is a sharp increase in the effluent NO concentration, approaching the feed value (500 ppm) during the latter part of the lean period and into the rich period. In fact, for the highest O_2 feed concentration case (S_N =1.87), the, NO concentration decreases slightly due to its oxidation to NO₂. With increasing S_N the NO decrease during the rich is slower and the breakthrough during the lean is quicker.



Figure 3.7 Effluent profile of NO, O₂, CO and CO₂ in cases with CO as reductant at 625°C, lean/rich switching frequency (a) 90/15s, (b) 60/10s. [Conditions: lean: 500 ppm NO, 700 ppm O₂, balance Ar; rich: 500 ppm NO, 2.5% CO, balance Ar].

This detrimental impact of O_2 on NO reduction is a result of oxidation of ceria by O_2 and a resulting decrease in the concentration of surface vacancies. Previous studies showed that both O_2 [85] and NO [94] can oxidize reduced ceria in a mixture, suggesting a competition between NO and O_2 for oxygen vacancies. Wang et al. [95] showed that NO

slipped before O_2 when NO and O_2 were fed together to a pre-reduced powder ceria under vacuum conditions in a TAP reactor. This issue was examined in more detail for the case of lean-rich cycling to a ceria-washcoated monolith at atmospheric pressure. The effluent concentrations of NO and O₂ were measured during cycling using a feed with S_N=0.48 (500 ppm NO, 700 ppm O₂), feed temperature of 625°C, and cycling times of 90s/15s (Fig. 3.7 (a)) and 60/10s (Fig. 3.7 (b)). In both experiments neither NO nor O₂ were detected at the beginning of the lean period. Eventually NO breakthrough occurred, followed by O₂. For the 90/15s cycle (Fig. 3.7 (a)), NO slipped ~ 29 s after the start of the lean feed while O_2 slipped after ~50 s. For the 60/10s cycle (Fig. 3.7 (b)) the NO and O_2 breakthrough occurred at ~ 25 and ~ 45 s after the start of the lean feed. The period of no NO or O₂ confirmed that both NO and O_2 adsorb and react at oxygen vacancies. The sequential slip of NO followed by O_2 suggests that O_2 is a more potent oxidant than NO. Furthermore, the somewhat later NO and O₂ slip for the 60/10s cycle compared to the 90/15 cycle suggests a more efficient regeneration with a shorter cycle. Figs. 3.7 (c) and 3.7 (d) shows the effluent profiles of CO and CO₂ with two cycling frequencies. Similar to the case without O_2 in lean feed (Fig. 3.2 (a)), CO reaches a maximum at the end of lean phase and keeps decreasing in rich phase. CO₂ reaches a maximum in rich phase and then keeps decreasing until the breakthrough time of NO (~45s for 90/15s case and ~35s for 60/10s case). Along with the breakthrough of NO, a small amount of CO_2 (100 ~ 200 ppm) is continuously generated, which could be contributed to the reaction between adsorbed CO and fed oxidants (NO and O_2). The late slip of CO_2 in the middle rich phase suggests that oxidants (NO and O₂) first react with surface vacancies than adsorbed CO on reduced ceria surfaces.



Figure 3.8 Cycle-averaged NO and CO conversion with CO as reductant and O₂ in lean stream. [Conditions: lean/rich: 90/15s, 60/10s, 30/5s, 6/1s; rich: 500 ppm NO, 2.5% CO; lean: (a) 500 ppm NO, 1400ppm O₂,; (b) 500 ppm NO, 2100ppm O₂].

When O_2 is introduced into the lean feed, an optimal lean/rich switching frequency exists which changes with feed temperature and feed composition (S_N). Fig. 3.8 compares the cycle-averaged NO and CO conversion as a function of feed temperature for cycle times spanning 90/15s, 60/10s, 30/5s and 6/1s at a fixed rich cycle duty (14.3%). Two different O₂ concentrations are considered; 1400 ppm corresponding to an overall rich feed case (S_N = 0.84; Figs. 3.8 (a), 3.8 (b)) and 2100 ppm corresponding to an overall lean feed case (S_N = 1.15; Figs. 3.8 (c), 3.8 (d)). For the rich case the longest cycle (90/15) gives the highest cycle-averaged NO conversion for feed temperatures at or below 500 °C, although the conversion is quite low for all the cycle times. On the other hand, above 500 °C a shortest cycle is most effective. In the latter regime the NO conversion increases significantly with decreasing cycle time, approaching nearly complete conversion for the 6/1 cycle at 625 °C. For the overall lean case the temperature regime giving short cycle enhancement is confined to 600 °C and higher. However, the optimal lean/rich cycle is 30/5 at a feed temperature of 500°C and 550°C. At lower temperatures the optimal cycle is 90/15s or 60/10s. In comparing Figs. 3.8 (a) and 3.8 (c, it is clear that the optimal lean/rich switching frequency changes from 6/1s to 30/5s as S_N increases from 0.84 to 1.15. The corresponding CO conversion for both cases (Figs. 3.8 (b), 3.8 (d)) do not show the transition as observed for NO.



Figure 3.9 Working mechanism for NO reduction over ceria with CO as reductant and O₂ in lean stream.

Based on these data and the relevant literature [85][91][96], a cyclic mechanism is proposed, depicted in Fig. 3.9, for NO reduction over ceria with CO as sole reductant and O_2 as an extra oxidant in lean. The mechanism assumes that N_2 is the main product of NO conversion. N₂O and NO₂ were detected as side products along with N₂. However, the amount of N₂O was within the detection limit of the FTIR (~5 ppm) and NO₂ yield was only ~1%. At the beginning of the lean phase, and when ceria is in its most reduced state during the cycle, fed NO is converted to N₂ through its decomposition on surface vacancies or reaction with CO that remains on the surface. O₂ competes with NO for said vacancies and adsorbed CO. During the rich feed, N₂ is generated by NO reduction and CO₂ by CO oxidation as ceria becomes more oxidized and surface vacancies filled, the reduction of NO to N₂ shifts to its oxidation by surface oxygen to NO₂. Upon the switch back to a reducing atmosphere, CO reacts with oxygen, first through scavenging adsorbed O₂ and any NO₂, and then with lattice oxygen. This leads to a progressive reduction of ceria at the more accessible surface region, enabling the commencement of NO decomposition and reaction with adsorbed CO. The proposed cyclic mechanism thus involves four processes; two during the lean feed -- ceria oxidation and oxygen adsorption, and two during the rich feed -- surface oxygen scavenging and ceria reduction by CO.

The cyclic mechanism helps to explain key data features, such as the dependence of the optimal lean/rich switching frequency on feed temperature in Fig. 3.8. At high temperatures (> 600° C), the rate of surface oxygen depletion is fast, which results in nearly instantaneous oxygen depletion at the start of the rich period. However, the reduction slows as the process shifts to one limited by solid state diffusion of lattice oxygen. The increase in NO conversion with higher lean/rich switching frequency results in a better utilization of the surface oxygen vacancies. Rather than waiting for subsurface vacancies to be generated, a switch to the lean feed exposes the NO/O₂ mixture to the most accessible surface sites. This avoids the slower reduction of a longer rich feed and the slower reoxidation during the lean feed. Accordingly, the optimal lean/rich switching frequency above 600° C in Fig. 3.8 (c) is always 6/1s. In contrast, at lower temperatures (< 500° C), a slower ceria reduction requires a longer rich feed to achieve sufficient regeneration of surface oxygen vacancies. A too short rich period leads to an inadequate concentration of vacancies and a lower conversion efficiency of NO during the subsequent lean feed. Thus, the optimal lean/rich switching frequency as shown in Fig. 7c is 30/5s at $550^{\circ}C$ and 90/15s at $450^{\circ}C$ respectively. Furthermore, for a fixed feed temperature, an increase in the O₂ concentration increases the exposure of O₂ to the ceria, which requires a longer rich feed to achieve sufficient regeneration. With insufficient rich time, oxygen vacancies cannot be efficiently generated nor can NO be efficiently reduced. Thus, the optimal lean/rich switching frequency at feed temperature of $550^{\circ}C$ is 6/1s and 30/5s with S_N as 0.84 and 1.15, respectively.

The two-step regeneration during the rich feed helps explain the effluent profile of NO shown in Fig. 3.6. NO fed during the rich feed can only be converted to N₂ through its decomposition at oxygen vacancies or through reaction with adsorbed CO. With an increased O₂ concentration during the lean feed (larger S_N), the ceria surface accumulates more oxygen by the end of lean phase. This requires more CO for subsequent surface scavenging and ceria reduction, further delaying NO reduction. The data show that at a feed temperature of 500°C, the decay of NO during the rich phase is slower with increased S_N.

Previous studies of the Di-Air system showed that upstream mixing of rich and lean feeds has a non-negligible impact on deNOx performance [76][97][30]. In this study, the upstream mixing of lean and rich feeds leads to additional CO consumption through its oxidation which decreases the amount of CO available to reduce the ceria. The adverse impact of mixing increases with increasing lean/rich switching frequency.

The proposed cyclic mechanism presumes the existence of multiple types of oxygen sites defined by their proximity to the external ceria surface. A CO uptake experiment was conducted to examine this issue. Before exposing the ceria catalyst to CO, a cyclic steady state was obtained during sustained lean/rich cycling at a switching frequency of 90/15s and S_N of 0.48. A continuous feed of 250 ppm CO and balance Ar was then applied at the end of the final lean phase upon establishment of the cyclic state.



Figure 3.10 (a) CO uptake profile at 600°C with an inlet gas composition of 250ppm CO.(b) Several possible oxygen sites on ceria: chemisorbed oxygen, surface oxygen sites and bulk surface sites.

The CO uptake profile is shown in Fig. 3.10. The start of the timeline corresponds to the commencement of CO feed. Prior to the run, pseudo steady state was obtained with switching frequency as 90/15s, rich condition as 500ppm NO, 2.5% CO, balance Ar, lean condition as 500 ppm NO, 700 ppm O₂, balance Ar. The CO transient effluent concentration can be broken into three periods in terms of CO uptake. In the first period

(between 0 and ~150s), negligible CO is detected. In the second period (from ~150s to ~500s), CO is detected with an accelerating slippage rate (i.e., to left of inflection point). In the third period (~500s to 3000s), the CO concentration rate continuously declines as it approaches the feed value of 200 ppm. The CO consumption during the first and second periods may be attributed to the consumption of surface adsorbed O_2 , which accumulates during the previous lean phase and surface lattice oxygen sites. The third and slow but observable CO consumption is attributed to consumption of subsurface oxygen within the ceria particles.

3.3 Impact of lean-rich mixing

During lean/rich switching in an NSR system, the extent of mixing has a significant impact on the overall NO conversion. Kabin et al. [45]showed that during lean-rich cycling to a lean NOx trap catalyst that the cycle-averaged NOx conversion approaches two limits when the total cycle time approaches limiting values for a fixed rich duty fraction (d_r). For long cycle time the conversion approaches a weighted average value given by $d_rX_{NOx,r}$ + $(1 - d_r)X_{NOx,l}$ where dr is the duty fraction and $X_{NOx,r}$ ($X_{NOx,l}$) denote the fractional steady state conversion for the rich (lean) feed. For short cycle time the conversion approaches that obtained if the lean and rich feeds are completely mixed.

The impact of the feed composition on the long and short cycle time limits was examined at a feed temperature of 600 °C with CO as reductant. Fig. 3.11 (a) shows that the short cycle time limit exceeds 45% when the feed S_N is equal or less than unity, and decreases sharply to 5% for S_N exceeding unity. This trend clearly shows that a stoichiometric excess of CO is effective in generating surface vacancies for NO

decomposition. In contrast, an excess of O_2 leads to oxidation of CO and inhibition of NO decomposition. The sharp decrease in the short cycle time limits when S_N exceeds 1 indicates that the axial dispersion has a smaller detrimental impact on NO conversion when the cycle-averaged lean feed is applied.



Figure 3.11 (a) short-cycle-time limits and (b) long-cycle-time limits as a function of S_N with CO as reductant at feed temperature of 600°C. [Conditions: rich: 500ppm NO, 2.5% CO; lean: 500 ppm NO, varied concentration of O₂].

Fig. 3.12 (b) shows that a long cycle time limit is much less sensitive to the feed composition, increasing from 14% to 17% as S_N increases from 0.14 to 1.87. Clearly the main factor is the large breakthrough of NO that occurs during a protracted lean feed. Even a very rich regeneration is not able to generate a sufficient supply of vacancies for the NO admitted during the ensuing lean feed.

Next examined is if the long and short cycle time limits were approached as the cycle time was lengthened and shortened, respectively. The NO conversions obtained with two sets of feeds with four different cycle times, 90/15s, 60/10s, 30/5s and 6/1s are compared with the long and short cycle time limits in Fig. 3.12.



Figure 3.12 Cycle-averaged NO conversion as a function of total cycle time at 600°C. The short and long cycle limits are shown as "x" and purple line respectively. [Rich: 500ppm NO, 2.5% CO; lean: 500 ppm NO, (a) 2100ppm or (b) 3600 ppm O₂].

For the lean feed containing 2100 ppm O₂ (Fig. 3.12 (a)) the NO conversion decreases monotonically from a maximum of ~60% at cycle time of 7 s (6/1 cycle). The conversion at 90/15 is 35% which exceeds the limiting value of ~15%. That the 6/1 cycle results in a conversion that is significantly higher than the well-mixed limit of ~5% underscores the benefit of cyclical operation. For the lean feed containing 3600 ppm O₂ (Fig. 3.12 (b)) the NO conversion exhibits a maximum between cycle time of 35 s (38% conversion) and 7 s (20% conversion). The increased O₂ concentration during the lean feed has a detrimental effect on the overall conversion. This trend is consistent with earlier results which showed that O₂ is a better oxidant than NO (Fig. 3.8). The higher O₂ concentration decreases the surface vacancies available for NO decomposition, lowering the NO conversion. Further, as the cycle time is shortened, upstream mixing of the lean and rich feeds has the effect of inhibiting NO conversion and oxidizing CO. The latter effect lessens the effectiveness of the ceria reduction.

3.4 Impacts of CO₂ and H₂O

In practice, lean gasoline and diesel vehicle exhaust contain excess O_2 as well as large amounts of CO_2 and H_2O [87]. CO_2 and H_2O were introduced into the system to more closely mimic real exhausts and to examine their impact on selected performance features.



Figure 3.13 Impact of H₂O and CO₂ on cycle-averaged NO conversion as a function of S_N at 550°C. [Conditions: lean: 500 ppm NO, 700 ppm O₂; rich: 500ppm NO, 2.5% CO. If required CO₂ and H₂O were added into both lean and rich streams.]

Fig. 3.13 shows the NO conversion as a function of S_N with CO as reductant for feeds with or without water and CO₂. The notation in the figure is defined as (%CO₂, %H₂O). The reference case corresponds to a feed devoid of CO₂ and H₂O (0, 0). S_N is varied by varying O₂ concentration in the lean phase. For the reference case NO conversion decreases with S_N (O₂ concentration in lean phase) because of the detrimental effect of O₂, which has been extensively presented and discussed earlier. The highest NO conversion is achieved for the reference case for the range of S_N considered. The effluent profiles of NO and NH₃ are plotted in Fig. 3.13 (a) and Fig. 3.13 (b) respectively. Fig. 3.13 (a) shows that compared to the base case (the blue line), NO slips faster with the addition of extra oxidant (either CO₂ or H₂O). Fig. 3.13 (b) shows that NH₃ is generated in rich phase and early lean phase when H₂O is introduced in feed.

The NO conversion obtained for the (0, 3.5) and (5, 0) feeds shows that both CO₂ and H₂O are detrimental to NO conversion. However, it is noted that for a fixed S_N, the NO conversion achieved in the (5, 3.5) feed is lower than that for the (0, 3.5) feed but higher than for the (5, 0) feed. Thus H₂O mitigates the detrimental effect of CO₂.

Binet et al. [86] and Otsuka et al. [98] showed that CO₂ and H₂O can function as mild oxidants and re-oxidize reduced ceria during cycling. This results in a decreased effectiveness. As NO decomposition over ceria is highly dependent on the degree of ceria reduction, the oxidation of ceria by CO₂ or H₂O is detrimental to NO conversion due to decreased availability of reducing components, which is validated by the earlier NO slip in cases with CO₂ and/or H₂O shown in transient plot Fig. 3.13 (a). The less detrimental impact of H₂O may be attributed to the NH₃ generation pathway. Ceria is known to be a good catalyst for water gas shift reaction, which converts CO and H₂O to H₂ and CO₂. As discussed before, H₂ fed into the rich is able to reduce NO to NH₃. Correspondingly, in cases (0, 3.5) and (5, 3.5), NO can be reduced to N₂ via oxygen vacancies or reduced to NH₃ via hydrogen-containing species. In contrast, in case (5, 0), with CO adsorption hindered by CO₂, NO is mainly reduced via oxygen vacancies. Therefore, although H₂O is detrimental to NO reduction by CO over ceria, H₂O can still mitigate the detrimental impact of CO₂.

3.5 Conclusions

The NO decomposition over ceria was studied under various reaction conditions, including several feed temperatures, reductant types and extra oxidants. The main findings are:

Under lean/rich switching operation, NO can be efficiently reduced by CO, H₂ or C₃H₆ at high temperatures (e.g., >550°C). The main nitrogen-containing products are N₂ and NH₃, the latter is generated only when hydrogen-containing reductants (H₂ or C₃H₆) are applied. The reductants (CO, H₂ or C₃H₆) fed in the rich phase can reduce NO fed in rich phase directly, as well as reduce NO fed in the lean phase indirectly. Active reducing components, including oxygen vacancies and adsorbed reducing components (such as adsorbed CO and adsorbed hydrogen), are created by reductants in the rich feed and further utilized for NO reduction in the lean phase. Therefore, the most effective region for NO reduction is the v rich phase and the beginning of the lean phase.

Oxygen vacancies are crucial to NO abatement performance. Based on the two-step reduction process of ceria particles (surface reduction and bulk oxygen diffusion), There are two types of oxygen sites (or oxygen vacancies) at different positions inside ceria particles; surface oxygen sites (or surface oxygen vacancies) and bulk oxygen sites (or bulk oxygen vacancies) by. The surface oxygen sites are easily reduced by the rich phase to generate surface oxygen vacancies, which are able to reduce NO in the whole cycle. While the bulk oxygen vacancies inside the ceria particles can hardly be created or used to reduce NO. The efficiency of the surface oxygen vacancies largely determines NO reduction performance. Faster lean/rich switching frequency results in more efficient generation of surface oxygen vacancies and thus higher NO conversion. O₂ is detrimental to NO decomposition for many possible reasons. The first reason is that O₂ competes with NO for effective reducing sites (both oxygen vacancies and adsorbed reducing intermediates) in the lean phase. The second reason is that generation of reducing components in the rich phase is inhibited by adsorbed O₂ from the lean phase. The third is the pre-mixing of the lean and rich streams before the ceria, causes additional reductant consumption. With smaller amount of reductants available in the rich phase, fewer active reducing components are created and NO have a lower chance to be reduced.

Two operation strategies, lean/rich switching and steady-state feeding are compared a fixed duty cycle rich. The effective creation and storage of active reducing components in the rich phase enables superior lean/rich switching operation. With a cycleaveraged lean feed, NO can hardly be reduced under steady-state operation because oxygen vacancies can hardly be created with excess oxidants. In contrast, the separation of lean and rich feeds under lean/rich switching operation leads to effective generation of oxygen vacancies, which contributes to NO abatement. The optimal lean/rich switching frequency eads to best NO abatement performance. The optimal lean/rich switching frequency depends on both reaction conditions (such as feed temperature and S_N) and setup restrictions (e.g., the distance between the injection point and the monolith).

CO₂ and H₂O are detrimental to NO conversion because they can and oxidize to some extent reduced ceria. When CO is used as the sole reductant, H₂O has less detrimental effect than CO₂, partly because that utilization of H₂O generates NH₃ apart from N₂ generation via oxygen vacancies.

In this study, NO reduction via ceria is tested using simulated exhausts under both lean/rich switching and steady-state operation. NO can be efficiently reduced via ceria with

a cycle-averaged rich feed while O₂ inhibits NO abatement. Compared with steady-state operation, faster lean/rich switching operation benefits NO abatement due to a better utilization of surface oxygen vacancies. The utilization of surface oxygen vacancies suggests improved catalyst synthesis, for example, smaller ceria particles increase NO reduction. This study on NO decomposition on ceria during lean and rich cycling helps understand the beneficial function of ceria on NOx reduction at high temperatures, which also provide guidance for optimization of catalyst formulation and operation strategies.

Chapter 4 Impact of Storage Material (BaO and CeO₂) and Cycling Frequency on NOx storage and reduction

In this chapter, the impact of oxygen and NOx storage materials (CeO₂, BaO) on NOx conversion during fast lean-rich switching. The deNOx performance of three catalysts, Pt/Al₂O₃, Pt/CeO₂/Al₂O₃, Pt/BaO/Al₂O₃, are systematically compared over a range of operating conditions, including cycling frequency, feed temperature, reductant type (H₂, C₃H₆), and oxidant (O₂, CO₂, H₂O) concentrations. The findings are interpreted to advance the understanding and application of fast cycling NSR.

4.1 Catalyst Characterization

Sorption (physisorption and chemisorption) tests are conducted for the three Ptcontaining samples, Pt/Al₂O₃ (PtA), Pt/CeO₂/Al₂O₃ (PCA) and Pt/BaO/Al₂O₃ (PBA). The characterized surface area is 119.9 m²/g, 112.1 m²/g and 99.7 m²/g for PtA, PCA and PBA respectively. Pt dispersion is determined by CO-chemisorption using a Micromeritics 3 Flex instrument. The characterized Pt dispersion is 5.3%, 12.4% and 3.4% for PtA, PCA and PBA respectively. That each of the dispersions is less than 15% is likely a result of the accelerated aging protocol employed. The Pt dispersion for PCA is higher than the values for PtA and PBA. This may be due in part to additional CO consumption by reduction of ceria and adsorption on ceria.

SEM tests are conducted to determine the washcoat thickness of the three Ptcontaining monolith catalysts. The peripherally-averaged thickness of PtA, PBA and PCA are 39 μ m, 43 μ m, 41 μ m respectively. Weisz-Prater modulus was calculated to assess the impact of internal diffusion. The washcoat diffusion cannot be isolated in this study but the diffusion impacts in the three samples would be similar, as the three samples has similar washcoat thickness and porosity.

4.2 Impact of Catalyst Formulation

In this section, overall NOx abatement performance over each of the catalysts is compared for a cycle-averaged lean feed ($S_N = 9.7$) conducted at the fastest cycling frequency (6/1s) and using H₂ and C₃H₆ as reductants. H₂O or CO₂ were excluded in these experiments to avoid interference from side reactions.

Fig. 4.1 compares the cycle-averaged NOx conversion for the three catalysts as a function of feed temperature with either H₂ (Fig. 4.1 (a)) or C_3H_6 (Fig. 4.1 (b)) reductant. For both H₂ and C₃H₆, PtA is inferior to PBA and PCA over the entire temperature range. This confirms the promotional impact of BaO in storing NOx and of CeO_2 in storing O_2 and NOx. For H₂, the NOx conversion using PtA or PCA decreases monotonically with feed temperature while for PBA the conversion exhibits a local maximum at ~300 °C. PCA outperforms PBA in the lower temperature range (T $< 300^{\circ}$ C) while PBA outperforms PCA for intermediate and high temperatures (T > 300° C). For C₃H₆, the NOx conversion obtained with both PBA and PCA exhibits a local maximum at an intermediate temperature; specifically ~50% at ~400°C for PCA, and ~65% at ~450°C for PBA. In contrast, the NOx conversion obtained with PtA is below 10% over the entire feed temperature range. The NOx conversion for PCA slightly exceeds that for PBA for feed temperatures below 400°C while PBA significantly outperforms PCA at higher temperatures. These trends are consistent with those reported by Yang et al. [28] who showed that the addition of ceria to Pt/BaO/Al₂O₃ promotes cycle-averaged NOx

conversion over a wide intermediate temperature range (175°C - 400°C). The promotional impact diminishes at high temperatures (~4% at 400°C). The specific differences in the NOx conversions for the three catalysts can be largely explained by their discrepant NOx storage capacities.



Figure 4.1 Cycle-averaged reactant (NOx and C₃H₆) conversions as a function of feed temperature. [Conditions: 6s lean/1s rich; lean: 300 ppm NO, 5% O₂; rich: 300 ppm NO, 6.21% H₂ or 0.69% C₃H₆, tested catalyst: PtA, PCA, PBA].

Fig. 4.1 (c) shows the cycle-averaged C_3H_6 conversion over each of the three catalysts as a function of feed temperature. (Note: The H₂ conversion in the H₂ experiments is not reported as the H₂ was not measured.) For each catalyst the C_3H_6 conversion remains low (< 15%) for temperatures below 300°C. The merging of the conversions in this range is reflective of the equal Pt loading (1 wt.%). Upon light-off, the C_3H_6 conversion rank is PCA > PBA > PtA. Propylene consumption occurs through its catalytic reaction with O₂ due in part to unavoidable upstream mixing between the rich and lean feeds. With its limited capacity to store NOx or O₂ in this temperature range, catalytic oxidation by gaseous O₂ is the primary C₃H₆ conversion pathway. Consumption also occurs through reaction of C₃H₆ with stored NOx and/or stored oxygen. The increased conversion obtained for PBA vs. PtA is probably due to its reaction with stored NOx. The much larger incremental increase for PCA is clearly a result of its reaction with oxygen stored by the ceria [33][38].



Figure 4.2 Calculated amount of adsorbed NOx on PtA, PCA or PBA as a function of feed temperature. [Conditions: 300 ppm NO, 5% O₂, balance Ar].

Fig. 4.2 shows the estimated amount of stored NOx on the three samples as a function of feed temperature. These were estimated from NOx effluent profile. Previous

NSR studies [12] [24][99] show that NOx storage involves at least three sequential steps. In the first step complete NOx storage occurs, evidenced by the absence of NO or NO₂ in the effluent. The second step, commences at NO and/or NO₂ breakthrough, involves an increasing effluent concentration of both species, and lasts for 10's of seconds. The third step is the much slower approach of the NOx concentration to its feed level and may last for several minutes to hours. Since the current study focuses on NOx abatement performance over a range of cycle times, the time period of interest is confined to 60 s. For temperatures below 350°C PCA has a slightly higher NOx storage than PBA and PtA. At temperatures exceeding 400°C PBA outperforms both PCA and PtA. Even at temperatures as high as 550°C PBA retains some NOx storage capacity while both PCA and PtA have none. These data are consistent with previous works [46][100][101]. Bulk barium nitrate and nitrite species decompose in air at 590 °C and 267 °C, respectively [12]. In contrast, the NOx storage contributed by CeO₂ [46][100][101] and Al₂O₃ [43][102] occurs at much lower temperatures. Ji et al. [46] reported that surface nitrates formed on Pt/CeO₂ remained stable at 300°C but disappeared upon heating to 400°C. Al₂O₃ may also contribute to the NOx adsorption at temperatures below 300°C [43]. These results are under "dry" conditions – NOx storage on PtA is much lower in the presence of H₂O. Nitrates and nitrites formed on Al₂O₃ with a co-feed of NO and O₂ but those are weakly bound and displaced by H₂O [103]. Nitrates and nitrites [12] formed on CeO₂ or BaO surface still survive with H₂O introduction, as CeO₂ and BaO possess relatively stronger basicity compared to Al₂O₃.

A comparison between the cycle-averaged NOx conversion and NOx storage provides insight into the working mechanism. With H₂ as reductant, the impact of catalyst composition on cycle-averaged NOx conversion (Fig. 4.1 (a)) follows the trends of the

short-time NOx storage data (Fig. 4.2) with two exceptions described below. For temperatures < 300°C, PCA has the highest NOx storage capacity (Fig. 4.2) and the highest NOx conversion (Fig. 4.1 (a)). In contrast, at higher temperatures (> 400°C), PBA exhibits the highest NOx storage (Fig. 4.2) and as a result outperforms PCA and PtA during fast cycling (Fig. 4.1 (a)). Two exceptions to the connection between storage and conversion are encountered at 150°C and 350°C. At 150°C, PBA has a higher NOx conversion but a lower NOx storage than PtA. This may be explained by the difference in the stability of nitrates or nitrites on PBA and PtA. That is, nitrate species formed on Al_2O_3 can be easily purged in an inert gas at the same temperature [43] while nitrate species formed on BaO remain stable during inert purging [12]. Thus, even though PtA traps more NOx during the lean feed, the loosely held NOx desorbs from the surface, preventing its reduction. At 350°C, PCA has a lower cycle-averaged NOx conversion but has a slightly higher NOx storage compared to PBA. This contradiction may be explained by the oxygen storage of PCA. Ren et al. [100] pointed out that on a ceria-containing NSR catalyst, the reductant reacts with both stored NOx and oxygen. Thus, in cyclic experiments with PCA, additional consumption of reductants may result in a lower reductant concentration and a lower cycleaveraged NOx conversion.

For C₃H₆ as reductant, the dependence of cycle-averaged NOx conversion (Fig. 4.1 (b)) also follows the fast NOx storage trends at temperatures exceeding the propylene light-off (e.g., $> 300^{\circ}$ C). With C₃H₆ as reductant PCA outperforms PBA over a wider range of temperature than with H₂; i.e., up to ~350°C. The promotional effect of ceria is through mitigation of the self-inhibited propylene oxidation on Pt. Previous NSR studies have shown that hydrocarbons are inferior to H₂ due to self-inhibition [104][105]. Lang et al.

[106] showed that the addition of ceria, albeit with Pd/Al_2O_3 , lowers the light-off temperature of C_3H_6 . In summary, the consistent dependence of cycle-averaged NOx conversion on the fast NOx storage capacity validates the importance of the conventional NSR mechanism at higher cycling frequency.

Figs. 4.1 (a) and 4.1 (b) show that PCA outperforms PtA over the entire feed temperature range with both H_2 and C_3H_6 as reductant. However, the difference diminishes at higher temperatures (> 400°C). In fact, the NOx conversion approaches \sim 14% for both PCA and PtA at feed temperatures exceeding 500°C. This value in fact corresponds to the fraction of the cycle that is rich; i.e., 1/7, showing that the NOx reduction only occurs during the rich part of the cycle at high temperature. The only slightly higher NOx conversion on PCA compared to PtA, i.e., 4% higher for H₂ and 8% for C₃H₆, suggests that the benefits of CeO₂ under lean conditions ($S_N = 9.7$) is limited. Reported in the previous study[70], the rate of NO decomposition/reduction over PGM-free ceria is greatly diminished due to the higher reactivity with oxygen vacancies of O_2 compared to NO. In the current study using $Pt/CeO_2/Al_2O_3$, the NOx conversion is almost certainly confined to the rich phase when there is a large excess of O_2 . These results suggest that ceria has only a limited promotional impact on the deNOx under fast cycling conditions. These conclusions are not likely to be much different if O₂ is present during the reductant injection. On the other hand, there is a sustained enhancement in the NOx conversion on PBA compared to PtA at high temperature. Figs. 4.1 (a) and 4.1 (b) show a NOx conversion enhancement at 600°C of ~15% and ~28% for H₂ and C₃H₆, respectively.

The performance with Pt/CeO₂/Al₂O₃ and Pt/BaO/Al₂O₃ confirm a decidedly minor role of oxygen storage material (CeO₂) while underscoring the critical role of NOx storage

material (BaO). These findings agree with those of Reihani et al. [22] who reported that the fractional NOx conversion achieved with a Pd-Rh TWC under fast cycling was only slightly higher than 15%, the percentage of rich time among the total lean-rich cycling time for a 15% duty cycle. They attributed the inferior deNOx performance to two factors; the low NOx storage due to lack of NOx storage material, and the inferior NO oxidation due to the absence of Pt.



Figure 4.3 Comparison of cycle-averaged NOx conversion over PCA or PBA with H₂ or C₃H₆ as the sole reductant. [Conditions: 6s lean/1s rich; lean: 300 ppm NO, 5% O₂; rich: 300 ppm NO, 6.21% H₂ or 0.69% C₃H₆].

Figs. 4.3 (a) and 4.3 (b) recast the cycle-averaged NOx conversion data for PBA and PCA, respectively, to more clearly show the impact of the reductant type. At low to intermediate temperature (< 400°C), H₂ is the superior reductant for both PBA and PCA.

This finding is consistent with previously-reported results and is attributed to the much lower light-off temperature of H_2 on Pt-containing catalyst [107]. At high temperature (> 450°C) there is no longer an advantage of H₂. In fact, to the contrary, the NOx conversion with C_3H_6 slightly exceeds by ~10% that obtained with H_2 on the PBA catalyst (Fig. 4.3) (a)). The NOx conversion enhancement with C_3H_6 under fast cycling has been previously reported [21][31][108][109]. Earlier studies attributed the enhancement to the formation of a thermally stable hydrocarbon surface intermediate that is selectively oxidized to N₂ during the lean part of the cycle [21][23]. Most recently Ting et al. [24] show via modeling of experimental results that the advantage of C₃H₆ is a result of its lower external mass transfer rate compared to H₂ and the resulting lower release of NO during the rich pulse. On PCA both H₂ and C₃H₆ give essentially the same 14% NOx conversion (Fig. 4.3 (b)) indicating that reduction only occurs during the rich feed. Earlier discussion pointed out that the redox pathway has only a minor contribution to the NOx reduction performance under net lean conditions ($S_N = 9.7$). For the PCA catalyst, the nearly identical NOx conversion of ~14% above 450°C for both H₂ and C₃H₆ suggests that any additional reduction on the ceria is negligible.

4.3 Role of CeO₂

As introduced earlier, the enhanced NOx conversion observed during fast cycling at high temperatures, is attributed to one of three mechanisms; (1) improved NOx storage utilization, (2) adsorbed hydrocarbon intermediate pathway, or (3) ceria redox pathway. The low NOx conversion obtained during lean-rich cycling on Pt/CeO₂ compared to Pt/BaO suggests that the redox pathway is secondary. To investigate this further, the overall and transient NOx abatement behavior over the PCA catalyst was compared for various cycling frequencies and feed conditions. Similar to the last set of experiments, H_2O or CO_2 were excluded from the feed to avoid complications from side reactions (e.g., water gas shift reaction) in order to isolate the impact of CeO₂.

4.3.1 Impact of O₂

Fig. 4.4 summarizes cycle-averaged NOx conversion (Figs. 4.4 (a), (b)), NH₃ yield (Figs. 4.4 (c), (d)) and N₂O yield (Figs. 4.4 (e), (f)) from PCA as functions of feed temperature for cycle time ratios spanning 90/15 s to 6/1 s and for two feed compositions, $S_N = 9.7$ (Figs. 4.4 (a), (c), (e)) and $S_N = 1.0$ (Figs. 4.4 (b), (d), (f)). The NOx conversion increases with decreasing cycle time over the entire feed temperature range for both lean and stoichiometric feeds. For the lean feed ($S_N = 9.7$), the beneficial impact of fast cycling diminishes at temperatures >500°C, due to the less effective NO decomposition in the presence of excess O₂. Hence NO is only reduced during the rich part of the cycle. In contrast, for the stoichiometric feed ($S_N = 1$) the NOx conversion approaches a plateau that incrementally expands beyond 14% with decreasing cycle time. For example, $X_{NOx} \sim 34\%$ for the 6/1 cycle.

The conversion increase with decreasing cycle time at lower temperatures is a result of the improved NOx storage utilization on the ceria. It is noteworthy that the lean feed gives a higher conversion than the stoichiometric feed. This is attributed to the higher yield of NO₂ from Pt-catalyzed NO oxidation, which is of positive order in O₂. Crocoll et al. [110] studied the NO oxidation over Pt/Al₂O₃ catalyst under oxygen excess conditions. It was found that the increase in the O₂ concentration from 1.5 vol.% to 6.0 vol.% led to a monotonic increase of NO conversion to NO₂ over a wide temperature range (150 °C – 500 °C). The NOx storage capacity results on PCA for the $S_N = 1.0$ and $S_N = 9.7$ cases are shown in Fig. 4.5. The results show that a higher O₂ feed concentration gives a higher NOx storage capacity on PCA when PCA still possesses NOx storage capacity (i.e., < 450 °C). In this case, the promoted NO oxidation due to the increase of O₂ concentration results in an enhanced NOx storage on PCA catalyst, which contributes to the higher NOx conversion under net rich conditions.



Figure 4.4 Cycle-averaged NOx conversion, NH₃ yield and N₂O yield over PCA as a function of feed temperature. [Conditions: lean: 300 ppm NO, 5% O₂ ($S_N = 9.7$) or 0.5% O₂ ($S_N = 1.0$); rich: 300 ppm NO, 6.21% H₂.]



Figure 4.5 Calculated amount of adsorbed NOx on PCA as a function of feed temperature. [Conditions: (a) $S_N = 9.7$: 300 ppm NO, 5% O₂, balance Ar; (b) $S_N = 1.0$: 300 ppm NO, 0.5% O₂, balance Ar.]

Figs. 4.4 (c) and 4.4 (d) show that the cycle-averaged NH₃ yield is a nonmonotonic function of temperature for both feeds at all cycle times. The maximum NH₃ yield occurs at an intermediate temperature ($250^{\circ}C \sim 400^{\circ}C$) and is slightly skewed to lower values for the lean feed. To the right of the maximum the yield approaches ~14%, indicating all the NO that reacts is converted to NH₃ under these conditions. The lone exception is the 6/1 cycle with the lean feed for which the yield limit is ~10%. For temperatures sufficiently left of the yield maximum, an increase in the cycle time decreases monotonically the NH₃ yield. This trend conveys that a more efficient oxidation accompanies the faster cycling. Previous NSR studies of Pt/BaO/Al₂O₃ have shown that during regeneration, NH₃ is generated upstream from the reaction of H₂ with stored NOx in reaction R4.1 as

$$Ba(NO_3)_2 + 8H_2 \rightarrow 2NH_3 + BaO + 5H_2O.$$
 (R4.1)

The NH₃ subsequently reacts with stored NOx downstream oxidized by NO and O_2 to N_2 by reaction R4.2 [111][112] as

$$3Ba(NO_3)_2 + 10NH_3 \rightarrow 8N_2 + 3BaO + 15H_2O.$$
 (R4.2)

N₂O may also form via reaction R4.3 [113] as

$$Ba(NO_3)_2 + 2NH_3 \rightarrow 2N_2O + BaO + 3H_2O.$$
 (R4.3)

Lietti et al. [114] identified the different temperature thresholds for the two steps on a Pt/BaO/Al₂O₃ catalyst and concluded that NH₃ formation (R4.1) is faster than NH₃ consumption (R4.2). This should increase the net formation of NH_3 (R4.1). Indeed, an increasing dependence of NH₃ yield with cycle frequency was observed in Pt/BaO/Al₂O₃ [71]. In contrast, with its oxygen storage capacity, PCA promotes NH_3 oxidation (R4.2) which decreases the net generation of NH₃. The decrease in NH₃ yield with shorter cycle time is attributed to enhanced (oxidation) reaction of NH₃. NH₃ formation occurs in the front part of the monolith during the rich H₂ pulse; the faster cycling increases the contact of the rich and lean feeds which results in the enhanced extent of reaction. This trend is consistent with Ting et al. [24] who used a NSR catalyst containing a higher loading of PGM (Pt + Rh) and mixture of BaO and CeO₂. The quantitative analysis here is not included here as tt is not feasible to do the quantitative analysis under fast cycles (e.g., 6s lean/1s rich), as the mixing inside the gas cell disables the precise distinguishing of FTIR data into lean and rich periods. The stoichiometries used here were adapted from previous studies [24][112][114][115], where quantitative analysis and modeling analysis were used.

Figs. 4.4 (e) and 4.4 (f) show that for both feeds, the N₂O formation only occurs at low temperatures (e.g., < 300°C) and its yield increases monotonically with decreasing cycle time for a fixed temperature. N₂O formation on PCA results from two paths; the first is a reaction between NO and reductant or surface-deposited reductive species over reduced PGM sites via the NSR pathway, while the second is reaction of NO over partially reduced ceria via the redox pathway. A shorter cycle leads to the faster oxidation/reduction transition of PGM sites and ceria, both of which promote N₂O formation and result in a higher N₂O yield.

The NOx and O_2 storage functionalities and their contributions to NOx reduction may be assessed by examining the transient species concentrations at 150°C and 550°C. Effluent transient profiles of nitrogen-containing species provide a more detailed look at the underlying chemistry during the lean-rich cycle (Fig. 4.6). The ceria NOx storage capacity decreases to a negligible value for temperatures above 400°C [46] while the oxygen storage is sustained at high temperatures on activated ceria (i.e., >150 °C for H₂) [116]. PCA exhibits oxygen storage function at both 150°C and 550°C but has NOx storage function only below 200°C. Therefore, the deNOx performance at 550°C presents the sole contribution from redox pathway. Ting et al. [24] pointed out that mixing inside the FTIR gas cell results in a protracted tail for ~20s in this experimental setup at the given flowrate. To suppress the interference from the tail, analysis of the transient data from the longest cycling time 90/15s is focused. The mass spectrometer (MS) signal of m/e = 28 includes contributions from both N_2 and N_2O when H_2 is the reductant and the feed is devoid of CO₂. The N₂ part of the m/e = 28 signal may be adjusted by subtracting the N₂O FTIR measured contribution The FTIR mixing effect prevents a complete deconvolution of the N_2O and N_2 contributions from the m/e = 28 signal.

To better understand the impact of O_2 on NOx reduction performance over PCA, a set of experiments was conducted with varied O_2 concentration in the lean feed for a 90/15 cycle at feed temperatures of 150°C and 550°C. Three lean feeds having different O_2 concentrations (0, 1400 ppm, 5%) were applied having the following respective values of S_N: 0.03, 0.30 and S_N = 9.7. The results of these experiments are shown in Fig. 4.6; i.e.,

NOx (Figs. 4.6 (a) and 4.6 (b)), N₂O (Figs. 4.6 (c) and 4.6 (d)), NH₃ (Figs. 4.6 (e) and 4.6 (f)), and m/e = 28 (Figs. 4.6 (g) and 4.6 (h)). The m/e = 28 signal intensity was converted to N₂ concentration using a N₂ calibration factor, by subtracting N₂O contribution from the overall m/e = 28 signal.



Figure 4.6 Effluent concentration profiles with PCA. [Conditions: 90s lean/15s rich; lean: 300 ppm NO, no O₂ ($S_N = 0.03$), 1400 ppm O₂ ($S_N = 0.30$) or 5% O₂ ($S_N = 9.7$); rich: 300 ppm NO, 6.21% H₂,; feed temperature: 150 °C or 550 °C].

The rich cycling feed ($S_N = 0.03$) serves as a reference in that no O₂ is contained in

the feeds. The NOx profile exhibits a similar pattern at 150°C (Fig. 4.6 (a)) and 550°C (Fig. 4.6 (b)) despite the widely different temperatures. After a quick decrease during the rich feed, the NOx remains undetected for ~10 s and ~30 s at 150 and 550 °C, respectively. Following breakthrough, the NOx slowly increases to its feed value. At both temperatures N_2 exhibits a continuous generation throughout the entire lean feed along with an additional small peak evident at the start of the rich feed. The protracted NH₃ tail during the lean feed exceeds the ~ 20s tail produced by the FTIR cell, suggesting that NH₃ is generated throughout the lean period. The reduction of NO and generation of NH₃ in rich involves the reaction of NO with adsorbed H during the rich feed; i.e.,

$$NO + 2.5H_2 \rightarrow NH_3 + H_2O.$$
 (R4.4)

Also, the reduction of ceria or PGM-containing ceria by H_2 leads to the formation of vacancies (R4.5) [33][38][86] and H adatoms (R4.6 and R4.7) [70], which may be utilized for NO reduction in lean period:

$$\mathrm{H}_{2} + \mathrm{Pt} - \mathrm{O} \to \mathrm{Pt} + \mathrm{H}_{2}\mathrm{O}, \tag{R4.5}$$

$$H_2 + CeO_2 \rightarrow HO - Ce - OH, \qquad (R4.6)$$

and
$$CeO_2 + HO - Ce - OH \rightarrow Ce_2O_3 + H_2O.$$
 (R4.7)

Reactions R4.8 - R4.10 describe NO reduction to N_2 and NH_3 over reduced Pt-CeO₂ during the lean period:

$$NO + Pt \to 0.5N_2 + 0 - Pt,$$
 (R4.8)

and
$$2NO + 2Ce_2O_3 \rightarrow N_2 + 4CeO_2$$
 (R4.9)

and
$$2NO + 5HO - Ce - OH \rightarrow 2NH_3 + 5CeO_2 + 2H_2O.$$
 (R4.10)

The similar NOx, N₂ and NH₃ effluent profiles indicates the existence of the redox pathway.

The impact of O₂ on NOx reduction at high temperature (i.e., 550°C) is discussed

first due to its comparative simplicity. Previous studies [25][95] pointed out that O_2 is a better oxidant than NO to re-oxidize ceria or Pt/CeO₂. Correspondingly, this study shows that the addition of O₂ has an inhibitory impact on NOx conversion. Fig. 4.6 (b) shows that the addition of O₂ to the lean feed leads to a large increase in unreacted NOx such as an earlier and sharper slip of NOx. For the $S_N = 9.7$ feed, NOx slips and reaches the feed level (300 ppm) almost immediately upon the switch from rich to lean feed. This suggests that NOx reduction only occurs during the rich feed and beginning of the lean feed. Accordingly, the addition of O₂ strongly inhibits N₂ formation during both the lean and rich feeds. This results in a smaller N_2 peak during the rich feed and a diminished N_2 formation period during the lean feed (Fig. 4.6 (h)). For example, for the first peak $N_2 \sim 50$ ppm and disappears after ~ 2s. At 550°C, NH₃ is mainly formed during the rich period with limited additional generation during the lean period. In comparison, for the $S_N = 0.03$ case, NH₃ has a large formation during the rich and as mentioned above is sustained for ~ 60s into the lean period (Fig. 4.6 (f)). Similar to N₂, the addition of O₂ decreases NH₃ generation during both the lean and rich feeds. The detrimental impact of O_2 on NOx conversion at 550°C is attributed to the competition between NO and O₂ for surface vacancies and hydroxyls.

At 150°C the NOx reduction data reveal classical NOx storage and reduction behavior (Fig. 4.6 (a)) [100][101]. For each of the feeds, the NOx decays quickly upon the switch from lean to rich and remains undetected in the remaining part of rich feed. This trend is consistent with H₂ reduction of co-fed NO and NOx trapped on the ceria phase during the lean period. NOx remains undetected for ~5s in the beginning of lean feed and then increases towards the feed concentration. The lean NOx slip is a nonmonotonic function of the O₂ concentration.

Previous studies [46][100][101] suggest that Pt/CeO₂/Al₂O₃ exhibits considerable NOx storage capacity under net lean conditions at medium and low temperatures (<400 °C). Haneda et al. [117] reported NO decomposition to N_2 and N_2O on reduced Pt/CeO₂ catalysts even at room temperature. Based on previous studies [46][100][101], the transient NO trend in the lean period has the following aspects. First NOx is trapped on sites close to the Pt crystallites. This is followed by slower trapping on distal and sub-surface sites. At the same time NO decomposition occurs on reduced Pt and ceria sites. The nonmonotonic dependence of NOx reduction conversion on O₂ concentration at 150°C is explained by the simultaneous involvement of two NOx reduction pathways; i.e., the conventional NSR pathway and the redox pathway. As such, for the NSR pathway, NOx is stored on the ceria during the lean feed and the NOx is reduced in the ensuing rich period. Previous studies [12][118] point out that NOx storage typically proceeds through the sequential NO oxidation to NO₂ which then is reactively stored as nitrates. An alternative route involves nitrite formation. Crocoll et al. [110] reported that Pt catalyzed NO oxidation is of positive order with respect to O_2 . Hence, an increase in the O_2 concentration should promote NOx storage on PCA. Thus, for the $S_N = 9.7$ feed the NSR pathway has a dominant contribution to the NOx conversion as the large excess of O₂ oxidizes the reduced PCA quickly and inhibits NO decomposition on PCA. At the other extreme is the $S_N = 0.03$ case for which the redox pathway mainly contributes to the NOx conversion as O_2 is excluded in feed. As O₂ is added into the mixture the NO decomposition is inhibited, resulting in a lower NOx conversion. However, compared to the $S_N = 9.7$ case, the low O₂ concentration in $S_N = 0.30$ case leads to a lower NO oxidation rate and NOx storage and inferior NOx reduction behavior. This explains the poor NOx abatement performance obtained for the $S_N = 0.30$

case.

Figs. 4.6 (c), 4.6 (e) and 4.6 (g) show the transient profiles of N-containing products at 150 °C. With the feed devoid of O_2 ($S_N = 0.03$), each of the N-containing products (N_2 , NH₃ and N₂O) is generated throughout the lean period, confirming the contribution from the redox pathway. The addition of O_2 shortens the generation period. For example, the increase of S_N from 0.03 to 9.7 shrinks the reduction period to the first 3s of the lean phase, with larger N₂ (~ 2500 ppm) and N₂O (~200 ppm) peaks detected. Recall that O₂ fed during the lean period competes with NO to decompose on vacancies and/or react with residue H₂ on the catalyst, an increase of O₂ concentration in the lean decreases the chance for NO reduction to N₂ and NH₃. Therefore, the generation period of N-containing products shrinks with the addition of O₂. With a large excess of O₂ in feed ($S_N = 9.7$), the NOx reduction pathway is dominated by the NSR pathway. The generation of N-containing species (N₂, NH₃, N₂O) during the lean period may be attributed to the reaction between the adsorbed reducing species (e.g., NH₃ and H adatoms) and NOx fed [119][120][121].

Transient profiles of nitrogen-containing species confirm the transition from the redox pathway to the NSR pathway with an increase in the O₂ concentration (S_N). The S_N increase from 0.03 to 9.7 shrinks the duration during which N-containing products (N₂, NH₃ and N₂O) are generated in the rich period and early lean period. Elimination of any N₂, NH₃ and N₂O generation during the late lean phase (i.e., after 15s in lean phase for the S_N = 9.7 case) shows a transition from some reduction to NOx storage. Correspondingly, the expanded difference between detected NOx and the feed level (300 ppm) is an indicator of NOx storage. Also, with the increase in S_N is the increased formation of nitrogen-containing products (N₂, NH₃ and N₂O) during the rich phase.

4.3.2 Impact of Reductant

The redox pathway involves NOx reduction on reduced ceria sites, including the ceria sites proximal to PGM particles and isolated ceria sites [26][95]. Previous studies show that the addition of Pt onto ceria leads to two additional active sites in addition to CeO₂ sites; namely, PGM sites and Pt/CeO₂ sites [33][38]. Each of these is able to reduce NO [25][95]. The previous study [70] showed that ceria reduced NO once activated at high temperatures (e.g., $> 450^{\circ}$ C). To differentiate the contribution from Pt and Pt/CeO₂ sites and to identify the role of Pt/CeO₂ sites, PCA and PtA were compared in targeted experiments described next.



Figure 4.7 Cycle-averaged reactant (NOx and C₃H₆) conversions and product (N₂O and NH₃) yields over PCA or PtA. [Conditions: 6s lean/1s rich; lean: 300 ppm NO, 0.5% ppm O₂; rich: 300 ppm NO, 6.21% H₂ or 0.69% C₃H₆;].

The deNOx performance over PCA and PtA for the $S_N = 9.7$ case was showed earlier. Such results suggests that the NOx storage capacity plays a significant role in NOx
conversion. Here the focus is the $S_N = 1.0$ case; the lower O_2 concentration attenuates the NOx reduction performance contributed by the redox pathway. H₂ and C₃H₆ reductants are used.

Fig. 4.7 (a) shows the cycle-averaged NOx conversion for the $S_N = 1.0$ cycle over PCA under the fastest cycling (6/1 s). Similar to the $S_N = 9.7$ case shown earlier (Fig. 4.7 (b)), H₂ outperforms C₃H₆ at low and intermediate temperatures ($150^{\circ}C - 400^{\circ}C$). At high temperature the behavior is different. The NOx conversion approaches 14% for both reductants for the $S_N = 9.7$ case. In contrast, the NOx conversion is ~ 35-40% for both reductants for the $S_N = 1.0$ case. This indicates that some reduction occurs during the lean part of the cycle. Further, $C_{3}H_{6}$ gives a slightly higher NOx conversion than H₂. As discussed earlier, deNOx achieved below 400 °C is a result of NOx storage and reduction. With PCA having a negligible NOx storage capacity but nonzero OSC at higher temperatures, the NOx reduction occurring during the lean feed is a result of the redox pathway. Accordingly, for both the $S_N = 9.7$ and $S_N = 1.0$ cases, the inferiority of C₃H₆ to H₂ below 400°C is a result of differences in their reactivities on Pt. On the other hand, the superiority of C_3H_6 to H_2 above 450°C for the $S_N = 1.0$ case is its higher reactivity than H_2 on CeO₂. Wang et al. studied the complete reduction process of CeO₂ [26] and Pt/CeO₂ [95] by H_2 and C_3H_6 and concluded that C_3H_6 leads to a higher extent of reduction on both CeO_2 and Pt/CeO_2 . They suggested that it is due to the deposition of carbonaceous species on the ceria surface. The results reported in Fig. 4.7 corroborate the Wang et al. findings; i.e., C_3H_6 provides more reducing sites on the CeO₂ (than H₂), either vacancies or carbonaceous material, for subsequent NO decomposition/reduction. Earlier results show that the deNOx attributed to the redox pathway is sensitive to the O_2 concentration; i.e.,

competition between NO and O₂ for reduced sites. The data indicate that a large excess of O₂ in the $S_N = 9.7$ case results in the fast oxidation of reduced sites by O₂, largely suppressing NO conversion. In the $S_N = 1.0$ case, the O₂ inhibition is somewhat less with a fraction of NO able to be reduced. As a result, an enhancement of NOx conversion by C₃H₆ exists in the $S_N = 1.0$ case but not in the $S_N = 9.7$ case.

To assess the contribution from Pt to that of CeO₂ or even of Pt/CeO₂, the PtA sample was evaluated using the same experimental conditions. Fig. 4.7 (a) shows the NOx conversion with PtA under 6/1 cycling. Similar to the $S_N = 9.7$ case (Figs. 4.1 (a) and 4.1 (b)), PCA is much more active than PtA for NOx conversion using either C₃H₆ or H₂ as the reductant. Over the entire temperature range, a higher NOx conversion is achieved with H₂ compared to C₃H₆ for PtA. In contrast, th previous study [70] showed that C₃H₆ gave a better deNOx performance than H₂ over CeO₂ under cyclic conditions. These findings suggest that the enhancement of NOx conversion over PCA by C₃H₆ above 450°C in the S_N = 1.0 case is a result of contribution of the Pt/CeO₂ and/or CeO₂ sites. Fig. 4.7 (b) shows the C₃H₆ conversion over PCA and PtA samples. The higher C₃H₆ conversion obtained on PCA shows the role of oxygen storage in enhancing oxidation. In the absence of ceria, a large fraction of the O₂ fed during the lean leaves the reactor unreacted.

Fig. 4.7 (c) shows the NH₃ yield over PCA and PtA with H₂ or C_3H_6 as reductant. For both PCA and PtA, H₂ is much more effective in providing H adatoms to react with NO to make NH₃. For PCA the NH₃ yield increases with feed temperature below 400°C and reaches a plateau above 450°C (~ 14% with H₂ and ~ 3% with C₃H₆). The nonmonotonic dependence of NH₃ yield on feed temperature for PCA may be attributed to the competing temperature dependent NOx and O₂ storage capacities, as discussed earlier. The NH₃ yield over PtA increases monotonically with feed temperature for H₂ feed while remaining at a negligible level for C₃H₆. Finally, Fig. 4.6 (d) shows the N₂O yield over PCA and PtA. The formation of N₂O is confined to lower temperatures ($<400^{\circ}$ C) with PtA giving a slightly higher N₂O yield.

4.4 Impact of Fast Cycling

As presented earlier, there are three principal pathways (conventional NSR pathway, HC intermediate pathway, redox pathway) that may contribute to deNOx performance during lean-rich switching. Earlier the dependence of NOx conversion and byproduct (NH₃ and N₂O) yield on cycling frequency for PCA catalysts was presented (Fig. 4.4). The results show that because PCA has NOx and O₂ storage capacity, both the NSR and redox pathways contribute to extents that depend on the operating conditions. The results for PBA reveal the importance of NOx storage in enhancing NOx conversion over a wide range of temperatures (i.e., 150 °C ~ 500 °C) [71]. A comparison of PBA to PCA indicates that the redox pathway may only contribute at high temperature and without an excess of O₂ (Fig. 4.1). The contribution of the hydrocarbon intermediate pathway is more difficult to assess. Recent findings indicate that it does contribute but its impact is secondary. In this section the impact of cycle frequency on the deNOx performance is discussed and the impact of the two pathways is explained.



Figure 4.8 Fast and slow NOx or oxygen storage sites. (a) fast and slow NOx storage sites on PBA; (b) (c) fast and slow oxygen storage sites on PCA. Here BaO and CeO₂ are chosen to represent the NOx and oxygen storage material respectively.

It is instructive to compare and contrast the storage and utilization of NOx and O₂. Fig. 4.8 shows schematics of the locale of an individual Pt and/or CeO₂ particle for the PBA and PCA catalysts. Fig. 4.8 (a) depicts the fast and slow NOx storage sites on the Pt/BaO (or Pt/CeO₂ at low temperature). Previous works have described how the local structure of the NSR catalyst defines at least two populations of sites; specifically proximal and distal NOx storage sites [12][24]. Kumar et al.[122] showed experimentally that the storage and regeneration of NOx during NSR involves an active interface at the contact line of the PGM crystallite and NOx storage material. These measurements provided an experimental underpinning of a coupled process of catalytic reaction and transport. Under conditions that the NO supply is limiting, the diffusion of stored or adsorbed NOx species to and from storage sites is the rate controlling process. The process was modeled at the crystallite scale by Bhatia et al. [115] and Shakya et al. [123]. A simplified picture (and model) comprises "fast" and "slow" NOx storage sites, the former of which are proximal site and the latter distal. The primary pathway for NOx storage involves sequential steps. First, NO and O₂ adsorb and react on the Pt, forming NO₂. The NO₂ then moves to a storage sites via the gas phase which involves desorption and gas phase transport, or via the surface, which involves spillover and surface or solid-state diffusion.

Fig. 4.8 (b) is a schematic picture of the Pt/CeO₂ catalyst which, instead of storing and consuming NOx, stores and consumes O₂. The PCA catalyst comprises fast and slow oxygen storage sites based on the analogous premise of proximity of the CeO₂ to the PGM crystallite [33]. Fast oxygen storage sites are defined as the proximal to Pt particles whereas slow oxygen storage sites are defined as storage sites far away from Pt particles. A second pair of fast and slow oxygen storage sites can be designated according to the position on/within a CeO₂ particle, as per Fig. 4.8 (c), following our previous study on NO decomposition over PGM-free ceria. The reduction of PGM-free ceria first undergoes a fast surface reduction process and then continues with slow consumption of oxygen diffusing from the bulk to the surface. As the surface oxygen is more accessible than bulk oxygen, the "fast" oxygen storage sites are the oxygen sites on the surface of ceria particles.

For both the NSR and redox pathways, enhancement in the NOx conversion by rapid pulsing with a reductant can be ascribed as the more efficient utilization of fast sites, be they NOx storage sites or oxygen storage sites. During cyclic NSR process, the occupation and regeneration starts with the utilization of fast NOx storage sites and then proceeds with slow NOx storage sites. As pointed out in previous studies [22][24], faster switching between lean and rich feeds through a shorter cycle results in less loss of NOx. That is, a longer lean period ultimately results in the breakthrough of NO/NO₂ as the diffusion to sites further removed from the PGM crystallite is too slow compared to the characteristic residence time of the flowing gas. As fast NOx storage sites offers easier accessibility and faster occupation/regeneration rates, fast cycling leads to a higher NOx conversion in the NSR pathway.

A similar picture is envisioned for the redox pathway. This involves the generation of reducing components (vacancies and accumulating surface intermediates) during the rich phase feed with the subsequent adsorption and decomposition/reduction of NOx during the lean feed. Faster switching between lean and rich streams enable a more efficient utilization of the oxygen storage sites. During cyclic experiments, the occupation and regeneration first starts with the utilization of fast oxygen storage sites and then proceeds with slow oxygen storage sites. As fast oxygen storage sites offers easier accessibility and faster occupation/regeneration rates, fast cycling leads to a higher NOx conversion via the redox pathway.

When $C_{3}H_{6}$ is applied as the reductant, the working mechanisms are more complex due to the potential involvement of surface hydrocarbon intermediate species. Compared to H₂, the injection of $C_{3}H_{6}$ onto both PBA and PCA results in a reduced PGM surface with accumulation of hydrocarbon species [21][26]. The adsorbed species may be further utilized for NOx reduction, either through interaction with adsorbed NOx for intermediates R-NOx and finally N₂ in NSR pathway [21][97], or through interaction with NO and/or O₂ for additional NO reduction in redox pathway. At high temperatures (> 550° C), the utilization of C₃H₆ results in a deeper reduction extent of ceria with accumulation of hydrocarbon intermediates [25] [26]. These intermediates on serve as additional reductant and enhance NO reduction via the redox pathway.



Figure 4.9 NOx conversions under cyclic or steady state operation on PCA at 550 °C. [Cyclic: 6s lean/1s rich; lean: 300 ppm NO, varied O₂ concentration; rich: 300 ppm NO, 6.21% H₂ or 0.69% C₃H₆; Steady state: 300 ppm NO, 0.887% H₂, varied O₂ concentration].

The promotion of C₃H₆ shows better resistance to O₂ during NSR. Enhancement of NOx conversion by C₃H₆ via a redox pathway decreases monotonically with increased O₂ concentration in the feed, or increased S_N (Fig. 4.9), eventually becoming negligible in a large excess of O₂ (e.g., S_N = 9.7, Fig. 4.9 (b), > 450°C). In contrast, the enhancement of NOx conversion by C₃H₆ during the NSR pathway is sustained in the S_N = 9.7 case (Fig. 4.3 (a)). The better resistance in the NSR pathway may be ascribed to the incorporation of stored NOx on storage sites (e.g., BaO). In the redox pathway, the hydrocarbon intermediates formed on PGM sites are rapidly consumed by NO and O₂ with O₂ exhibiting a better oxidation capability on reduced surface. With a large excess of O₂ in the feed,

hydrocarbon intermediates accumulating on the PCA will be first scavenged by O_2 , diminishing the likelihood of NO reduction. In contrast, over NSR catalyst (e.g., PBA), any accumulated hydrocarbon intermediates PGM are able to react directly with stored NOx, which enables enhanced NOx conversion by C_3H_6 at high temperatures in a lean atmosphere.

4.5 Conclusions

Experiments of NOx reduction under fast lean/rich cycling over Pt/Al₂O₃, Pt/CeO₂/Al₂O₃ and Pt/BaO/Al₂O₃ provide insight into the underlying mechanism and elucidate the beneficial impacts from storage components (i.e., BaO and CeO₂). The impacts of catalyst formulation, reductant type, O₂ concentration, and cycling time were evaluated.

With cycle-averaged lean feeds ($S_N = 9.7$) and H_2 as reductant, Pt/CeO₂/Al₂O₃ (PCA) exhibits the highest NOx conversion below 300°C while Pt/BaO/Al₂O₃ (PBA) surpasses PCA above 300°C. Above 450°C, NOx reduction over PCA is largely confined to only the rich feed but PCA still surpasses Pt/Al₂O₃ (PA) for a small enhancement in the NOx conversion. Generally, the overall NOx conversion over the three catalysts parallels the corresponding NOx storage capacity. The dependence of NOx conversion on NOx storage capacity underscores the necessity of NOx storage functionality under lean conditions. In contrast, the oxygen storage functionality only shows rather confined promotion. Pathways involved in adsorbed NOx, including the conventional NSR pathway and the hydrocarbon intermediate pathway, are responsible for the effective NOx reduction during fast cycling. The redox mechanism plays a rather minor role.

NO reduction over PCA by H₂ can be achieved in both lean and rich with anaerobic feeds within the whole temperature range (150°C ~ 600°C). With the addition of excess O₂ NOx conversion over PCA increases below 400°C but decreases above 400°C. The opposing trends can be attributed to the dependence of NOx storage and/or oxygen storage capacity of PCA on temperatures. PCA mainly exhibits NOx storage capacity at lower temperatures (i.e., < 400°C) and the enhancement from excess O₂ comes from the increased NOx storage rates. At higher temperatures (i.e., > 400°C), PCA only exhibits oxygen storage capacity. The detrimental impact from excess O₂ results from competition between NO and O₂ for reduced sites (vacancies and adsorbed reducing intermediates).

Fast cycling enhances NOx conversion over PBA in the lean case and over PCA for the stoichiometric case within the whole temperature range using H₂ as the reductant. The promotional impact over PCA for the lean case only exists at low temperatures (< 450°C), when PCA maintains NOx storage capacity. The promotional impact from fast cycling can be ascribed to the better utilization of fast NOx or oxygen storage sites from the conventional NSR pathway or redox pathway correspondingly. With a cycle-averaged rich and stoichiometric feed, lean/rich cyclic operation is inferior to steady state operation. However, lean/rich cyclic operation surpasses steady state operation with the presence of slightly excess O₂.

Enhanced NOx conversion was also observed by adopting fast cycling and/or C_3H_6 as reductant over PBA in the lean case or over PCA in the stoichiometric case. Compared to H₂, reduction of PBA and PCA by C_3H_6 results in surface-deposited hydrocarbon fragments on Pt and/or ceria, which can be further utilized by stored NOx on PBA or gaseous fed NO in rich. The additional reduction extent of PBA and PCA provided by C_3H_6 may account for the enhancement of overall NOx conversion by C_3H_6 . The enhancement from C_3H_6 is more resistant to O_2 in NSR pathway than the redox pathway. The presence of H₂O and CO₂ inhibits the enhancement by C_3H_6 in both PBA and PCA cases mainly due to the competition for NOx or oxygen storage sites.

This study confirms the prevalence of the conventional NSR mechanism and the hydrocarbon intermediate pathways during fast cycling over NSR catalysts. A redox pathway is validated but proven to extend a rather limited impact on NOx abatement under excess O₂. Fast cycling exhibits enhancement over PBA in $S_N = 9.7$ case and over PCA in $S_N = 1.0$ case, thanks to the improved utilization of fast NOx storage and oxygen storage (or vacancy) sites respectively. C₃H₆ leads to an enhanced NOx conversion over PBA in the $S_N = 9.7$ case and over PCA in the $S_N = 1.0$ case. The benefits from C₃H₆ may be ascribed to the deposition of hydrocarbon fragments on Pt sites, which serve as additional reduction of stored NOx or gaseous NO in NSR or redox pathway respectively.

Chapter 5 Impact of Oxygen Storage Material and Catalyst Architecture on Three-Way Catalyst Performance

This chapter presents performance evaluation results of simultaneous conversion of CO, NO and C₃H₆ on OSM (Oxygen Storage Material) - containing catalyst, characterization tests of OSM as well as mechanism discussion. CZO (Ce_{0.3}Zr_{0.7}O₂) and spinel Mn_{0.5}Fe_{2.5}O₄) are selected as two model OSMs. The investigated impacts of OSM type (CZO and spinel Mn_{0.5}Fe_{2.5}O₄), operation mode (steady-state and modulation) as well as catalyst design (PGM deposition on OSM and separation of PGM and OSM) provide insight into the performance and design of catalysts for TWC applications.

5.1 Characterization Results

5.1.1 XRD Test

The MFO spinel is prepared by incipient wetness impregnation and the spinel crystallites grow in the pores of the Al₂O₃ support. The MFO particle size is determined by XRD measurement. The XRD data (Fig. 5.1) show that MFO has a cubic structure with a lattice constant of 8.314 Å. The size of MFO particle is estimated as ~ 20 nm based on the Scherrer equation [124]. Fig. 5.1 shows the XRD results of the MFO/Al₂O₃ particles. The spinel peaks are indicated by the vertical yellow lines with the corresponding Miller indices indicated. The unassigned peaks come from the alumina based support. Based on three main peaks at $2\theta = 30.23$, 35.65 and 43.14 with d-spacing as 2.954, 2.516, 2.095 Å, respectively, the lattice parameter is determined as a = b = c = 8.341 Å in a cubic crystal system. The full width at half maximum (FWHM) from the most intense peak at $2\theta = 35.65$ is 0.502. Accordingly, the crystal size is estimated to be 19.4 Å by the Scherrer equation.



Figure 5.1 XRD results of MFO/Al₂O₃ (Results are provide by CDTi Inc).

5.1.2 Surface area and PGM dispersion

Surface areas of the OSM powder samples are reported in Table 5.1. Physisorption measurements show that the surface areas correspond to the particular oxide, be it alumina (A), CZO, or MFO. For example, for samples A and PA the surface area is that of γ -Al₂O₃ while for CZO and PC the surface area is that of Ce_{0.3}Zr_{0.7}O₂. On the other hand, for samples SA and PS, the reported surface area is mainly from Al₂O₃ with a smaller contribution from MFO. XRD results (not included here) show that MFO has a cubic structure with the lattice constant of 8.314 Å. Based on the Scherrer equation [124], the estimated crystallite size of MFO is ~20 nm. Assuming the MFO resides on the Al₂O₃ as spheres with no porosity, the estimated surface area of the MFO is ~30 m²/g (25 wt.% MFO/Al₂O₃ basis). CO chemisorption measurements reveal a PGM dispersion for the PA sample of 11%. The consumption of CO was used to estimate the amount of PGM oxide from which the PGM dispersion was determined. However, for PS or PC, the OSM (MFO

and CZO) caused a much higher CO consumption compared to the PA, giving rather unreliable results. Hence the results for PS and PC are excluded.

Table 5.1 DET Sufface Area						
Powder Catalyst	Α	CZO	SA	PA	PC	PS
BET Surface Area (m ² /g)	170.1	76.3	93.2	164.6	73.3	95.2

Table 5.1 BET Surface Area

5.1.2 Surface area and PGM dispersion

SEM was used to characterize the washcoat thickness of monolith catalysts. The peripheral-averaged thickness was calculated to account for the different washcoat thickness on monolith walls or in monolith corners. The washcoat thickness for single-layered monolith is $20 \sim 30 \,\mu\text{m}$ while the washcoat thickness for dual-layered monolith is $\sim 50 \,\mu\text{m}$.

5.1.3 TPR and TPD

The TPR and TPD results (Fig. 5.2) show the signal intensities in consumption/generation rates to enable a clear comparison of the temperatures where there are notable peaks. The values on the vertical axes represent the net rate for any of the subplot (i.e., the dashed line represent zero for any of the subplot). The rate values were changed arbitrarily to ensure easier comparison between CZO and MFO. The TPR data are used to elucidate the OSM reduction process by identifying the temperatures giving notable intensity changes; the magnitude of the signals are less important. Fig. 5.2 shows that the uptake magnitude is ~10 times higher for SA compared to CZO using CO as the reductant, which reflects the higher OSC for MFO. A quantitative comparison of the more important DOSC is presented in Chapter 6.

The H₂-TPR show significant differences between the samples. The data for PA (Fig. 5.2 (a)) show that the oxide associated with the PGM supported on Al₂O₃ is reduced in the relatively lower temperature range of 100 °C to 350 °C. The H₂ consumption is attributed to the reduction of PtO_x and PdO [58]. In contrast to the other samples, the rather broad peak indicates a lower amount of stored oxygen. Malet et al. [75] pointed out that the merging of multiple peaks into a single peak is likely for higher values of β/C_0 ratio, where β and C₀ represent temperature ramp rate and reductant concentration respectively. A higher H₂ concentration did not help to overcome the measurement challenge due to the limited amount of oxides. The noise in the results can be attributed the relatively high signal-to-noise ratio of the mass spectrometer detector.



Figure 5.2 (a) H₂-TPR results [Conditions: 60 sccm, 10 °C/min, 10% H₂/Ar for CZO, PC, SA, PS; 4000 ppm H₂/Ar for PA]; (b) CO-TPR results [Conditions: 60 sccm, 10 °C/min, 10% CO/Ar]; (c) O2-TPD [Conditions: 60 sccm, pure Ar].

The TPR data show considerable differences in the CZO containing catalysts. For sample CZO, both H₂-TPR (Fig. 5.2 (a)) and CO-TPR (Fig. 5.2 (b)) show reductant uptake starting from a relatively low temperature (~ 200 °C), with a large peak appearing at higher temperature (~ 400 °C). These data are consistent with previous studies that report reduction of surface and bulk oxygen species occurring at low temperature (~ 450 °C) and high temperature (~ 750 °C), respectively [33][37][125]. With the addition of PGM to the CZO (sample PC) an easier reduction is enabled. Specifically, H₂-TPR shows reductant consumption starting at ~100 °C (Fig. 5.2 (a)) while CO-TPR (Fig. 5.2 (b)) shows consumption starting at ~175 °C. Previous studies [126][127][128] report that the metalsupport interaction between PGM and CZO enables an easier utilization of oxygen. During H₂-TPR on PC, the large peak at ~100 °C is attributed to sites near PGM (Pt and Pd). Similarly, during CO-TPR on PC, the two reduction peaks at ~175 °C and ~275 °C are attributed to adsorbed oxygen located near the Pt and Pd crystallites, while the two other more subtle higher temperatures reduction peaks at ~425 °C and ~600 °C are attributed to the surface oxygen sites further from PGM and bulk oxygen sites, respectively.

For sample SA, both H₂-TPR and CO-TPR (Figs. 5.2 (a) and 5.2 (b)) show multiple peaks. H₂-TPR (Fig. 5.2 (a)) shows a minor H₂ consumption peak at ~150 °C and a major H₂ consumption peak at ~425 °C, with continuous H₂ consumption up to 700 °C (upper temperature limit). In CO-TPR (Fig. 5.2 (b)), detectable CO consumption starts at ~150 °C, with three peaks observed at ~375 °C, ~435 °C and ~570 °C. The multiple peaks in H₂-TPR and CO-TPR suggest the existence of multiple metal oxide species. This is attributed to the multi-valent nature of MFO (Mn_{0.5}Fe_{2.5}O₄); both Mn and Fe cations can exist in the +2 and +3 oxidation states. In a reducing atmosphere, the Mn and Fe cations are reduced to lower oxidation states (i.e., Mn(III) \rightarrow Mn (II) and Fe(III) \rightarrow Fe (II) \rightarrow Fe⁰). This is accompanied by the loss of lattice oxygen to gaseous products (i.e., CO, CO₂ and H₂O). Two overall reactions are as follows:

$$Mn_{0.5}Fe_{2.5}O_4 + CO \rightarrow 0.5 MnO + 2.5 FeO + CO_2$$
 (R5.1)

and
$$Mn_{0.5}Fe_{2.5}O_4 + 3.5 CO \rightarrow 0.5 MnO + 2.5 Fe + 3.5 CO_2.$$
 (R5.2)

Reaction R5.1 corresponds to 1 mol O/mol MFO while R5.2 corresponds to 3.5 mol O/mol MFO.

Quantification of the CO consumption over different temperature ranges provides deeper insight into the progressive reduction of the MFO spinel. For example, $OSC_{CO}^{50-700^{\circ} C}$ represents the integral CO consumption per mole of MFO from 50 °C to 700 °C. Our calculations show that $OSC_{CO}^{50-475^{\circ} C}$ and $OSC_{CO}^{50-700^{\circ} C}$ are ~ 0.9 mol O/mol MFO and ~ 3.1 mol O/mol MFO, respectively. $OSC_{CO}^{50-475^{\circ}C}$ ~ 0.9 mol O/mol MFO suggests the first phase of CO reduction given by reaction R4; i.e., Mn(III) and Fe(III) to Mn(II) and Fe(II). Above 475 °C, the CO-TPR shows only one peak, suggesting reduction of Fe(II) to Fe. The calculated $OSC_{CO}^{50-700^{\circ}C}$ value of 3.1 mol O/mol MFO is slightly smaller than the stoichiometry value of 3.5 from reaction R5.2 which suggests incomplete reduction of MFO during the CO-TPR. Full reduction may be achieved at higher temperature but this was not pursued due to experimental constraints.

PGM addition to the MFO generally lowers the peak temperatures during H₂-TPR and CO-TPR (Figs. 5.2 (a) and 5.2 (b)), although the decreases are rather small. For PS, both H₂ and CO-TPR show some reductant consumption from ~175 °C but the major reductant consumption occurs at higher temperatures (i.e., ~600 °C for H₂ and ~540 °C for CO). This suggests that PGM deposition onto the MFO provides limited promotion for oxygen activation from the MFO. This point is also supported by DOSC results discussed later in Section 5.5.

O₂-TPD was conducted to rule out the possibility of thermal decomposition of the OSM. Thermal decomposition of ceria occurs at the rather high temperature of ~1000 °C [94]. Fig. 5.2 (c) shows that SA releases O₂ under inert flow above 550 °C, suggesting desorption of pre-adsorbed O₂ or decomposition of MFO. The OSCC (oxygen storage capacity, complete) [36] can be calculated by assuming that all Mn (III) is reduced to Mn (II) and all Fe (III) are reduced to Fe⁰. The total amount of released O₂ only accounts for ~0.1% of the OSCC of SA. Thus, the extent of thermal decomposition is quite limited in the temperature range of 550 °C -700 °C. Therefore it can be concluded that reduction of CZO and MFO occurs mostly from reaction between reductant and oxygen contained in the OSM rather than from OSM thermal decomposition.

5.2 Steady-State Results

In this Section, CO, NO, and C₃H₆ abatement behavior for the simulated exhaust under steady-state conditions is compared for all seven monolith catalyst samples (CZO, SA, PA, PC, PS, PAC_DL, PAS_DL). These data help to assess the contributions from the PGM and OSM components, as well as the impact of the catalyst architecture.

5.2.1 Reference Catalysts

Three catalysts (CZO, SA and PA) serve as reference materials to understand the contributions from PGM and CZO components.



Figure 5.3 Reactant (NO, CO, C₃H₆) conversions as a function of feed temperature under steady-state operation using PA, SA or CZO [Conditions: 0.17% H₂, 0.52% CO, 400 ppm C₃H₆, 500 ppm NO, 0.5% O₂, 7% H₂O, 7% CO₂, balanced Ar].

Fig. 5.3 compares the NO (5.3 (a)), CO (5.3 (b)), and C_3H_6 (5.3 (c)) conversion for the three reference catalysts spanning the feed temperature range spanning 200 °C to 500 °C. Clearly, PA is the most active of the three catalysts, which is not surprising given that it is the lone reference catalyst containing PGM. With PA, the T₈₀ (the feed temperature giving 80% conversion) for NO, CO and C₃H₆ are ~375 °C, ~345 °C and ~365 °C, respectively. Both CZO and SA give rather low NO and CO conversions (< 20%) over the tested temperature range, with SA having a consistently higher, albeit slight, activity than CZO. SA is much more active for propylene oxidation than CZO; e.g., ~60% conversion for SA at feed temperature at 500 °C compared to only ~12% conversion for CZO. In summary, the PGM is much more active than the OSM materials. CZO itself has a negligible activity in converting NO, CO and C₃H₆ below 500 °C while the MFO spinel catalyzes C₃H₆ conversion at relatively low temperatures (e.g., > 350 °C).

5.2.2 PGM and OSM-containing catalysts

As described earlier, two types of catalyst architectures were employed to incorporate the PGM and OSM functions onto the monolith substrate. The first architecture comprised PGM deposited directly onto the OSM. The second architecture comprised OSM and PGM as two separate washcoat layers. Figs. 5.4 and 5.5 shows the NO, CO, and C₃H₆ conversions for the PGM-only (PA) and PGM + OSM-containing catalysts (PC, PAC_DL, PS, PAS_DL) under steady-state conditions based on either feed temperature (Fig. 5.4) and monolith temperature (Fig. 5.5). The PGM-only sample (PA) serves as the reference to evaluate the contribution from OSM addition. The performance of the samples are evaluated based on feed temperature and monolith temperature. Results for the CZO-based catalysts are provided in Figs. 5.4 (a) ~ 5.4 (c) (feed temperature) and Figs. 5.5 (a) ~ 5.5 (c) (monolith temperature); results for the MFO-based catalysts are provided in Figs. 5.4 (d) ~ 5.5 (f) (monolith temperature).

Results based on feed temperature are considered first. For all the catalyst samples the NO, CO, and C₃H₆ conversions span <20% at feed temperatures below ~200 °C to >95% at post light-off temperatures (> 350 °C). Between those limits the activities of the catalysts vary significantly. Table 5.2 provides the T_{80} values for NO, CO and C_3H_6 conversions. In general, the addition of OSM decreases T_{80} (from the PA reference value) for each of the reactants. The PC sample exhibits the largest T_{80} decrease; i.e., ~65°C, ~85°C, and ~80 °C for NO, CO and C_3H_6 , respectively. In contrast, a considerably smaller T_{80} decrease of ~15 °C is evident for the dual-layer PAC_DL sample.



Figure 5.4 Reactant conversions on CZO (a - c) and spinel (d - f) - containing catalysts under steady-state operation. [Conditions: 0.17% H₂, 0.52% CO, 400 ppm C₃H₆, 500 ppm NO, 0.5% O₂, 7% H₂O, 7% CO₂, balanced Ar].

A different trend is observed with the MFO-containing catalysts. For sample PS, the T₈₀ for NO, CO and C₃H₆ is lowered by ~35 °C, ~25°C, and ~45 °C, respectively, from



the PA reference value. For the dual-layer sample PAS_DL, T_{80} for NO and CO is lowered by another ~15 °C and 30 °C compared to PS, while the T_{80} for C₃H₆ remains unchanged.

Figure 5.5 Reactant conversions on CZO (a - c) and spinel (d - f) - containing catalysts under steady-state operation. [Conditions: 0.17% H₂, 0.52% CO, 400 ppm C₃H₆, 500 ppm NO, 0.5% O₂, 7% H₂O, 7% CO₂].

	/				0
Catalyst	PA	РС	PAC _DL	PS	PAS_ DL
T ₈₀ (NO) (°C)	~375	~310	~355	~340	~325
T ₈₀ (CO) (°C)	~345	~260	~335	~320	~290
$T_{80} (C_3 H_6) (^{\circ}C)$	~365	~285	~345	~320	~320
T _{80,m} (NO) (°C)	~450	~380	~425	~410	~400
T _{80,m} (CO) (°C)	~390	~330	~390	~350	~330
$T_{80,m}(C_{3}H_{6})(^{\circ}C)$	~430	~360	~410	~385	~390

Table 5.2 T₈₀ and T_{80,m} of NO, CO and C₃H₆ for PGM-containing Catalysts

Oxidation of reductants (H₂, CO, C₃H₆) generate an exotherm with a temperature rise proportional to their feed concentrations. This increases the catalyst temperature and reaction rates. For the multiple reaction system used, the temperature rise between the feed and the midpoint of monolith approached ~80 °C at complete conversion. To account for the temperature rise, the reactant (NO, CO, C₃H₆) conversions obtained with the PGM + OSM-containing catalysts are plotted as a function of monolith temperature (Figs. 4g – 4l). The monolith temperature based light-off temperature, T_{80,m}, was measured for NO, CO and C₃H₆ for the five catalysts. The results are summarized in Table 5.2. For CZOcontaining samples, PAC_DL gives a T_{80,m} about ~10 °C higher than T₈₀, compared to PA. PC gives a large decrease (~70 °C) in T_{80,m} for NO, CO and C₃H₆ compared to PA. The spinel containing catalysts PAS_DL and PS have ~40 °C lower T_{80,m} for C₃H₆ oxidation compared to PA. The PGM-deposited MFO sample (PS) has a T_{80,m} for NO and CO conversion that is ~40 °C lower than that obtained for PA. PAS_DL gives a further decrease ~10 °C to T_{80,m} for NO and CO compared to PS.

To summarize, the steady state findings show that the preferred architecture giving the best overall abatement of NO, CO, and C_3H_6 depends on the OSM material. For CZO the preferred architecture is single layer of CZO-supported PGM while for the MFO spinel the preferred architecture is the dual-layer PGM + spinel. This point is discussed in later Sections.

5.3 Promotion by OSM

In the last section the steady-state performance for the PGM-only, OSM-only and PGM + OSM containing catalysts is compared. The catalyst comparisons conclusively

show that the OSM (CZO or MFO) promotes the activity for most of the catalysts. In this section, OSM contributions to the simultaneous removal of NO, CO and C_3H_6 is further discussed. It is useful at this point to provide the global reactions that occur for the feed containing NO, CO and C_3H_6 (R5.3 ~ R5.5). These are as follows:

$$H_2 + 0.5 O_2 \rightarrow H_2O$$
 $\Delta H_{298K}^{\Theta} = -241.8 \text{ kJ/mol},$ (R5.3)

$$CO + 0.5 O_2 \rightarrow CO_2 \qquad \Delta H^{\Theta}_{298K} = -283.0 \text{ kJ/mol}, \quad (R5.4)$$

$$C_{3}H_{6} + 4.5 O_{2} \rightarrow 3 CO_{2} + 3 H_{2}O \qquad \Delta H^{\Theta}_{298K} = -1928.3 \text{ kJ/mol}, \quad (R5.5)$$

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad \Delta H_{298K}^{\Theta} = -41.2 \text{ kJ/mol}, \qquad (R5.6)$$

$$C_{3}H_{6} + 3 H_{2}O \rightarrow 3 CO + 6 H_{2} \qquad \Delta H^{\Theta}_{298K} = 371.64 \text{ kJ/mol}, \quad (R5.7)$$

and CO (or H₂ or C₃H₆) + NO \rightarrow N₂ (or N₂O or NH₃) + CO₂ (and H₂O)*

In addition to the oxidation reactions, NO reduction (R5.8), water gas shift (WGS, reaction 5.6), and C_3H_6 steam reforming (C_3H_6 SR, reaction 5.7) occur, the latter two when O_2 is completely consumed. The oxidation reactions R5.3 to R5.5 provide exothermic reaction heat of reaction to drive endothermic reactions such as steam reforming of propylene or the reverse water gas shift reaction (reverse of R5.6).

5.3.1 Impact of water gas shift and C₃H₆ steam reforming

The catalytic performance of the water gas shift reaction and C_3H_6 steam reforming reaction were tested for the CZO and MFO-based catalysts.

Vehicular exhaust contains large amounts of H₂O and CO₂, deep oxidation products of the fuel combustion. For this reason, reactions involving H₂O provide alternative routes for the conversion of reductants (CO and C₃H₆), namely water gas shift reaction (WGS, Reaction 5.6) and C₃H₆ steam reforming (C₃H₆ SR, Reaction 5.7). The reversible and exothermic WGS reaction is thermodynamically favored and kinetically limited at low temperature [129]. WGS catalysts include Fe₂O₃-Cr₂O₃, Cu-ZnO-Al₂O₃, Rh-CZO, Pt-CZO, among others [129][130]. Fig. 5.6 (a) compares the WGS performance over monolith catalysts PA, PC, PS, SA and PAS_DL. The model feed contains the same CO, H₂O and CO₂ concentrations as the simulated exhaust. Conversions are shown as a function of feed temperature as the temperature rise is relatively small. The H₂ yield is defined as

$$Y_{H_2}(\%) = \frac{[H_2]_{effluent}}{[CO]_{feed}} \times 100\%.$$
 (5.1)

Included in Fig. 5.6 (a) is the H₂ equilibrium yield. With WGS being exothermic, the equilibrium yield is a monotonic decreasing function of temperature.

Clearly, the best WGS catalyst is PC with the H₂ yield greatly exceeding that obtained for all other catalysts. The actual H₂ yield approaches the equilibrium value when temperatures reach ~350 °C. Above 350 °C, the H₂ yield decreases with temperature, following the equilibrium curve. The impressive activity of CeO₂ supported PGM results from the strong interaction between ceria and PGM [37][131]. Fu et al. [132] reported that nonmetallic platinum species strongly associated with surface Ce-O groups (e.g., Pt-O-Ce) are responsible for the WGS activity. The three other catalysts considered show rather poor WGS activity. In fact, the SA and PA show almost negligible H₂ yield below 500 °C. PS and PAS_DL starts to catalyze WGS around 500 °C with limited H₂ yield as ~18%, which is very much lower than the equilibrium yield as ~80%.

Among the three reductants used in this study (H₂, CO, C₃H₆), H₂ is the most easily converted. As just discussed above, PC is an active WGS catalyst while PA and spinelcontaining catalysts (PS, SA, PS, PAS_DL) exhibit negligible WGS activity below 500 °C. To this end, the WGS activity of PC provides another conversion pathway for CO beyond its oxidation path. A comparison of the feed temperature dependence of H₂ yield during WGS (Fig. 5.6 (a)) and of CO conversion during oxidation (Fig. 5.5 (a)) suggests that oxidation is in part enabled by reaction of CO with H₂O. Both the H₂ yield and CO conversion are ~50% at ~325 °C. In contrast, for PA and spinel-containing catalysts, the WGS route has an apparent negligible contribution to CO oxidation before light-off.



Figure 5.6 Performance of (a) water gas shift reaction (WGSR) and (b) C₃H₆ steam reforming (C₃H₆ SR) using selected catalysts (PA, PC, PS, PAD_DL and SA). [Conditions: (a) 0.52% CO, 7% H₂O, 7% CO₂; (b) 400 ppm C₃H₆, 7% H₂O].

The endothermic C_3H_6 SR reaction is thermodynamically favored at high temperatures. Fig. 5.6 (b) shows the expected monotonic increasing dependence of C_3H_6 conversion with temperature over PA, PC, PS, SA and PAS_DL. The model feed contained

the same C₃H₆ and H₂O concentrations as the full simulated exhaust. Similar to the WGS results (Fig. 5.6 (a)), PC gives a higher C₃H₆ conversion than PA and spinel-containing catalysts over the entire temperature range. In addition, PA and the spinel-containing catalysts (SA, PS and PAS_DL) have negligible C₃H₆ SR activity (i.e., < 5% up to 500 °C). This suggests that the C₃H₆ SR pathway has a negligible contribution to C₃H₆ consumption when using the O₂ containing feed. For the PC sample, while up to 20% conversion of C₃H₆ is obtained by 500 °C, its contribution during the full feed is small. Fig. 5.5 showed that T_{80,m} for C₃H₆ oxidation light-off with PC (Fig. 5.5 (c)) is ~360 °C. At that temperature may not be ignored. This is consistent with the findings of Dubien et al. [133], who showed that C₃H₆ SR started to promote C₃H₆ conversion above ~ 350 °C.

As a summary, PC shows excellent WGS promotion (from 300 °C) and limited C₃H₆ SR promotion. In contrast, PA or MFO-containing catalysts (SA, PAS_DL and PS) show negligible WGS or C₃H₆ SR activity below 500 °C. Among the three reductants used (H₂, CO, C₃H₆), H₂ is the most reactive. The WGS and C₃H₆ SR activity of PC provides additional conversion pathways for CO and C₃H₆ beyond the oxidations. In contrast, WGS and C₃H₆ SR routes have almost negligible contribution to CO and C₃H₆ conversion on MFO based catalysts, at least before light-off.

5.3.2 OSM Conversion Enhancement

Catalysts containing PGM supported on ceria (or CZO) are well known for their oxidation activity [33][37][134]. For example, the rate of CO oxidation over PGM-Al₂O₃ catalysts suffers from self-inhibition at low temperatures (before light-off) [135][106]. The

-1 order with respect to CO is well established [106]. Previous studies [135][106][136] show that addition of a sufficient amount of ceria (or CZO) to PGM-Al₂O₃ catalysts can mitigate the detrimental impact of CO self-inhibition. It is generally accepted that reaction occurs between CO adsorbed on PGM sites with oxygen adatoms supplied by CeO₂ to the PGM through a spillover process. Previous reported results [106][136] also show that PGM-CZO based catalysts (e.g., Pt/CeO₂/Al₂O₃ and Pd/CZO) also promote C₃H₆ light-off. The mechanism is thought to involve oxygen supplied via ceria (or CZO). The effective utilization of oxygen atoms from CZO is due to a favorable metal-support interaction between PGM and CZO. This was reported in earlier studies [33][37][134] and corroborated by TPR results described earlier (Fig. 5.2 (b)). The beneficial interaction clearly depends on the presence of the PGM-CZO interface where catalysis occurs. For this reason, catalysts in which the oxygen storage materials and PGM crystallites are not in close proximity are inferior to those that are. In order to maximize the promotional effect of CZO, the design with PGM directly deposited onto CZO should be used.

For MFO spinel-containing catalysts a different picture emerges. The oxidations of CO and C_3H_6 by O_2 are mainly responsible for the overall conversion of CO and C_3H_6 , as MFO-containing catalysts show rather poor WGS and C_3H_6 SR performance (Fig. 5.6). Before discussing the promotional impact of MFO for both the single-layer PS and dual-layer PAS_DL, it helps to examine the oxidation activity of alumina-supported spinel (SA) and alumina-supported PGM (PA).



Figure 5.7 CO or C₃H₆-TPO using PA or SA [Conditions: (a) 0.52% CO, 0.26% O₂, balanced Ar; (b) 400 ppm C₃H₆, 0.18% O₂, balanced Ar; (c) 0.52% CO, 400 ppm C₃H₆, 0.44% O₂, balanced Ar; Ramp rate: 10 °C/min].

			1.
Catalyst	PA	SA	
T _{50,m} (CO) (°C)	~ 290	~ 475	
$T_{50,m} (C_3 H_6) (^{\circ}C)$	~410	~ 410	

 Table 5.3 T_{50,m} of CO or C₃H₆ in CO or C₃H₆-TPO on PA and SA Samples

Figs. 5.7 (a) and 5.7 (b) respectively show the TPO of individual components CO and $C_{3}H_{6}$. Table 5.2 provides the light-off temperatures ($T_{50,m}$) of CO and $C_{3}H_{6}$ during their oxidations. PA is clearly the more active of the two catalysts, with a ~185 °C lower $T_{50,m}$ for CO oxidation compared to SA, while achieving 100% CO conversion by ~320 °C. These data suggest that CO oxidation is faster on the PGM sites. In contrast, C₃H₆ oxidation performance on SA is comparable to that on PA; both SA and PA have a similar T_{50,m} for C₃H₆ oxidation of ~410 °C. For PA, detectable C₃H₆ conversion starts from ~225 °C. Before light-off, a plateau in C_3H_6 conversion occurs over the 250 ~375 °C temperature range. A similar feature was reported for propylene oxidation on Pd/CeO₂ [106]. The sharp feature may be due to ignition of accumulated carbonaceous species on the PGM sites [106][137]. Compared to PA, SA has a smoother but less steep C₃H₆ light-off curve. Further, while complete C₃H₆ conversion is not reached until quite high temperature (550 °C) for SA, C₃H₆ conversion is detectable starting at temperatures as low as ~300 °C. In fact, over a narrow temperature range (340 °C ~410 °C), SA has a higher C₃H₆ conversion than PA. Additionally, CO appears as a byproduct from partial oxidation of C₃H₆ on SA.

In order to decipher the data for the supported MFO spinel catalyst (SA), it is instructive to conduct a set of TPO experiments of single component and two components to identify inhibition effects. The TPO results for H₂, CO, C₃H₆ for single- and co-oxidations are provided in Fig. 5.6. Table 5.3 gives the measured light-off temperatures for H₂, CO and C₃H₆ in single oxidation and co-oxidation experiments. The O₂ feed concentration is adjusted in all cases to maintain overall stoichiometric feeds.



Figure 5.8 TPO performance of SA in stoichiometric feeds [Reductant concentration: (I) Sole oxidation: 0.17% H₂/0.52% CO/400 ppm C₃H₆; (II) Co-oxidation: combination of 0.17% H₂, 0.52% CO and 400 ppm C₃H₆; 10 C/min].

The data show that CO oxidation is inhibited by H₂ and/or C₃H₆, while C₃H₆ oxidation is unaffected by H₂ and/or CO. For the single component oxidations, the T_{50,m} for H₂, CO and C₃H₆ are 410 °C, 475 °C and 410 °C, respectively. The addition of a second reductant to H₂ (CO or C₃H₆) results in a higher T_{50,m}, showing cross inhibition (Fig. 5.8

(a)). A similar result happens for CO when either H₂ or C₃H₆ are added (Fig. 5.8 (b)). In contrast, the C₃H₆ conversion and light-off remains unaffected by the addition of CO or H₂ (Fig. 5.8 (c)). TPO results (not included here) with a ternary mixture having a stoichiometric concentration of O₂ also shows unaffected C₃H₆ light-off but inhibited oxidations of CO and H₂. Earlier it is showed that CO oxidation is preferred on PGM sites. For H₂ oxidation, PA gives T_{100, m} ~50 °C while SA gives T_{50,m} ~410 °C. The TPO results using SA confirm that C₃H₆ oxidation occurs on both PGM and MFO sites while CO and H₂ oxidation is preferred on PGM sites.

Doductont	$T_{50,m}$ for desired reductant (°C)					
Keuuctant	Sole-oxidation	With 0.17% H ₂	With 0.52% CO	With 400 ppm C ₃ H ₆		
\mathbf{H}_2	410		450	500		
СО	475	525		540		
C3H6	410	410	410			

Table 5.4 Light-off temperatures for H₂, CO and C₃H₆ on SA

The previous literature shows that CO and C₃H₆ inhibit each other during light-off on both Pt/Al₂O₃ and Pd/Al₂O₃ catalysts [106][137][138]. Fig. 5.9 shows the single oxidations of CO and C₃H₆ as well as co-oxidations while keeping the O₂ concentration at the neutral stoichiometric condition. At the feed concentrations considered for the single oxidations (0.52% CO or 400 ppm C₃H₆) CO lights off at ~300 °C while C₃H₆ lights off at ~410 °C. The addition of the other reductant increases the light off temperature for each by ~150 °C for CO and ~50 °C for C₃H₆, demonstrating mutual inhibition.



Figure 5.9 CO or C₃H₆-TPO using PA, PAS_DL or PS [Conditions: (a) 0.52% CO, 0.26% O₂, balanced Ar; (b) 400 ppm C₃H₆, 0.18% O₂, balanced Ar; Ramp rate: 10 °C/min].

With the catalytic activity of MFO established for C_3H_6 oxidation and the mutual inhibition on the particular PGM formulation demonstrated, the better performance of the dual-layer PGM + spinel catalyst (PAS_DL) can be more clearly understood. The PGM sites are active for both the oxidations of CO and C_3H_6 . Thus, the addition of the MFO to the PGM catalyst mitigates the mutual inhibition between CO and C_3H_6 . This is a result of the oxidation of C_3H_6 on the MFO-only catalyst. Fig. 5.7 (c) compares the co-oxidation performance of CO and C_3H_6 oxidation over PA and PAS_DL. The addition of the base MFO (PAS_DL) lowers the $T_{80,m}$ for C_3H_6 and CO by ~85 °C and ~65 °C. The enhancement in the C_3H_6 conversion is attributed to the additional oxidation that occurs on the MFO sites of the dual-layer catalyst (Fig. 5.7 (b)). In contrast, the enhancement in the CO conversion results from a higher rate of CO oxidation on PGM as we shown earlier that SA exhibits negligible CO oxidation activity below 375 °C (Fig. 5.7 (a)). However, in this temperature range the dual layer catalyst has a higher C₃H₆ conversion, which lowers the local C₃H₆ concentration. This in turn lessens the detrimental inhibition of CO oxidation by propylene on the PGM sites (Fig. 5.9). In addition, CO that is generated through C₃H₆ partial oxidation over SA may be catalytically converted in the adjacent top PGM layer. Hence, CO conversion in co-oxidation using PAS_DL is enhanced compared to PA. The CO and C₃H₆ oxidation results over PA and PAS_DL are consistent with earlier results in Fig. 5.4, that show PA and PAS_DL give nearly equal NO, CO and C₃H₆ conversions below ~310 °C. Above 310 °C NO, CO and C₃H₆ conversions on PAS_DL exceed those on PA.

The enhanced conversion of CO and C₃H₆ oxidation by PS (vs. PA) is attributed to two factors. The first factor is that MFO is a supplier of oxygen to the PGM at the PGM-MFO interface, akin to the role of CZO for the PC catalyst. The second factor is an active MFO. Fig. 8a compares the CO TPO results for PA, PAS_DL and PS. Compared to PA, both PAS_DL and PS have slightly lower T_{50,m}; i.e., ~ 5 °C and ~ 30 °C, respectively. We discussed earlier that the MFO has poor CO oxidation activity below 375 °C (Fig. 5.7 (a)). Accordingly, the dual-layer PAS_DL shows similar CO oxidation performance to the PA. The enhancement obtained with PS relies on the interaction between the spinel and PGM. Earlier CO-TPR data (Fig. 5.2 (b)) show that the addition of PGM directly onto the MFO spinel slightly promotes oxygen activation from MFO, i.e., the CO consumption peak is lowered by 35 °C, from 570 °C to 535 °C. In comparison, the CO-TPR data (Fig. 5.2 (b)) show that PGM deposited on CZO dramatically enhances oxygen activation from CZO, with the peak temperature lowered by ~200 °C, from ~375 °C to ~175 °C. This difference suggests that the interaction between PGM and MFO is quite a bit weaker than between PGM and CZO. Fig. 8b compares the C₃H₆ TPO results for PA, PAS_DL and PS. Compared to PA, both PAS_DL and PS give better C₃H₆ oxidation performance, with T_{50,m} lowered by ~ 80 °C and ~ 70 °C, respectively. Again, as shown earlier the MFO spinel itself catalyzes C₃H₆ oxidation (Fig. 5b). With PS and PAS_DL having the same MFO loading, the second role of MFO as an oxidation catalyst should be comparable for both catalysts. However, the inferior C₃H₆ TPO performance of PS compared to PAS_DL suggests a detrimental PGM-MFO interaction that negatively impacts the C₃H₆ oxidation. This result is quite different than the enhancement achieved with the CZO-supported PGM which promotes C₃H₆ oxidation [106][137][138].

Finally, with a full mixture (CO, C₃H₆, NO and O₂), the overall performance is more complicated due to the potential inhibition among reactants. A thorough understanding of the effects will require combined experimental and modeling, a subject for future study. Additionally, MFO spinel needs to be screened for desired reaction activities, such as HC oxidation and NO decomposition.

5.3.3 Promotion for NO reduction

Figs. 5.4 (a) and 5.4 (d) showed that addition of OSM to PA enhances NO conversion for both CZO- and MFO-containing catalysts. For the former, previous researchers reported additional NO reduction pathways, including NO decomposition on reduced ceria and PGM/CZO [71][139] as well as direct NO reduction by reductant (CO or H₂) [70][95]. To this end, NO reduction performance over MFO-containing catalysts is tested with CO as the model reductant.



Figure 5.10 NO reduction performance by CO using selected catalysts as a function of feed temperature. [Conditions: 500 ppm NO, 600 ppm CO, balanced Ar].

Fig. 5.10 shows the NO conversion as a function of temperature over PA, PS and SA with CO as the reductant for the nearly equimolar mixture (CO/NO = 6/5). Overall the PS sample is the most active for NO conversion while SA is nearly inactive. Between 200 °C to 400° C, the NO conversion is <10%, suggesting that MFO by itself offers little or no NO reduction activity. In addition, the MFO-free PGM sample PA is only moderately active. Clearly the addition of PGM onto the MFO spinel gives a large enhancement in the NO conversion. This is not simply a result of the addition of precious metal crystallites but the creation of an active co-catalyst, likely at the PGM-MFO interface. Interestingly, earlier results in Fig. 4j showed that PAS_DL promotes NO conversion compared to PA. The somewhat counterintuitive result suggests that the interaction does not require a large interface between the two functions. For PA, only PGM sites are available to catalyze the chemistry. In such a case all of the reactants (H₂, CO, C₃H₆, O₂, NO) compete with each other for adsorption and reaction on PGM sites. For PAS_DL, the MFO provides additional

sites for desired reactions, particularly C_3H_6 oxidation. This lessens the competition between reactants and as a result makes NO reduction more efficiently on PGM sites.

5.4 Impact of Modulation

The exhaust from combustion engines switches between fuel-lean and fuel-rich conditions due to the imperfect control of the air/fuel ratio. Hence, a more realistic testing condition is a cycle-averaged near-stoichiometric feed with periodic variation between lean and rich composition. An intriguing extension would be optimized feed policies that maximize catalysts performance, minimize precious metal content, or a combination of both.

Cycle-averaged NO, CO, C₃H₆ conversions under modulated feeds over PA and PGM+OSM containing catalysts are shown as a function of the feed temperature in Fig. 5.11. The feed always contain 0.17% H₂, 0.52% CO, 400ppm C₃H₆, 7% H₂O and 7% CO₂. In steady state operation, O₂ concentration is fixed as 0.5%. In modulation operation, O₂ concentration in lean and rich is chosen as 0.7% and 0.3% respectively. For the latter, results over PC and PAS_DL were used for comparison, as we previously showed that the PC sample is the best for CZO-containing catalysts while the PAS_DL is the best for MFO-containing catalysts. For each of the three catalysts performance under a steady-state feed is included as the reference.

For the PA sample (Fig. 5.11, left column), modulation only slightly increases the NO and C_3H_6 conversions before light-off (< 350 °C), while the CO conversion is nearly unaffected. Enhancement in the conversions of NO and C_3H_6 under modulation is consistent with the study of Muraki et al. [140] who reported NO and C_3H_6 conversion
enhancement under modulation with a Pt/Al₂O₃ catalyst. Silveston [141][142] reviewed the impacts of modulation on TWC performance, showing that forced modulation might enhance conversion of some reactants at low and medium temperatures (< 400 °C). Other studies [143][144][145] point out that the impacts from modulation are complex, with dependence on several parameters, including catalyst compositions (e.g., PGM type), reaction conditions (e.g., reductant type, space velocity, axial dispersion), and modulation modes (e.g., modulation frequency and amplitude). Conversion (or rate) enhancement by forced modulation is a result of a nonlinear coupling between the transient feed composition and the rate of consumption. In general, the dependence of output and input reactant concentration must be concave and the modulation must be sufficiently fast relative to the catalyst response time [146].



Figure 5.11 Reactant conversions under steady-state or modulation operation over PA, PAS_DL and PC; solid lines: steady-state; dashed lines: modulation. [Conditions: space velocity: 70,000 h⁻¹; 4s lean/4s rich].

The PA data reveal that at high temperatures (>350 °C), modulation suppresses the NO, CO and C₃H₆ conversions by ~20%, ~12% and ~7%, °C respectively. Silveston [141][142] also showed that periodic forcing suppresses conversions at high temperatures (i.e., 400 °C - 800 °C). Suppression of conversion by modulation at high temperatures results from insufficient oxidation of reductants (CO and C₃H₆) during the rich feed and insufficient reduction of NO during the lean feed. The mathematical condition for suppression of the rate is a convex rate dependence on the reactant concentration [146].

These findings on the effect of modulation on the performance of the reference PA catalyst motivates an investigation of the impact of OSM addition on the catalyst performance [147]. Trapping and release of oxygen is expected to have an impact since the rates of oxidation and reduction (of NO) are typically sensitive to the O_2 concentration. In this study a longer cycle (4s/4s) is chosen to amplify the decrease by modulation at high temperatures in order to clearly illustrate the role of OSM. The experiments reveal that addition of OSM (either CZO or MFO) mitigates the detrimental impact of modulation in the high conversion and temperature regimes. For example, with PAS_DL (Fig. 5.11 second column) or PC (Fig. 5.11, third column III) the NO conversion under modulation is ~10% lower than under steady-state operation. Thus the gap between steady state and modulated operation is smaller. For CO conversion the OSM benefit is clearly evident for both CZO and MFO. In fact, CZO addition eliminates the modulation suppression completely, whereas for propylene conversion the MFO addition nearly eliminates the suppression. For the PAS_DL sample, modulation has a negligible impact on $C_{3}H_{6}$ conversion above 350 °C while for PA the conversion dropped up to 20% from the steadystate level.

5.5 Dynamic Oxygen Storage Capacity (DOSC)

Modulation results show that CZO and MFO-containing catalysts exhibit resistance to different reductant conversions; i.e., PC is resistant for CO conversion while MFO is resistant for C₃H₆ conversion. Such features result from different reduction capability of CO and C₃H₆ on the CZO and MFO. To further understand the impacts of modulation and OSC addition, DOSC measurements was conducted to evaluate the oxygen storage and release performance of CZO and MFO using reductants CO and C₃H₆ under lean/rich switching. The measured oxygen uptake was calculated from the data as a molar ratio for each OSM; i.e., mole O/mole CZO or MFO.

The cycle-averaged DOSC results for CZO or MFO based catalysts (OSM-only and PGM-OSM catalysts) with CO or C₃H₆ as the probe gas are shown in Fig. 5.12. Before showing the results it is instructive to define two limiting OSC values. The "OSC complete" (OSCC) [36] is the maximum oxygen consumption determined by the OSM stoichiometry. OSCC for both CZO and MFO spinel were estimated. For CZO it is assumed that that all Ce cations in Ce_{0.3}Zr_{0.7}O₂ are reduced from Ce(IV) to Ce(III). The OSCC is calculated to be 0.15 mol O/mol CZO. Similarly, the OSCC for MFO is estimated as 3.5 mol O/ mol MFO by assuming that all Mn cations are reduced to a Mn(II) and all Fe ions are reduced to Fe⁰. The second limiting OSC value is the "reductant limiting OSC" (or OSCR) in moles of O consumed/mole OSM during complete reductant consumption in the DOSC experiment. Figs. 5.12 (a) and 5.12 (b) show this limiting value when feeding in CO or C₃H₆ at the equivalent level of reduction intensity based on the oxidation stoichiometries (CO/C₃H₆ = 9). For CZO the OSCR value is 0.034 mol O/mol CZO while for MFO the

OSCR value is 0.225 mol O/mol MFO. Again, this estimate assumes 100% conversion of the injected CO (or C_3H_6) and O_2 .



Figure 5.12 Calculated DOSC of selected catalyst. (a) CZO based catalysts (CZO and PC);
(b) Spinel-based catalysts (SA and PS) [Conditions: carry Ar: 150 sccm; probe gas: 1.8% CO/Ar (or 0.2% C₃H₆/Ar) and 0.9% O₂/Ar; sampling loop: 5 mL].

Fig. 5.12 (a) compares the DOSC performance for CZO and PC. Over the temperature range considered (200 °C - 600 °C), CO gives a consistently higher DOSC than C_3H_6 for the CZO and PC catalysts. PGM addition dramatically enhances the utilization efficiency of oxygen from CZO, which is undoubtedly a result of the established

beneficial coupling between the PGM and CZO [33][37]. For example, DOSC for PC at 350 °C with CO as probe gas is ~0.028 mol O/mol CZO, accounting for ~18% of the OSCC, which is ~14 times higher than DOSC for the CZO-only sample at the same conditions (~ 0.002 mol O/mol CZO). The measured DOSC for PC for both CO and C₃H₆ approaches ~0.03 mol O/mol CZO at high temperature, which is slightly smaller than the OSCR value of 0.034 mol O/mol CZO. The slight difference may be attributed to diffusion impacts. The inferior DOSC by C₃H₆ at lower temperatures (< 450 °C) is attributed to the lower reactivity of C₃H₆ on either CZO or PGM-CZO [38][148].

Fig. 5.12 (b) compares the DOSC performance for the MFO and PS catalysts. Both MFO and PS exhibit dynamic oxygen exchange at the relatively lower temperature, i.e., $\sim 200 \,^{\circ}$ C for CO case and $\sim 250 \,^{\circ}$ C for C₃H₆. Further, over the same temperature range, CO and C₃H₆ give comparable DOSC. In contrast to CZO materials, PGM deposition onto the spinel OSC shows limited enhancement for DOSC, suggesting an ineffective activation of MFO spinel by the PGM, consistent with the earlier TPR results. For example, the DOSC for PS at 350 °C with CO as the probe gas is ~0.07 mol O/mol MFO, amounting to ~2% of the OSCC; this is ~1.5 times higher than the DOSC for the SA at the same conditions (~ 0.047 mol O/mol MFO). These measured DOSC values are slightly smaller than the OSCR value of 0.225 mol O/mol MFO at high temperature.

The transient profiles of effluent CO_2 concentration in the CO-DOSC measurements for the MFO spinel in Fig. 5.13. Figs. 5.13 (a) and 5.13 (b) show the CO_2 generation during the rich pulse (CO) and lean pulse (O₂), respectively. The rich CO_2 generation, which results from MFO reduction by CO. The almost negligible lean CO_2 generation comes from the reaction between injected O_2 and adsorbed carbonaceous

species from the previous CO injection. The fraction of CO₂ generation in rich/lean phases during CO-DOSC for three studied catalysts are summarized in Table 5.4. Generally, CO₂ generation limits in rich phase for SA, PS and CZO while considerable amount of CO₂ is generated in both rich and lean phase for PC. Evidence of lean CO₂ generation occurs only for PC below 350 °C, in agreement with previous studies [63][64].



Figure 5.13 Effluent CO₂ concentration in (a) rich and (b) lean during CO-DOSC measurement with spinel. [Conditions: Carry Ar flow rate: 150 sccm; probe gases: 1.8% CO/Ar and 0.9% O₂/Ar; sampling loop size: 5 mL].

Catalyst	Phase	Temperature (°C)								
		200	250	300	350	400	450	500	550	600
SA	Rich	99.1%	99.2%	99.0%	99.3%	99.1%	99.7%	99.9%	100%	100%
	Lean	0.9%	0.8%	1.0%	0.7%	0.9%	0.3%	0.1%	0%	0%
PS	Rich	99.1%	99.0%	99.1%	99.0%	99.2%	99.6%	100%	100%	100%
	Lean	0.9%	1.0%	0.9%	1.0%	0.8%	0.4%	0%	0%	0%
CZO	Rich	98.6%	98.3%	98.6%	98.4%	98.9%	99.1%	100%	100%	100%
	Lean	1.4%	1.7%	1.4%	1.6%	1.1%	0.9%	0%	0%	0%
PC	Rich	78.8%	84.9%	90.0%	94.1%	97.0%	98.2%	99.1%	99.9%	100%
	Lean	21.2%	15.1%	10.0%	5.9%	3.0%	1.8%	0.9%	0.2%	0%

Table 5.5 Fraction of Lean/Rich CO₂ Generation in CO-DOSC Tests on SA

A different trend is observed in C₃H₆-DOSC tests, where products from partial or total oxidation are generated in both rich and lean phases for SA, PS and PC at low and medium temperatures (e.g., < 450 °C).



Figure 5.14 (a) Effluent CO, CO₂, H₂, C₃H₆, O₂ concentration during C₃H₆-DOSC measurement with spinel at 450 °C; (b) (c) Effluent CO₂ concentration in rich and lean during C₃H₆-DOSC measurement with spinel.

Fig. 5.14 shows selected transient results for the C₃H₆-DOSC experiments with the MFO spinel. Fig. 5.14 (a) is the transient profile of effluent concentrations for reactants (C₃H₆ and O₂) and products (CO, H₂ and CO₂) at 450 °C. During the rich pulse, besides CO₂ as major product, CO and H₂ are generated as the byproduct from C₃H₆ oxidation. During the early rich, CO₂ is the only oxidation product, suggesting that C₃H₆ consumes easily accessible oxygen from Mn_{0.5}Fe_{2.5}O₄, likely surface oxygen. Generation of CO and H₂ in the later rich suggests less effective C₃H₆ oxidation by reduced Mn_{0.5}Fe_{2.5}O₄, which may be due to the difficulty in utilizing bulk oxygen. During the O₂ pulse, CO₂ is generated while CO or H₂ are undetected. For OSM-only sample (Spinel or CZO) and PS, CO is

generated as the main byproduct from 400 °C while H₂ yield approaches zero. However in PC case, CO and H₂ are generated with a ratio of ~1:1, suggesting the pathway of C₃H₆ partial oxidation. The generation of CO and H₂ may occur on less oxidized catalyst surface. Note that in DOSC calculation, the impacts of CO and H₂ were eliminated.



Figure 5.15 Schematic illustration of simultaneous removal of NO, CO and C₃H₆ over PC and PAS_DL during modulation.

Figs. 5.14 (b) and 5.14 (c) show the transient profiles of effluent CO₂ concentration during C₃H₆-DOSC for the MFO spinel for a wide range of temperatures. Considerable CO₂ is generated during both lean and rich pulses, particularly below 450 °C. DOSC results for PS and PC also show considerable CO₂ generation during both the lean and rich pulses below 400 °C. Previous studies [38][148] reported the "retention" of hydrocarbons on CZO-containing material, suggesting that hydrocarbon adsorption and reduction on CZOcontaining material results in formation of carbonaceous species. Such carbonaceous species are responsible for lean CO₂ generation observed in DOSC measurements for spinel and PC.

Fig. 5.15 depicts the envisioned process for CZO (a) and MFO spinel (b). The OSM is reduced by CO and C₃H₆ during the rich phase, generating vacancies and possibly depositing carbonaceous species in the case of propylene. The vacancies and carbonaceous species serve as active sites for NO and O₂ reduction during the following lean phase. As shown, the consumption of reductants (H_2 , CO and C_3H_6) with a modulated exhaust feed occurs via reaction with oxidants (O_2 and H_2O), as well as reaction with the OSM itself. The preference of reductant oxidation on the CZO-promoted PGM is in the order: $H_2 >$ $CO > C_3H_6$ [106][137]. Earlier described results (Figs. 5.6 (a) and 5.6 (b)) showed that PC has high WGS activity but negligible C₃H₆ SR activity. The DOSC results (Figs. 5.12 (a) and 5.12 (b)) show that CO results in a higher DOSC than C₃H₆ for both CZO and PC catalysts. Hence, under modulation conditions, CO is preferred to be converted over PC via oxidation by oxidants (O₂ and H₂O) and CZO than is C₃H₆. Accordingly, for PC (Fig. 5.11, Column III), CO conversion is more resistant to modulation than C₃H₆. The dual layer catalyst (PAS_DL) contains PGM as the active component and MFO as the promoter. The conversions of CO and C₃H₆ depend almost entirely on oxidation by O₂ and oxygen supplied by the MFO spinel since the catalyst has rather poor WGS and $C_{3}H_{6}$ SR activity (Fig. 5.6). As discussed earlier, with regards to co-oxidation of CO and C₃H₆ by O₂, PGM sites are favorable for CO oxidation while the MFO shows preference C₃H₆ oxidation. $C_{3}H_{6}$ inhibits CO oxidation on both PGM and spinel while $C_{3}H_{6}$ oxidation is inhibited by CO on PGM, but unaffected by CO on spinel. The DOSC results (Fig. 5.12 (b)) show that CO and C₃H₆ give similar DOSC for spinel. Collectively this suggests that the addition of the MFO to PA enhances C_3H_6 oxidation and increases the resistance of C_3H_6 conversion to modulation. If the promotion from spinel is sufficient C_3H_6 conversion remains almost the same under modulation compared to under steady-state operation (Fig. 5.11, Column II).

5.6 Conclusions

This experimental study of the simultaneous removal of NO, CO and C₃H₆ elucidates the promotion of precious metal catalyst from ceria- and spinel oxygen storage materials. The investigated impacts of OSM type (CZO and spinel Mn_{0.5}Fe_{2.5}O₄), operation mode (steady-state and modulation) as well as catalyst design (PGM deposition on OSM and separation of PGM and OSM) provide insight into the performance and design of catalysts for TWC applications.

The best PGM-OSM catalyst designs for CZO or spinel are direct deposition of PGM on CZO (PC) and dual-layer PGM-MFO structure (PAS_DL), respectively. Compared to PGM/Al₂O₃ (PA), PC and PAS_DL decreases T_{80,feed} (feed temperature giving 80% conversion) for NO, CO and C₃H₆ for ~70 °C and ~50 °C respectively. H₂ and CO-TPR results show strong interaction between PGM and CZO but weak interaction between PGM and spinel. Deposition of PGM onto CZO ease the activation and utilization of oxygen from CZO, especially oxygen proximal to PGM. PC shows promotion for oxidation of reductants (CO and C₃H₆), reduction of NO, water gas shift reaction and minor promotion for C₃H₆ SR promotion, all of which contribute to simultaneous removal of NO, CO and C₃H₆. In contrast, PA and MFO-containing PGM catalysts show rather confined WGS and C₃H₆ SR performance. The weak interaction between PGM and spinel indicates

that deposition of PGM onto spinel may not be the optimal design. Compared to PA, promotion from MFO-containing PGM catalysts mainly results from additional active catalytic sites ($Mn_{0.5}Fe_{2.5}O_4$), where desired reactants can be converted, especially via C₃H₆ oxidation by O₂.

At high temperatures (i.e., after light-off), modulation decreases NO, CO and C₃H₆ conversions simultaneously over PGM-Al₂O₃. Such a detrimental impact from modulation is lessened by OSM addition. PC and PAS_DL are more resistant to CO or C₃H₆ modulation respectively. Dynamic oxygen storage capacity (DOSC) measurements were conducted to evaluate the fast oxygen release/storage in OSM. Results show that the MFO spinel exhibits ~20 times higher DOSC than CZO with either CO or C₃H₆ as the probe reductant. Results show that CO and C₃H₆ have comparable reactivity with spinel but CO is better for CZO and PGM-deposited CZO. Experimental and modeling research of DOSC behavior of CZO and spinel are still on-going.

The study provides insight into the benefits of OSM and provides guidance for optimization of TWC catalyst formulation. Although spinel (Mn_{0.5}Fe_{2.5}O₄) may not be the optimal OSM for TWC design, spinel-containing PGM catalysts may be used in other applications. For example, concurrent studies at the University of Houston revealed that the dual-layer PGM-spinel catalysts exhibit comparable or even better CH₄ oxidation performance to PGM/CZO catalysts.

Chapter 6 Modeling of Dynamic Oxygen Storage Capacity on CZO and MFO Spinel

6.1 Reduction/Oxidation Kinetics of CZO and MFO spinel

The reduction behavior of $Mn_{0.5}Fe_{2.5}O_4$ (MFO) spinel is discussed in previous section. CO-TPR (Fig. 5.2) results show that MFO reduction occurs through multiple steps. Two overall reactions of MFO reduction by CO are listed as follows:

$$Mn_{0.5}Fe_{2.5}O_4 + CO \rightarrow 0.5 MnO + 2.5 FeO + CO_2 \text{ (or } Mn_{0.5}Fe_{2.5}O_3 + CO_2\text{)}$$
 (R6.1)

and 0.5 MnO + 2.5 FeO + 2.5 CO (or $Mn_{0.5}\text{Fe}_{2.5}\text{O}_3 + 2.5 \text{ CO}$)

$$\rightarrow$$
 0.5 MnO + 2.5 Fe + 2.5 CO₂ (or Mn_{0.5}Fe_{2.5}O_{0.5} + 2.5 CO₂). (R6.2)

Reaction R6.3 can be considered as a combination of steps R6.1 and R6.2 as

$$Mn_{0.5}Fe_{2.5}O_4 + 3.5 \text{ CO} \rightarrow 0.5 \text{ MnO} + 2.5 \text{ Fe} + 3.5 \text{ CO}_2$$

(or Mn_{0.5}Fe_{2.5}O_{0.5} + 3.5 \text{ CO}_2). (R6.3)

Similarly, the reduction reactions with H₂ as the reductant can be listed as follows:

$$Mn_{0.5}Fe_{2.5}O_4 + H_2 \rightarrow 0.5 MnO + 2.5 FeO + H_2O \quad (or Mn_{0.5}Fe_{2.5}O_3 + H_2O) \tag{R6.4}$$

and 0.5 MnO + 2.5 FeO + 2.5 H₂ (or Mn_{0.5}Fe_{2.5}O₃ + 2.5 H₂)

$$\rightarrow$$
 0.5 MnO + 2.5 Fe + 2.5 H₂O (or Mn_{0.5}Fe_{2.5}O_{0.5} + 2.5 H₂O). (R6.5)

Reaction R6.6 can be considered as a combination of steps R6.4 and R6.5 as

$$Mn_{0.5}Fe_{2.5}O_4 + 3.5 H_2 \rightarrow 0.5 MnO + 2.5 Fe + 3.5 H_2O$$

$$(\text{or } \text{Mn}_{0.5}\text{Fe}_{2.5}\text{O}_{0.5} + 3.5 \text{ H}_2\text{O}).$$
 (R6.6)

For brevity, the Mn and Fe mixed oxides in its complex oxide format are considered as $Mn_{0.5}Fe_{2.5}Ox$, with x varying between 0.5 and 4, which later will be further simplified as MFOx. The molar site fraction of $Mn_{0.5}Fe_{2.5}Ox$ species is defined as

$$\theta_{MFO_{0.5}} = \theta_{Mn_{0.5}Fe_{2.5}O_4} = \frac{N_{Mn_{0.5}Fe_{2.5}O_4}}{N_{Mn_{0.5}Fe_{2.5}O_4} + N_{Mn_{0.5}Fe_{2.5}O_3} + N_{Mn_{0.5}Fe_{2.5}O_{0.5}}} \text{ here } x = 0.5, 3, 4. (6.1)$$

Based on such definition, rate expressions of reaction R1 and R3 are proposed as:

$$r_{CO,MFO,R1} = k_{OSC,MFO,CO,1} \Omega_S \theta_{MFO_4} x_{CO}, \qquad (6.2)$$

and
$$r_{CO,MFO,R3} = k_{OSC,MFO,CO,2} \Omega_S \theta_{MFO_3} x_{CO},$$
 (6.3)

where Ω_S represent the site density of MFO spinel in the washcoat.

Similarly, the rate expressions for MFOx reduction by H₂ can be written as:

$$r_{H_2,MFO,R1} = k_{OSC,MFO,H_2,1} \Omega_S \theta_{MFO_4} x_{H_2}^{1/2}$$
(6.4)

and
$$r_{H_2,MFO,R3} = k_{OSC,MFO,H_2,2} \Omega_S \theta_{MFO_3} x_{H_2}.$$
 (6.5)

The reaction order for H_2 in reaction R3 is determined by experiments as $\frac{1}{2}$. This may be due to the involvement of H_2 dissociation steps on spinel surface.

The two-step oxidation reaction of MFOx can be written as

$$MFO_3 + 0.5 O_2 \rightarrow MFO_4 \tag{R6.7}$$

and MFO_{0.5} + 1.25 O₂
$$\rightarrow$$
 MFO₃. (R6.8)

And the rate expressions for MFOx oxidation by O₂ can be written as

$$r_{O_2,MFO,R4} = k_{OSC,MFO,O_2,1} \Omega_S \theta_{MFO_3} x_{O_2}$$
(6.6)

and
$$r_{O_2,MFO,R5} = k_{OSC,MFO,O_2,2} \Omega_S \theta_{MFO_{0.5}} x_{O_2}.$$
 (6.7)

Experimental results show that PGM – PGM oxides pairs (e.g., Pt-PtO_x, Pd and PdO) have almost negligible contribution on DOSC. Hence, only the redox mechanism from MFO is considered in DOSC functionality for PGM-spinel dual-layer monolith.

For CZO sample, the overall redox steps are considered as

$$Ce_{0.3}Zr_{0.7}O_2 + 0.15 CO (or H_2) \rightarrow Ce_{0.3}Zr_{3}O_{0.85} + 0.15 CO_2 (or H_2O),$$
 (R6.6)

and
$$Ce_{0.3}Zr_{3}O_{0.85} + 0.075 O_{2} \rightarrow Ce_{0.3}Zr_{0.7}O_{2}$$
. (R6.7)

In zirconia-stablized ceria, Zr is added into CeO₂ lattice to improve the oxygen mobility inside lattice [33], but Zr or ZrO₂ doesn't provide OSC. Hence, in equation R6.6 and R6.7, only contribution from CeO₂ is considered.

The global reaction rate expression are considered as:

$$r_{CO,CZO} = k_{OSC,CZO,CO} \Omega_C \theta_{CeO_2} x_{CO}, \tag{6.8}$$

$$r_{H_2,CZO} = k_{OSC,CZO,H_2} \Omega_C \theta_{CeO_2} x_{H_2}, \tag{6.9}$$

and
$$r_{O_2,CZO} = k_{OSC,CZO,O_2} \Omega_C \theta_{Ce_2O_3} x_{O_2}.$$
 (6.10)

During the reduction/oxidation process, bulk diffusion of oxygen or vacancy inside the lattice will play an important role. Therefore, the actual kinetic rate expression used in the model may be modified from the aforementioned equations.

6.2 Experimental and Modeling DOSC Results in Fixed-Bed Reactor

In this section, a stepwise approach is used to model the transient reductionoxidation performance of the two OSMs considered in this study (MFO spinel and CZO). First, the transient redox performance of each is examined during a long period cycle (i.e., 60s) in the fixed-bed reactor. Then the same kinetic parameters are applied for modeling of fast cycle (2s or 0.8s) lean-rich (CO) modulation performance on OSM powders, and lastly on a PGM-spinel dual-layer monolith.

6.2.1 Experimental and Modeling DOSC Results of CZO

During modulation operation, feed gas composition usually changes in several Hz. Still, it is necessary to first evaluate the long-term reduction/oxidation behavior to understand the redox behavior and acquire kinetic parameters.



Figure 6.1 (a) effluent CO concentration, (b) total cumulative CO consumption and (c) cumulative CO consumption per mole OSM during 60s 1.8% CO/Ar pulse at 550 °C. [Conditions: 150 sccm; OSM: 15 mg CZO or 25wt% MFO/Al₂O₃].

Fig. 6.1 (a) shows the transient effluent CO concentration over CZO and SA samples during a continuous 60s 1.8% CO/Ar pulse at 550 °C. The inlet and effluent CO concentrations reveal the effectiveness of the CO reduction, or equivalently the effectiveness of the OSM in releasing oxygen. The sharper CO breakthrough for CZO compared to SA shows that the MFO spinel has a larger release and consumption of O_2 (CO). The cumulative CO consumption (in µmoles) and normalized consumption mol

CO/mol OSM are plotted in Figs. 6.1 (b) and 6.1 (c), respectively. The latter plot is useful for comparing different materials. Over the entire reduction period it is evident that the MFO spinel releases more oxygen and consumes more CO. This is consistent with what discussed in Chapter 5 [61].

The cumulative 60s-OSC results suggest that CO reduction on both CZO and MFO span a fast then a slow regime. For example, the CO reduction rate of SA, proportional to the slope of the cumulative OSC curve, during the first 5 s period is clearly much faster than during the final 20 s period. This is consistent with the following sequence of processes. At the start of the reduction, surface oxygen anions are consumed by CO. As these deplete, bulk oxygen anions must diffuse to the surface to sustain reduction. Diffusion of the reductant CO to the underlying oxygen is less likely; both MFO and CZO have a dense cubic lattice structure [36]. Surface oxygen anion diffusion rate is typically much slower than the surface reaction, the overall rate eventually becomes limited by the slower solid-state diffusion.

There are two types of models that can be applied to describe the oxide reduction process; namely, the nucleation model (NM) and the shrinking-core model (SCM) [149]. The NM applies for those reduction processes in which the reduction degree versus time plot is sigmoidally shaped and the instantaneous reduction rate versus time plot exhibits a maximum (Fig. 6.2). In contrast, for those reduction processes described by the SCM, the reduction rate monotonically decreases with time from the start. Since the experimental data (Fig. 6.1) reveal a declining reduction rate with time (i.e., slope of cumulative OSC) for both the MFO spinel and CZO, first attempt is to apply the SCM to model the transient

reduction/oxidation performance. There have been previous attempts to use the SCM to describe the performance features of catalytic converters. Hepburn et al. [150] and Olsson [151] applied the SCM to simulate periodic storage and release of NOx during lean/rich cycling in a LNT (lean NOx trap). More recently Jian et al. [69] applied the SCM to describe the oxygen storage and reduction behavior of CZO from a commercial TWC catalyst.



Figure 6.2 Relationship between reduction extent vs. time in gas solid reactions: (a) nucleation model; (b) shrinking-core model (Here α represents the extent of reduction). [149]

Three main assumptions are made to apply the SCM: (i) the OSM particle (CZO or MFO particle) is spherically shaped; (ii) an outer layer (shell) of reduced OSM (Ce_{0.3}Zr_{0.7}O_{1.85} for CZO; Mn_{0.5}Fe_{2.5}O_x for MFO) encapsulates an inner core of oxidized OSM (Ce_{0.3}Zr_{0.7}O₂ for CZO; Mn_{0.5}Fe_{2.5}O₄ for MFO); (iii) reacting species (reductant during reduction; O₂ during oxidation) must diffuse through the surface layer to the inner core for reaction. Fundamental studies [33][38] show that the reduction of CeO₂ before complete reduction (i.e., to Ce₂O₃) leads to formation of a group of oxygen-deficient non-stoichiometric oxides, including higher cerium oxides (CeO_{1.74} – CeO₂) with fluorite-

related structures (e.g., phase α , β , γ etc.) and lower cerium oxides (CeO_{1.5} – CeO_{1.74}) with dominant body-centered cubic structure. Development of a kinetic model that predicts all of these features is beyond the scope of this study. Instead, it is simply considered a onestep reduction of CeO₂ to Ce₂O₃ and replace the diffusion resistance of oxygen ions inside lattice with diffusion resistance of reactant gas (CO or O₂) inside a "hypothetical" surface layer. In spinel case, it is default to determine the diffusional impacts on reduction behavior due to the lack of literature. Similar to CZO case, the diffusional impacts resulted from reactant gas (CO or O₂) is considered to be inside a (hypothetical) surface layer. Aggregation [152] is reported for ceria or CZO particles during synthesis and causes different particle sizes in samples. For ease of modeling, an averaged particle size is used to apply shrinking-core model. The average particle size for CZO is determined as 350 nm by SEM tests. The MFO particle size is determined by XRD measurement. The XRD data (Fig. 5.1) show that MFO has a cubic structure with a lattice constant of 8.314 Å. The size of MFO particle is estimated as ~ 20 nm based on the Scherrer equation [124].

Here the CZO case is first considered. With the aforementioned assumptions, the reaction rates for CO and O₂ consumption on OSM particle (CZO or MFO spinel) can be derived as

$$r_{CO} = k_1 \frac{\frac{C_{CO,r_p}}{r_p^{2(1-\theta_{CZO_2}^{1/3})\theta_{CZO_2}^{2/3}}} \Omega_C \theta_{CZO_2}, \tag{6.11}$$

and
$$r_{O_2} = k_2 \frac{c_{O_2, r_p}}{1 + k_2 \Omega_C (1 - \theta_{CZO_2})} \frac{r_p^{2(1 - \theta_{CZO_2}^{1/3})}}{\frac{3D_{p,O_2} \theta_1^{1/3}}{2}} \Omega_{OSM} (1 - \theta_{CZO_2}).$$
 (6.12)

where k_1 and k_2 are the rate constants for CO reduction or O₂ oxidation, respectively, C_{CO,r_p} (C_{O_2,r_p}) is the CO (O₂) concentration on the external particle surface, Ω_C is the site density of CZO (mol/m³ cat), r_p is the radius of CZO particle, $D_{p,CO}$ is the CO diffusivity in the CZO_{1.85} shell, θ_{CZO_2} is the fraction (dimensionless) of CZO₂ inside CZO particles. Note that if it is assumed the CZO particle has a uniform molar density regardless of its reduction extent, then θ_{CZO_2} can be further expressed as the volume fraction of oxidized CZO (i.e., CZO₂) in the overall particle. Derivation details of the SCM equations are provided in the Appendix.

Tuble off Temperature dependent variables							
Parameter	Value	Parameter	Value				
u _{f,fixed-bed}	0.1989×(T/273.15) m/s	D_{f,O_2}	$1.13 \times 10^{-9} T^{1.7019} (\text{m}^2/\text{s})$				
$u_{f,monolith}$	0.2362×(T/273.15) m/s	D_{f,co_2}	$8.25 \times 10^{-10} T^{1.7148} \text{ (m}^2\text{/s)}$				
D_{f,H_2}	$5.83 \times 10^{-9} T^{1.6725} (m^2/s)$	D_{f,H_2O}	$1.62 \times 10^{-9} T^{1.7033} (\text{m}^2/\text{s})$				
D _{f,CO}	$1.13 \times 10^{-9} T^{1.7148} (m^2/s)$						

Table 6.1 Temperature-dependent variables

ParameterValueParameterValue d_{CZO} 350 nm ε_p 0.06 m³ SA or CZO pellet/ m₃
catalyst bed d_{MFO} 20 nm L_b 0.01 m

 Ω_{C}

 Ω_S

360 µm

 $0.45 \text{ m}^3/\text{m}^3$ catalyst bed

d_{pellet}

ε_b

22500 mol/m³ pellet

 $2150 \text{ mol/m}^3 \text{ pellet}$

Table 6.2 Constant parameters used in fixed-bed reactor simulation

For modeling of reduction/oxidation performance on CZO using CO, equations from species balance (Eqns. 2.9, 2.11) and site balance (Eqns. 2.14 and 2.15) are solved simultaneously for species concentrations in fluid phase ($x_{f,i}(z,t)$, here i = CO, O₂, CO₂), species concentrations in solid phase ($x_{s,i}(z,r,t)$, here i = CO, O₂, CO₂), as well as site coverages of CZO₂ and CZO_{1.85} ($\theta_{CZO_2}(z,r,t)$, $\theta_{CZO_{1.85}}(z,r,t)$). Applied boundary and initial conditions are listed as Eqns. 2.19 ~ 2.22. Applied reaction rate expressions are Eqns. (6.11) and (6.12). The temperature-dependent and fixed parameters are listed in Table 6.1 and Table 6.2 respectively.

Figs. 6.3 (a) - (d) respectively compare the experimental data and model predictions of the effluent profiles of CO and CO₂ from the fixed-bed of CZO particles during sequential 60s CO/60s O₂ pulsing. The flowrate of carry Ar and weight of CZO pellets were 150 sccm and 15 mg respectively. The probe gas was 1.8% CO/Ar. The total flowrate was 150 sccm. Probe gas was 1.8% CO/Ar and tested OSM was 15 mg CZO pellets. Figs. 6.3 (a) and (c) respectively show the transient effluent CO and CO_2 concentrations for CZO; Fig. 6.3 (b) is an expanded view of Fig. 6.3 (a). The monotonic increase in the effluent CO concentration shows the aforementioned two regimes while the effluent CO₂ concentration shows the finite supply of accessible oxygen and inaccessible lattice oxygen. The temporal effluent CO plots enable estimate of the apparent activation energy of the reduction. This is accomplished by plotting the ln (apparent rate) versus 1/T for several different temperatures. The fitted data for CO oxidation gives an apparent activation energy of 51.4 kJ/mol, which is slightly lower than the value reported by Gong et al. (65.0 kJ/mol) [69]. The difference may results from the different morphology and composition of CZO (e.g., Ce/Zr ratio) [33]. Aneggi et al. [73] studied the CO oxidation kinetics on a group of polycrystalline ceria powders and pointed out that the activation energy for CO oxidation on ceria is dependent on many factors, including surface area, crystal surface (e.g., {111}) or {100}) reactivity. In contrast, the fitted data in the diffusion region gives an apparent activation energy of 0 kJ/mol, identical to the findings from Gong et al. [69]. A constant diffusivity with value of 4.0×10^{-12} m²/s is used in the modeling. The value is close to the value previously reported by Gong et al. $(8.0 \times 10^{-11} \text{ m}^2/\text{s})$ [69].



Figure 6.3 Comparison of experimental and modeling results of 60s CO pulse on CZO pellets: (a) & (b) transient effluent CO concentration; (c) transient effluent CO₂ concentration; (d) site coverage θ_{CZO_2}

Fig. 6.3 (d) shows the predicted site coverage of CZO pellets during the 60s CO

pulse. Assuming the OSM particle and the oxidized core are spherical, θ_{CZO_2} is given by

$$\theta_{CZO_2} = \frac{V_{core}}{V_{particle}} = \frac{r_1^3}{r_p^3}.$$
(6.13)

The detailed derivation is included in Appendix. Here r_1 and r_p represent the radius of oxidized core and CZO particle respectively. The shell thickness is a function of θ_{CZO_2} as

$$l_p = \frac{V_{core}}{V_{particle}} = r_p (1 - \theta_{CZO_2}^{1/3}).$$
(6.14)

For example, a site coverage θ_{CZO_2} at 5s of ~ 0.95 gives a shell thickness of ~5.8 nm. Ceria has the fluorite structure with the lattice parameter as 0.541nm. As a rough estimation, if

0.541nm is taken as the lattice parameter for the CZO sample used in this study, at 5s the shell thickness is ~ 10 layers of CZO.

A similar attempt to apply the SCM was made for the reduction/oxidation performance of MFO spinel. The size of MFO particle is estimated as ~ 20 nm based on the Scherrer equation [124]. With this estimated particle size, the MFO particle is too small for use with the SCM model. An alternative analysis method for the spinel is considered instead.

6.2.2 Experimental and Modeling DOSC Results of MFO Spinel Powder Catalysts

For modeling of reduction/oxidation performance on MFO spinel using CO, equations from species balance (Eqns. 2.9, 2.11) and site balance (Eqns. 2.16, 2.17, 2.18) are solved simultaneously for species concentrations in fluid phase ($x_{f,i}(z, t)$, here i = CO, H₂, O₂, CO₂ and H₂O), species concentrations in solid phase ($x_{s,i}(z, r, t)$, here i = CO, O₂, CO₂), as well as site coverages of MFO₄, MFO₃, MFO_{0.5} ($\theta_{MFO_4}(z, r, t)$, $\theta_{MFO_3}(z, r, t)$ and $\theta_{MFO_{0.5}}(z, r, t)$). Applied boundary and initial conditions are listed as Eqns. 2.19 ~ 2.22. Applied reaction rate expressions are Eqns. 6.2 ~ 6.7. The temperature-dependent and fixed parameters are listed in Table 6.1 and Table 6.2 respectively. Table 6.3 summarizes the kinetic parameters used in multiple reduction/oxidation steps of MFO.

No.	Reaction	Activation Energy (kJ/mol)	Pre-exponential Factor
R1 (CO)	$MFO_4 + CO \rightarrow MFO_3 + CO_2$	52.3	$1.59 \times 10^5 (s^{-1})$
R3 (CO)	$MFO_3 + 2.5 \text{ CO} \rightarrow MFO_{0.5} + 2.5 \text{ CO}_2$	61.0	$5.50 \times 10^4 (s^{-1})$
R1 (H ₂)	$MFO_4 + H_2 \rightarrow MFO_3 + H_2O$	69.2	$7.09 \times 10^5 (s^{-1})$
R3 (H ₂)	$MFO_3 + 2.5 H_2 \rightarrow MFO_{0.5} + 2.5 H_2O$	115.0	$3.51 \times 10^6 (s^{-1})$
R4	$MFO_3 + 0.5 O_2 \rightarrow MFO_4$	42.5	$4.50 \times 10^5 (s^{-1})$
R5	$MFO_{0.5} + 1.25 \text{ O}_2 \rightarrow MFO_3$	45.0	$9.00 \times 10^5 (s^{-1})$

Table 6.3 Kinetic parameters used in MFO DOSC modeling



Figure 6.4 (a) effluent CO₂ concentration and (b) H₂ consumption during 60s reductant pulse on SA at 600 °C. [Conditions: Carry Ar flow rate as 150 sccm; probe gas concentration: 2.5%, 1.8% or 1.0%; OSM: 15 mg 25wt% MFO/Al₂O₃].

Fig. 6.4 shows the effluent CO₂ concentration (Fig. 6.4 (a)) and H₂ (Fig. 6.4 (b)) consumption for the SA samples during a 60s reductant (CO or H₂ with multiple concentrations) pulse at 600 °C. Fig. 6.4 (a) shows that for all three CO concentrations (1.0%, 1.8% and 2.5%), the generated CO₂ appears right after CO is introduced and quickly

goes through a maximum (i.e., at ~ 5s for 1.0%; ~ 3s for 1.8%; ~2s for 2.5%). Beyond the maximum, the CO₂ concentration drops quickly for the two higher CO feed concentrations and approaches a non-zero plateau ~ 1000 ppm after 20s. A similar trend is seen for the H₂ case (Fig. 6.4 (b)). The H₂ consumption reaches a maximum at ~ 5s for 1.0%, ~ 3s for 1.8% and ~ 2s for 2.5% and the H₂ uptake reaches a nonzero plateau of ~ 2000 ppm. Accordingly, the reduction of the alumina-supported MFO spinel consists of two stages; the first stage is characterized by a large reductant (CO or H₂) consumption upon its introduction (i.e., first 10s); the second appears after ~20s characterized by a much lower consumption rate. As discussed earlier, the first stage is kinetically-controlled while the second slower stage is diffusion-controlled. The kinetic regime is short-lived, occurring during the first ~ 20 s. Considering that the modulation period is typically less than a few seconds (i.e., frequency of 0.5 - 2 Hz), it is crucial to evaluate the redox behavior of the MFO spinel in the kinetic-controlled region.

A quantitative analysis of the extent of CO reduction of MFO helps to identify the rate controlling regimes. Here "fast oxygen storage capacity", $\text{FOSC}_{\text{red.conc.}}^{t_1-t_2}$ is defined as the integral reductant consumption during the time period "t₁ - t₂" using reductant "red." at the prescribed concentration "conc.". The end of the first period (t₂) is defined as the point at the start of the plateau in the CO₂ effluent (Fig. 6.4 (a)) or H₂ consumption (Fig. 6.4 (b)) curves. For CO, $\text{FOSC}_{\text{CO,1.0\%}}^{0~20s}$, $\text{FOSC}_{\text{CO,1.8\%}}^{0~20s}$ and $\text{FOSC}_{\text{CO,2.5\%}}^{0~20s}$ are estimated as 13.5 µmol, 13.6 µmol and 14.2 µmol, respectively. For H₂, $\text{FOSC}_{\text{H_2,1.0\%}}^{0~20s}$, $\text{FOSC}_{\text{H_2,1.8\%}}^{0~20s}$ and $\text{FOSC}_{\text{H_2,2.5\%}}^{0~20s}$ are estimated as 12.8 µmol, 13.5 µmol and 14.1 µmol, respectively. In this set of DOSC experiments the reactor contained 15 mg of 25 wt.% Mn_{0.5}Fe_{2.5}O₄/Al₂O₃ spinel powder; this corresponds to 16.2 µmol MFO. XRD results show that MFO has a cubic structure

with the lattice constant of 8.31 Å. Further, recall that the particle size of the MFO was estimated as ~ 20 nm based on the Scherrer equation [40]. Assuming that the MFO particles are spherical and the particle density is uniform, the amount of MFO (in μ mol) in the first surface layer is estimated as

$$N_{surface MFO} = 16.2 \ \mu mol \times \left[1 - \frac{\left(\frac{20}{2}nm - 0.831nm\right)^3}{\left(\frac{20}{2}nm\right)^3} \right] = 3.73 \ \mu mol.$$
(6.15)

In Chapter 5, the maximum reduction extent of MFO is determined as 3.5 mol O/mol MFO. Therefore, the maximum theoretical amount of reducible oxygen in the first layer of the Mn_{0.5}Fe_{2.5}O₄ particle is ~ 13 µmol. This value is very close to the calculated FOSC values described above for both CO and H₂ reduction. The estimated O consumption for other feed temperatures consistently show a FOSC very close to 13 µmol (Table 6.4 and Table 6.5). At low and medium temperatures (e.g., < 550 °C), the FOSC values is somewhat lower than 13 µmol.

Table 6.4 Calculated FOSC values with CO as the reductant Temperature (°C) 500 550 600 FOSC^{0~50}_{CO,0.5%} (μmol) 11.81 12.43 13.13 FOSC^{0~30}_{C0,1.0%} (µmol) 12.10 12.54 13.55 $FOSC_{C0,1.8\%}^{0\sim20}$ (µmol) 12.74 14.12 13.63

Table 6.5 Calculated FOSC values with CO as the reductant				
Temperature (°C)	500	550	600	
$FOSC_{H_{2},0.5\%}^{0\sim50}$ (µmol)	11.01	11.58	12.91	
FOSC ^{0~30} _{H2} ,1.0% (µmol)	11.12	12.78	12.82	
$FOSC^{0\sim 20}_{H_{2},1.8\%}$ (µmol)	11.71	13.59	13.54	

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An analysis of the CO-TPR profiles for the MFO spinel provides further insight. Specifically, the CO-TPR profiles (Fig. 5.2) have three CO uptake peaks at ~ 350 °C, ~ 425 °C and ~ 575 °C. At low to moderate temperatures (e.g., < 550 °C), the reduction rate is not high enough and thus the DOSC will be smaller than 13 µmol. Given that the higher temperature DOSC values were obtained with two different reductant types (CO, H₂) and different reductant concentrations (1 - 2.5%) but each give similar values of 13 µmol (the maximum available O at the MFO surface) for FOSC, it is concluded that the reduction is transport limited and complete surface consumption is achieved. In the modeling of the MFO spinel, only the reduction or oxidation contribution from the first layer of MFO particle is considered. In other words, only 23.6% of the MFO is considered for reaction. Assume the MFO particles are perfect sphere, the 23.6% is calculated (using Eqn. (33)) based on the volume fraction of first layer inside the total MFO particle as

$$\frac{V_{\text{surface layer}}}{V_{\text{crystal}}} = \frac{\frac{\pi}{6} [d_{crystal}^3 - (d_{crystal} - 2a)^3]}{\frac{\pi}{6} d_{crystal}^3} = \frac{(19.4nm)^3 - (19.4nm - 2 \times 0.8314nm)^3}{(19.4nm)^3} = 0.236. \ (6.16)$$

Kinetic parameters for the reduction of MFO₄ to MFO₃ by reactions R1 and R2 as well as the reoxidation by R4 and R5 are determined using the following methodology. CO-TPR results (Fig. 5.2) show that reaction R1 occurs at low to moderate temperatures (i.e., 100 °C < T < 475 °C) while the deeper reduction R2 occurs at higher temperatures (i.e., T > 475 °C). Accordingly, the long cycle experimental data below 450 °C are used to estimate the R1 kinetic parameters. Cumulative OSC results within 60 s (similar to Fig. 6.1 (b)) from 200 °C to 450 °C are considered. The R1 activation energy is determined from the Arrhenius plot using logarithm of CO₂ production rate versus reciprocal of temperature; this gives 52.3 kJ/mol for the first CO reduction step (MFO₄ \rightarrow MFO₃). The deeper reduction (R2), MFO₃ \rightarrow MFO_{0.5} is effectively the reduction of FeO to metallic Fe.

Accordingly, the activation energy is chosen based on literature reported values. Chen et al. [153] reported the activation energy as 60.9 kJ/mol for FeO reduction to Fe using iron ore fines in a micro-fluidized bed. Liu et al. [154] studied the reduction kinetics of wustite by H₂ or CO and estimated an activation energy for FeO to Fe is (64 ± 8) kJ/mol. The activation energy used for the reduction (MFO₃ \rightarrow MFO_{0.5}) is 61.0 kJ/mol. The activation energies for R4 and R5 are determined using the same method described earlier. The Arrhenius plot of the O₂ consumption rate gives an activation energy as 42.5 kJ/mol for R7. The reaction R5, MFO_{0.5} \rightarrow MFO₃ is effectively the oxidation of metallic Fe to FeO. Grosvenor et al. [155] conducted experimental study reported (32 ± 6) kJ/mol as activation energy for iron oxidation by O₂. Roberts [156] reported an activation energy of (54 ± 8) kJ/mol from oxidation experiments of iron films by O₂. Based on the reported value, here 45 kJ/mol is selected as activation energy for the R8. During the entire 60s reduction of 0.5% CO, the cumulative OSC is smaller than 13 μ mol, suggesting that the MFO reduction is limited inside the first surface layer and bulk oxygen/vacancies do not participate in reactions. Pre-exponential factors were manually adjusted to fit the 0.5% CO data. The parameters were validated for experiments at higher CO concentrations (1.0% and 1.8%) at 60s pulse for validation.

Fig. 6.5 shows the experimental and modeling results of 60s 0.5% CO/60s 0.9% O₂ lean-rich cycling experiments. In experiments, flowrate of carry Ar was fixed as 150 sccm and SA weight was selected as 15 mg. Probe gases in rich and lean were 0.5% CO/Ar and 0.9% O₂/Ar respectively. Figs. 6.5 (a) ~ 6.5 (c) compare the measured and predicted results of transient effluent CO, O₂ and CO₂ concentrations while Figs. 6.5 (d) ~ 6.5 (f) report the fraction of three sites (MFO₄, MFO₃ and MFO_{0.5}) at end of the catalyst bed during the

reduction/oxidation cycles. The tuned model does a satisfactory job of predicting the main trends of reduction/oxidation behavior of MFO spinel, with some minor deviations. These deviations may arise from several factors. For example, the non-uniform pellets size and MFO crystal sizes can cause deviations. The experimentally prepared pellets have the size between 40 to 60 meshes (0.42 mm ~ 0.25 mm) while a fixed size number as 0.36 mm was used in modeling for brevity. In addition, the MFO crystals on support may have non-uniform distribution, therefore the reaction speed may vary among crystals. Another factor is that the rate expressions used in this study (Eqns. 6.2 and 6.3) may be too simple to capture all details of the performance. A microkinetic reaction model considering every elementary step may give a better prediction. However, this requires more fundamental studies. Current global kinetic model can capture most of the OSC or DOSC features (e.g., Fig. 6.6 and Fig. 6.8 discussed later) so these equations (Eqns. 6.2 and 6.3) were kept.



Figure 6.5 Experimental and modeling results of 60s/60s CO/O₂ pulses on SA: (a) transient effluent CO concentration; (b) transient effluent O₂ concentration; (c) transient effluent CO₂ concentration; (d) ~ (f) site coverages of MFO₄, MFO₃ and MFO_{0.5}.

The model-predicted site coverage results (Figs. 6.5 (d) ~ 6.5 (f)) provide deeper insight about the reduction/oxidation process. Fig. 6.5 (d) shows that the MFO4 site coverage decreases towards zero during the rich feed (i.e., CO). Upon the switch to the lean feed (i.e., O₂) the MFO4 site coverage returns to its maximum value of unity. In contrast, the partially reduced MFO3 site coverage shown in Fig. 6.5 (e) exhibits a maximum at higher temperatures (e.g., at ~20s into the rich period), increasing from 0 at the beginning of the rich feed but then decreasing as deeper reduction occurs. The maximum is not reached till the rich-to-lean switch at the lower temperatures (< 400 °C) due to the slower reduction rate. At all temperatures, upon the switch to the lean feed, reoxidation occurs with the MFO3 site coverage decreasing towards zero. The descent increases with temperature. Fig. 6.5 (f) shows that during the rich feed, the site coverage of the most reduced spinel (MFO0.5) remains zero for ~ 5s and then increases. During the lean feed, the MFO0.5 fraction remain unchanged for several seconds and then decreases to zero.

Overall, the redox behavior exhibited during the cycling conveys the sequential behavior associated with the multiple oxidation states of the MFO spinel; i.e., MFO₄ + CO \rightarrow MFO₃ (R1) followed by MFO₃ + 2.5 CO \rightarrow MFO_{0.5} (R2). During the reduction halfcycle, MFO₄ only takes part in R1 and therefore its site coverage decreases monotonically with time during reduction. Similarly, MFO_{0.5} is only generated in R2 and therefore its site coverage increases monotonically. In contrast, MFO₃ is generated in reaction R1 and consumed in reaction R2. The maximum in the MFO₃ fraction achieved during the rich feed is a result of by the balance between its generated from the reduction of MFO₄ and MFO₃ site coverage increases. As the reduction proceeds, MFO₃ is further reduced to MFO_{0.5}, decreasing the MFO₃ site coverage. Similar reasoning can be drawn for site coverage trends during the lean feed. The two-step oxidation steps are MFO₃ +0.5 O₂ \rightarrow MFO₄ (R7) and MFO_{0.5} + 1.25 O₂ \rightarrow MFO₃ (R8). During the oxidation half-cycle, MFO₄ is only generated by reaction R7 while MFO_{0.5} is only consumed by R8. As a result, the MFO₄ site coverage increases with time while the MFO_{0.5} site coverage decreases with time. Figs. 6.5 (e) and 6.5 (f) show that MFO₃ and MFO_{0.5} site coverages remain nearly unchanged during first several seconds of lean. This is because the fed O₂ is totally consumed, or stored in an upstream section of the catalyst bed. When the flow reaches the end of catalyst bed, no O₂ is available for reaction. As the reaction proceeds, the downstream vacant sites are gradually occupied, and the MFO_{0.5} sites at the end of the bed eventually consumed (by oxidation). As MFO₃ sites have both the generation and consumption terms, MFO₃ site coverage exhibit a maximum.

The spinel reactivity during the long-cycles are helpful in determining the kinetic parameters. On the other hand, the fast cycling with period on the order of seconds is more important in the vehicle application. Fig. 6.6 compares the measured and predicted transient effluent CO, O₂ and CO₂ profiles during a 2s CO/2s O₂ cycle for three CO feed concentrations (0.5% and 1.8%) and several temperatures between 200 °C to 600 °C. Overall the tuned model captures the transient behavior quite satisfactorily.



Figure 6.6 Experimental and model-predicted effluent concentration of CO, O₂ and CO₂ during CO/O₂ cycles on SA. [Conditions: 150 sccm carry Ar; lean: 0.9% O₂/Ar; rich: 0.5 % or 1.8% CO/Ar; pulse time: 2s; OSM: 15 mg 25wt% MFO/Al₂O₃].

It is important to note that the assumption of confined reduction inside the surface first layer of MFO crystal is not universal. It can only be applied in cases when the reduction/oxidation extent is very small (i.e., < 23.6% for MFO spinel), for example, reduction/oxidation of MFO at high temperature (e.g., 550 C) in a very short pulse (e.g., several seconds) or at low temperature in a relatively long pulse (e.g., tens of seconds). In these cases, the reaction extent is so small that gas-solid reaction is limited on MFO surface and the bulk oxygen/vacancy will not participate in reactions. In other cases when the reduction/oxidation is very high (i.e., >> 23.6% for MFO spinel) or even approaching 1, such as chemical looping processes, the observed reaction rate will be slowed by solid diffusion when surface oxygen/vacancies are depleted. Then impacts from slow diffusion also need to be considered in the whole reaction process.



Figure 6.7 Model predicted site coverage of MFO_x in rich during periodic CO/O₂ cycles on SA. [Conditions: 150 sccm carry Ar; lean: 0.9% O₂/Ar; rich: 0.5 % or 1.8% CO/Ar; pulse time: 2s; OSM: 15 mg 25wt% MFO/Al₂O₃].

Fig. 6.7 shows the predicted MFOx site coverages during rich feed under 2s CO/2s O₂ cycle. For each of the CO feed concentrations, the MFO₄ site coverage monotonically from 1, while the MFO₃ and MFO_{0.5} site coverages increase monotonically from 0. This again reflects the sequential nature of the reduction process involving reactions R1 and R2. At a fixed temperature (e.g., 500 °C), the MFO₃ and MFO_{0.5} site coverages approach higher levels as the CO concentration increases, as higher reductant concentration leads to a higher extent of reduction. That said, even for the highest CO concentration (1.8% CO/Ar) and temperature (600 °C), the MFO₄ coverage still exceeds 0.5 by the end of the rich feed (e.g., ~0.4 at 600 °C) while the MFO_{0.5} coverage is still quite small (e.g., ~0.03 at 600 °C). This shows that during the short CO pulse the reduction of MFO spinel is confined to the first particle layer and is still very limited to the first reduction step R1. Considering the modulation tests within several Hz (e.g., in hundreds of ms), which is the typical modulation operation condition in vehicles, the reduction extent of MFO will be even smaller and the dominant reduction step will be the fast reduction from MFO₄ to MFO₃ (reaction R1).

Experiments were conducted to quantify the cycle-averaged DOSC defined as

$$DOSC = \frac{\int_0^{t^*} [F_{CO,in}(t) - F_{CO,out}(t)]dt}{N_{cycle} \times N_{MFO}}.$$
(6.17)

The DOSC metric evaluates the effectiveness of the OSM to store O₂ under dynamic conditions. Fig. 6.8 (a) and (b) compares the measured and predicted DOSC for the MFO spinel over a wide range of feed temperatures and three CO feed concentrations, for 4 s cycle (Fig. 6.8 (a)) and 1.6 s cycle (Fig. 6.8 (b)). The experimental DOSC values were obtained from data collected at cyclic steady-state over five cycles. Each of the cases show a monotonic increasing dependence of the DOSC on the feed temperature. Further, for a

fixed temperature the DOSC increases with CO feed concentration. Overall these trends convey an increasing rate of O₂ exchange with temperature and a higher rate of reduction for higher CO concentration. Each of the curves approaches a theoretical upper bound value given corresponding to the "reductant limited OSC", or OSCR, indicated by the dashed horizontal segments. The OSCR reports the moles of O consumed/mole OSM during complete reductant consumption in the DOSC experiment. Overall, the tuned model predicts the DOSC satisfactorily with better agreement obtained for the shorter cycle experiments.



Figure 6.8 Experimental and model-predicted cumulative DOSC results in CO or H₂ DOSC tests (a)(c) 2s/2s and (b)(d) 0.8s/0.8s [Conditions: 150 sccm Ar; lean: 0.9% O₂/Ar; rich: 0.5 %, 1.0 %, 1.8 % CO or H₂/Ar; OSM: 15 mg 25wt% MFO/Al₂O₃].

The CO conversion during the periodic tests can be calculated from dividing the measured DOSC values by the corresponding OSCR values. The data show that cycle-averaged CO conversion increases slightly a decrease in the CO feed concentration. For

example, for a 2s pulse at 600 °C the CO conversions for 0.5% CO and 1.8% CO are ~ 81% and 75%, respectively. The slight increase of CO conversion is due to the better utilization of MFO₄ sites. It is previously discussed that CO reduces MFO₄ and MFO₃ sites sequentially with the first reduction (MFO₄ \rightarrow MFO₃) faster than MFO₃ reduction. At a lower CO feed concentration, the reduction is more likely to be confined in the first step (MFO₄ reduction). This is seen in Fig. 6.7, which shows that at 600 °C, MFO_{0.5} site coverage during 0.5% CO pulsing is nearly zero while the MFO_{0.5} site coverage reaches ~ 0.03 at end of 1.8% rich CO pulse. With lower CO feed concentration, the higher contribution from first reduction step enhances the overall reduction efficiency and accordingly enhances CO conversion.

Besides CO, H₂ was also used as the probe reductant in DOSC evaluation for MFO spinel. Fig. 6.9 shows the transient experimental and modeling results of H₂ and the model-predicted MFOx site coverages during either 60s (first column) or 2s (second column) 1.0% H₂ pulses. Fig. 6.8 (c) and (d) summarizes the cycle-averaged experimental and modeling H₂-DOSC results with multiple H₂ feed concentrations (0.5%, 1.0% and 1.8%) and two pulsing times (2s and 0.8s). The two plots show that current model and applied kinetic parameters are adequate to predict the transient and cycle-averaged results in H₂-DOSC tests with varied feed concentrations, feed temperatures and pulsing times.



Figure 6.9 Experimental and modeling results of H₂/O₂ OSC tests on SA. Row 1: effluent H₂ profile; Row 2 ~ 4: predicted MFO_x coverage in rich [Conditions: 150 sccm; 1.0% H₂/Ar (rich) and 0.9% O₂/Ar (lean); OSM: 15 mg 25wt% MFO/Al₂O₃].

Similar to CO case, only consider the reduction of MFO spinel within its first crystal layer is considered in the model. The activation energy for reaction R3 with H₂ is
estimated from literature. Jozwiak et al. [157] reported the activation energy for FeO reduction by H₂ is 104 kJ/mol through H₂-TPR tests. Hayashi et al. [158] studied the FeO reduction kinetics by H₂ using iron oxide fines and reported 110 kJ/mol as the activation energy. Based on literature reported values and the experimental DOSC data, 115.0 kJ/mol is used as the activation energy for FeO (i.e., reaction R3) in this study. In short cycle cases (2s), MFO_{0.5} site coverage is almost zero and the reduction of MFO spinel is very limited to the first reduction step (i.e., MFO₄ \rightarrow MFO₃).

It is worth mentioning that the aforementioned simplification of reduction inside the surface first layer of MFO is only valid when the reduction/oxidation cycles occurs in short time periods, or in other words, when the reduction/oxidation process is totally kinetic controlled. In those cases when diffusion can be dominant (i.e., long-time cycles such as reduction-oxidation cycles in chemical looping processes), the impacts from slow diffusion needs to be considered.

6.4 Experimental and Modeling DOSC Results of PGM-Spinel Dual-Layer Monolith

In emission control systems, the catalytic converter is comprised of a washcoated monolithic substrate due to its resilience to vibration, low pressure drop and high catalyst contacting area per unit volume. Here the findings of the oxygen storage and release from the MFO spinel is applied for a monolith supported material. Earlier work from our group investigated the methane oxidation performance of the dual-layer monolith consisting a top layer of Pt+Pd/Al₂O₃ and a bottom layer of MFO spinel/Al₂O₃ [40]. That study showed that the combination of spinel addition and lean-rich modulation results in an appreciable

decrease in the light-off temperature for methane oxidation. To examine the generality of those findings and to better understand the role of O₂ storage and release, CO oxidation and modulation performance on the same PGM/spinel dual-layer monolith is evaluated. First, CO oxidation performance is evaluated on PGM and spinel. Then the combined CO oxidation kinetics and OSC kinetics are incorporated into a whole modeling block for modulation tests.

Table 0.0 Constant parameters used in mononth reactor simulation						
Parameter	Value	Parameter Value				
$R_{\Omega,1}$	215 μm	Nu	3			
$R_{\Omega,w}$	140 µm	C _{pf}	1086 J/mol/K			
δ_{PA}	36 µm	C_{pw}	1000 J/mol/K			
δ_{SA}	18 µm	$ ho_f$	1.784 kg/m^3			
ϵ_{PA}	0.4	$ ho_w$	2000 kg/m^3			
ϵ_{SA}	0.4	k_w	2 W/m/K			
λ	30	Ω_{C}	1300 mol/m ³ washcoat			
L_m	0.02 m	Ω_S	31.8 mol/m ³ washcoat			
$Sh_{e,\infty}$	4.36					

Table 6.6 Constant parameters used in monolith reactor simulation

For DOSC modeling of the dual-layer PGM-MFO monolith using CO, equations from species balance (Eqns. 2.23, 2.25, 2.26), energy balance (Eqns. 2.28, 2.29) as well as site balance (2.16, 2.17, 2.18) are solved simultaneously for species concentrations in fluid phase ($x_{f,i}(z, t)$, here i = CO, O₂, CO₂), species concentrations in solid phase ($x_{wc,i}(z, y, t)$), here i = CO, O₂, CO₂), fluid temperature ($T_f(z, t)$), solid temperature ($T_s(z, t)$), as well as site coverages of MFO₄, MFO₃, MFO_{0.5} ($\theta_{MFO_4}(z, y, t)$, $\theta_{MFO_3}(z, y, t)$ and $\theta_{MFO_{0.5}}(z, y, t)$). Applied boundary and initial conditions are listed as Eqns. 2.30 ~ 2.41. Applied reaction rate expressions are Eqns. 6.2, 6.3, 6.6, 6.7, 6.18, and 6.21. The temperature-dependent and fixed parameters are listed in Table 6.1 and Table 6.6, respectively.

6.4.1 CO Oxidation Results

A Pt-catalyzed CO oxidation kinetic model developed by Raj et al. [80] is adopted in the current study. The global Langmuir-Hinshelwood rate expression (Eqn. 6.18) follows the experimental-observed reaction order with respect to CO, +1 in the low pressure regime and -1 in CO inhibition regimes:

$$R_{CO,PA} = \frac{k_{1,PA} x_{CO} x_{O_2}}{(1 + K_{CO} x_{CO})^2},\tag{6.18}$$

$$k_{1,PA} = A_{1,PA} \exp(-\frac{E_{1,PA}}{RT}),$$
 (6.19)

and
$$K_{CO} = A_{CO} \exp(-\frac{\Delta H_{CO}}{RT}).$$
 (6.20)

Here $E_{1,PA}$ and $(-\Delta H_{CO})$ represent the activation energy for the lumped rate constant and heat of CO adsorption respectively.

The rate of CO oxidation on MFO spinel is given by

$$R_{CO,SA} = k_{1,SA} x_{CO} x_{O_2}, (6.21)$$

where $k_{1,SA}$ represents the rate constant and is defined by

$$k_{1,SA} = A_{1,SA} \exp(-\frac{E_{1,SA}}{RT}).$$
 (6.22)

The aforementioned DOSC kinetics are also included in the MFO oxidation model. The global kinetic oxidation model is sufficient to capture the oxidation behavior under near stoichiometric conditions. Kinetic parameters for CO oxidation are summarized in Table 6.7.

		1			0
$E_{1,PA}$	$A_{1,PA}$	ΔH_{CO}	A _{CO}	$E_{1,SA}$	$A_{1,SA}$
119.90	3.35×10^{15}	7.79 kJ/mol	1.75×10^{3}	60.70	1.55×10^{7}
kJ/mol	$(mol/m^3 \cdot s)$			kJ/mol	$(m^3/mol \cdot s)$

Table 6.7 Kinetic parameters used in CO Oxidation modeling



Figure 6.10 Comparison of experimental and model-predicted CO-TPO results for (a) & (b) PA monolith and (c) & (d) SA monolith [Conditions: GHSV: 40 k hr⁻¹; feed: 0.8% CO, 0.4% O₂, balance N₂; ramp rate: 3 °C/min].

The $E_{1,PA}$ and $(-\Delta H_{CO})$ are selected as 119.90 kJ/mol and 7.79 kJ/mol, respectively, based on the study by Raj et al. [80]. Fig. 6.10 (a) compares the experimental and modeling results of the effluent CO concentration during a CO-TPO test using a stoichiometric feed under 3 °C/min ramp rate. The pre-exponential factors were manually tuned to fit the experimental TPO results. The CO light-off performance is evaluated using either the measured feed or monolith temperature. The sigmoidal-shaped CO light-off curve shows that CO starts to react with O₂ from ~ 250 °C, with 50% and 100% conversion reached at feed (monolith) temperatures of 290 °C (340 °C) and 310 °C (380 °C), respectively. The relatively high light-off temperature is due to the rather low PGM loading (i.e., 30 g/ft³). The model predicted results match well with experimental results at low and medium temperature (i.e., monolith temperature $< 340 \,^{\circ}$ C) with some minor discrepancy at high temperatures. The discrepancy may be due to the heat loss in the furnace, which is not considered in current model.

For CO oxidation on the MFO spinel, a simple rate expression (Eqn. 6.21) that assumes first- order for CO and O₂. Fig. 6.10 (b) compare the experimental and modeling results of the effluent CO concentration during the CO-TPO test using a stoichiometric feed under 3 °C/min ramp rate. The results show that CO starts to react from 150 °C and reaches 50% conversion at a feed (monolith) temperature of 325 °C (360 °C). Given that the modulation conditions spans a range of CO and O₂ concentrations, the kinetic expression (Eqn. 6.21) was tested under a similar range of CO and O₂ concentrations (CO concentration from 0 to 0.8% and O₂ concentration from 0 to 0.4%).

6.4.2 Modulation Results on PGM-Spinel Dual-Layer Monolith

With kinetic expressions and parameters determined in previous sections, the modulation performance of a PGM/spinel dual-layer monolith is tested in a flow reactor. In the model, both DOSC kinetics and CO oxidation kinetics are considered and the kinetic parameters are exactly the same as previous discussed parts. The experimental conditions were selected based on the previously reported experimental study by Kang et al. [40] but here only CO is used as the reductant. Generally the applied model and kinetic parameters are able to capture the cycle-averaged and transient results.



Figure 6.11 Experimental and modeling results of modulation tests on a PGM-Spinel monolith: (a) cycle-averaged CO conversion, (b) effluent CO concentration (c) model-predicted site coverage of MFOx at feed temperature as 300 °C.

Overall, tuned model is able to capture the cycle-averaged and transient results. Fig. 6.11 summarizes the cycle-average and transient modulation results from both experiments and modeling. The gas-hourly space velocity was controlled as 40,000 hr⁻¹ and the

modulation frequency was controlled as 1.5s rich/1.5s lean. CO concentration remained the same as 0.8% CO/N₂ in both rich and lean feeds while O₂ concentration was controlled as 0.8% O₂/N₂ and 0% O₂/N₂ in rich and lean feeds respectively. All reported results are collected at pseudo steady state.

Fig. 6.11 (a) shows the cycle-averaged CO conversions reaches 50% at a feed temperature of ~ 265 °C. This is lower than the $T_{50,feed}$ (feed temperature when CO conversion reaches 50%) in PA or SA oxidation cases, because both PGM and spinel sites contribute to CO oxidation in the dual-layer monolith. Fig. 6.11 (b) compares the transient effluent CO concentration under 1.5s/1.5s modulation at several feed temperatures. At low temperature (e.g., 150 °C), the model predicted CO concentration remains nearly constant, as the temperature is too low for CO to react with O_2 . As the feed temperature increases, the cycle-averaged CO concentration decreases, due to the reaction by O_2 by either direct gaseous oxidation or indirect oxidation through redox cycle on MFO spinel. When CO oxidation is activated (i.e., feed temperature above 200 °C), the effluent CO concentration fluctuates continuously. As temperature increases further, the fluctuation amplitude of the effluent CO concentration first increases (e.g., from 150 °C to 250 °C) and then decreases (e.g., from 275 °C to 350 °C). The fluctuation is due to the different reaction extent of CO oxidation under periodically changed feed. During reaction, CO can react with either O_2 supplied directly from the gas phase or from oxygen supplied from the spinel. During the rich feed, CO essentially reacts only with oxygen supplied from the MFO spinel; a negligible amount reacts directly with O₂ from axial mixing. The lack of O₂ in rich phase leads to a low CO conversion and accordingly a high effluent CO concentration. In contrast, the excess O_2 during the lean phase enables a higher CO conversion and a lower CO

effluent concentration. At low temperature (< 150 °C), reaction rates of CO oxidation with both gaseous O₂ and oxygen from the spinel are very slow, hence CO concentration stays almost around the feed value with very small fluctuations. At high temperatures (e.g., 350 °C or higher), CO can almost readily react with gaseous O₂ and oxygen from spinel, hence CO conversion is high and effluent CO concentrations shows small fluctuations.

Fig. 6.11 (c) shows the model predicted site coverages of the MFOx species at a feed temperature of 300 °C. During modulation, the site coverage of MFO_{0.5} is near zero, suggesting that the periodic reduction/oxidation during modulation is limited to the reaction pair between MFO₄ and MFO₃. This is similar to results discussed earlier. This limited utilization of oxygen from spinel during modulation suggests that it may be feasible to lower the spinel loading in the PGM/spinel dual-layer monolith while ensuring satisfactory reductant conversion under modulation conditions. Moreover, from the standpoint of material design, it is critical to design spinel materials which possess fast reduction/oxidation kinetics. It is still a necessary task to design materials with low oxygen ion diffusion barrier, but this will be the secondary task.

6.5 Conclusions

This coupled experimental and modeling study of dynamic oxygen storage capacity reveals the transient reduction/oxidation behavior and determines the reaction kinetics. The proposed kinetic model is capable to capture the cycle-averaged and transient DOSC performance with varied OSM types (CZO and Mn_{0.5}Fe_{2.5}O₄ spinel), reductant types (H₂ and CO, reductant concentrations and catalysts architectures (OSM pellets and PGM-spinel dual-layer monolith). The main findings of this study are as follows:

- For both CZO and spinel, the reduction (or oxidation) process under goes firstly a fast kinetic-controlled process and then a slow diffusion-controlled process.
- The classic shrinking-core model incorporates the gas-solid diffusivity inside the global reaction rate expression and successfully captures the transient reduction/oxidation performance in CZO case.
- Analysis of the experimental data show that the fast reduction of spinel occurs in ~
 20s upon pulse introduction and is limited in the first surface layer of spinel particles. As such, the shrinking-core model is not applicable during fast cycling but instead a surface progressive model is used.
- A progressive model only considering reactions inside first surface layer of spinel particles is developed based on transient DOSC performance under long cycle conditions (i.e., 60s reduction pulse). In the reaction model, spinel reduction or oxidation is considered as two sequential steps, MFO₄ ≠ MFO₃ and MFO₃ ≠ MFO_{0.5}. The model with fitted parameters is also capable to capture the transient DOSC performance under short cycles (i.e., 2s or 0.8s) with multiple reductant concentrations with either CO or H₂ as the model reductant.
- Model predicted results show that during fast modulation (e.g., ~ 2s), the reduction of spinel is mostly confined in the first reduction step (MFO₄ → MFO₃). Moreover, the reaction extent of the first reduction step inside the first spinel particle layer is far smaller than one (e.g., ~ 0.2 at maximum). This confirms that the utilization of oxygen from spinel during fast modulation conditions is very limited to surface oxygen and thus it is reasonable to consider reactions only in first spinel layer for modulation modeling.

• Considering the limited utilization efficiency of oxygen from spinel, it may be practical to lower the spinel loading in catalyst design and also for spinel screening of potential OSM candidate in three-way or four-way catalysts,

This study evaluates the reduction/oxidation behavior of OSM under periodic cycling conditions and provides guidance for model construction. The applied method to quantify and assess the OSC in Mn_{0.5}Fe_{2.5}O₄ provides insights for OSC evaluation of other potential spinels. The determined kinetic parameters can also be accommodated into the modeling study of CH₄ oxidation using PGM-spinel catalysts.

Chapter 7 Conclusions and Recommendations for Future Work

7.1 Conclusions

The main objective of this work is to determine and the contribution from storage material in two processes, NOx storage and reduction (NSR) as well as three-way catalysts (TWC). The impacts of NOx storage material (NSM) and oxygen storage material (OSM) are compared in NSR processes, especially under fast cycling conditions. The promotional impacts from novel OSM spinel in TWC process are evaluated. The main findings of this study are summarized as follows.

7.1.1 Storage Material in NOx Storage and Reduction Process

- (1) NO can be reduced by reductants (CO, H₂ or C₃H₆) over ceria at high temperatures (e.g., >550°C). The main nitrogen-containing products are N₂ and NH₃, latter of which is generated only when hydrogen-containing reductants (H₂ or C₃H₆) are applied. Under lean/rich switching operation, NO is reduced by several components, including fed reductants, oxygen vacancies and adsorbed components (such as adsorbed CO and adsorbed hydrogen).
- (2) O₂ is detrimental to NO decomposition over ceria, mainly due to the competition between NO and O₂ for effective reducing components. In fact, as O₂ is a better oxidant than NO, NO reduction is very limited if large excess of O₂ exits in feed. Considerable NO conversion can only be achieved with rich or near stoichiometric feed. CO₂ and H₂O are also detrimental to NO conversion because they can and oxidize to some extent reduced ceria.

- (3) For Pt-containing catalysts (Pt/Al₂O₃, Pt/BaO/Al₂O₃ and Pt/CeO₂/Al₂O₃), the overall NOx conversion with cycle-averaged lean feeds (e.g., S_N = 9.7) generally parallels the corresponding NOx storage capacity. For example, Pt/CeO₂/Al₂O₃ (PCA) exhibits the highest NOx conversion below 300°C while Pt/BaO/Al₂O₃ (PBA) surpasses PCA above 300°C.
- (4) PCA shows both NOx and oxygen storage functionality. NO reduction over PCA can be achieved in both cycle-averaged lean and rich feeds between 150°C and 600°C. Below 400 °C, cycle-averaged NOx conversion increases with O₂ concentration, as PCA mainly exhibits NOx storage capacity and O₂ promotes NOx storage on PCA. At high temperatures (> 400 °C), cycle-averaged NOx conversion decreases with O₂ concentration, as PCA only exhibits oxygen storage capacity and O2 competes with NO for reducing sites (vacancies and adsorbed reducing intermediates).
- (5) In fast NSR processes, NOx storage material related pathways, including the conventional NSR pathway and the hydrocarbon intermediate pathway, are responsible for the effective NOx reduction. The redox mechanism is validated but shown to only play a rather minor role.
- (6) Two operation strategies, lean/rich switching and steady-state feeding are compared a fixed duty cycle rich. Fast cycling exhibits enhancement over ceria in near stoichiometric case, PBA in $S_N = 9.7$ case and over PCA in $S_N = 1.0$ case, thanks to the improved utilization of fast NOx storage and oxygen storage sites. The fast and slow sites in ceria are defined as the oxygen (or vacancy) sites on surface or in bulk of ceria particles. The fast and slow sites in PBA and PCA are

defined as the NOx or oxygen storage sites near or far away from Pt atoms.

(7) Compared with steady-state operation, faster lean/rich switching operation benefits NO abatement over ceria due to a better utilization of surface oxygen vacancies. The utilization of surface oxygen vacancies suggests improved catalyst synthesis, for example, smaller ceria particles increase NO reduction. This study on NO decomposition on ceria during lean and rich cycling helps understand the beneficial function of ceria on NOx reduction at high temperatures, which also provide guidance for optimization of catalyst formulation and operation strategies.

7.1.2 Oxygen Storage Material in Three Way Catalyst

- (1) With same loading of precious group metal (PGM) and oxygen storage material (OSM), the best PGM-OSM catalyst designs for CZO (Ce_{0.3}Zr_{0.7}O₂) or MFO spinel (Mn_{0.5}Fe_{2.5}O₄) are direct deposition of PGM on CZO (PC) and dual-layer PGM-MFO structure (PAS_DL), respectively.
- (2) The strong metal-support interaction between PGM and CZO is responsible for the deposition design. Deposition of PGM onto CZO ease the activation and utilization of oxygen from CZO, especially oxygen proximal to PGM. This is confirmed from TPR tests and performance evaluation tests of desired reactions, including oxidation of reductants (CO and C₃H₆), reduction of NO and water gas shift reaction and minor promotion for C₃H₆ SR promotion.
- (3) TPR results show rather weak interaction between PGM and spinel. Promotion from MFO-containing PGM catalysts mainly results from additional active

catalytic sites ($Mn_{0.5}Fe_{2.5}O_4$), where desired reactants can be converted, especially via C_3H_6 oxidation by O_2 .

- (4) At high temperatures (i.e., after light-off), modulation decreases NO, CO and C₃H₆ conversions simultaneously over PGM-Al₂O₃. Addition of OSM mitigates the detrimental impacts from feed modulation. Specifically, PC and PAS_DL are more resistant to CO or C₃H₆ modulation respectively.
- (5) Oxygen storage capacity (OSC) measurements with both long and short time periods (e.g., 60s or 2s) were conducted to evaluate the oxygen release/storage in OSM. For both pulsing time (60s and 2s), MFO spinel exhibits ~20 times higher DOSC than CZO with either CO or C₃H₆ as the probe reductant. Results from dynamic oxygen storage capacity (DOSC) tests also shows that spinel provides similar DOSC with either CO or C₃H₆, while CZO provides higher CO-DOSC values.
- (6) Experimental results from 60s OSC tests show that the reduction (or oxidation) process under goes firstly a fast kinetic-controlled process and then a slow diffusion-controlled process for both CZO and MFO spinel. Analysis of the experimental data show that the fast reduction of spinel occurs in ~ 20s upon pulse introduction and is limited in the first surface layer of spinel particles.
- (7) The classic shrinking-core model incorporates the gas-solid diffusivity inside the global reaction rate expression and successfully captures the transient reduction/oxidation performance in CZO case.
- (8) In MFO spinel case, a progressive model only considering reactions inside first surface layer of spinel particles is developed based on transient DOSC performance

under long conditions (e.g., 60s reduction pulse). The reaction steps of spinel is considered based on TPR results as two sequential steps, $Mn_{0.5}Fe_{2.5}O_4 \neq Mn_{0.5}Fe_{2.5}O_3$ and $Mn_{0.5}Fe_{2.5}O_3 \neq Mn_{0.5}Fe_{2.5}O_{0.5}$. The model with fitted parameters is also capable to capture the cycle-averaged and transient DOSC performance under short cycles (i.e., 2s or 0.8s) with multiple reductant concentrations with CO or H₂ as the model reductant.

(9) Model predicted results show that during fast modulation (e.g., ~ 2s or less), the reduction of spinel is mostly confined in the first reduction step (MFO₄ → MFO₃). Moreover, the reaction extent of the first reduction step inside the first spinel particle layer is far smaller than one (e.g., ~ 0.2 at maximum). This suggests that the utilization of oxygen from spinel during fast modulation conditions is very limited to surface oxygen and thus it is reasonable to consider reactions only in first spinel layer for modulation modeling.

7.2 Recommendations

Based on the results and insights from current work, several recommendations for future experimental and modeling work are listed as follows:

- (1) The Di-Air or fast NSR system cannot provide satisfactory deNOx performance until medium temperatures (i.e., > 200 °C). It is recommended to study the performance of system of combined NSR and other low temperature deNOx processes (e.g., PNA).
- (2) The fast cycling or modulation operation leads to feed change in very short periods (e.g., hundreds of milliseconds), which imposes demanding requirements for the

time resolution of characterization equipment. For example, FTIR usually generates signals every second and mass spectrometer can lower the detection time to hundreds of milliseconds. Further experimental work is recommended to study the underlying mechanism during fast cycling with the aid of more advanced detection equipment.

- (3) Current DOSC modeling models for MFO spinel only considers CO and H₂ as reductants (Chapter 6), it is recommended to develop modeling blocks and determine kinetics for hydrocarbons, especially for CH₄, as spinel-contained catalysts show unexpected superior CH₄ activation performance [40].
- (4) A kinetic model considering reactions on both PGM and spinel sites need to be developed to capture and predict the performance of simultaneous removal of CO, NO and hydrocarbons on PGM-Spinel dual-layer catalysts, especially during modulation operation.
- (5) It is recommended to conduct experimental and simulation work for spinel, including material screening, composition optimization and structure tuning, to design spinels for improved the TWC or FWC performance.
- (6) Modeling results show that the utilization efficiently of surface oxygen sites in MFO spinel is very limited. It is recommended to optimize the spinel and PGM loading in PGM-Spinel dual-layer monolith catalysts.

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Appendix

Appendix A: Equation Derivation for SCM

The schematic of shrinking-core model is shown in Fig. A1. Here considered is the reduction process of an OSM particle which has the perfect sphere shape. Originally the OSM particle is fully oxidized and has the radius of r_p . During reduction, the reduced OSM is formed and surrounds the unreacted oxidized core in a layer uniformly. The reduced OSM layer has the thickness of l_p and the inner oxidized core has the radius of r_1 . The reductant (for example, CO), needs to diffuse through the reduced OSM layer to the oxidized OSM core, for reaction.



Fig. A1 Schematic of shrinking core model0

As an example, CZO reduction by CO (CZO₂ \rightarrow CZO_{1.85}) is considered here. The rate of CO consumption during reduction is given by

$$r_{CO} = k_1 \Omega_{C,oxi} C_{CO} = k_1 \Omega_C \theta_{CZO_2} C_{CO}. \tag{A.1}$$

Here r_{CO} is the reaction rate of CO based on CZO volume and has the unit of mol/(s•m³), k_1 is the rate constant of CO reduction, Ω_C is the site density of the CZO, and θ_{CZO_2} is the site (or volume) fraction of oxidized OSM in total OSM (i.e., θ_{CZO_2} for CZO).
The molar rate of diffusion at any radical position r (within the shell) is defined as molar flux times area, i.e.,

$$R_{diff. shell,CO} = D_{p,CO} (4\pi r^2) \frac{dc}{dr} \qquad \qquad for r_1 < r < r_p. \qquad (A.2)$$

Here $D_{p,CO}$ is the diffusivity of CO inside the reduced CZO (i.e., CZO_{1.85}) shell. As the rate of diffusion inside the shell is constant at any point, R_{diff, shell} can be further expressed as

$$R_{diff.\ shell,CO} = \frac{4\pi D_{p,CO}}{l_p} (C_{CO,r_p} - C_{CO,r_1}) r_p r_1 \qquad r_1 < r < r_p.$$
(A.3)

For reaction at the surface of the oxidized core, the rate expression is written as Eqn. A.4. Even though it is assumed that reaction occurs on the core surface, the rate expression of reduction (Eqn. A.4) contains the volume term (i.e., $\frac{4}{3}(\pi r_p^3)$) rather than the surface area term because the reduction rate is defined based on the CZO particle volume, i.e.,

$$R_{rxn.\ surface,C0} = \frac{4}{3} (\pi r_p^3) k_1 C_{C0,r_1} \Omega_C \theta_{CZO_2} \qquad at\ r = r_1.$$
(A.4)

Assuming the reduction is shell layer diffusion controlled, the CO diffusion rate is equal to the rate of CO consumption for the core of radius r_1 as

$$R_{rxn. \ surface, CO} = R_{diff. \ shell, CO} \qquad at \ r = r_1. \tag{A.5}$$

Substituting Eqns. A.3 and A.4 into Eqn. A.5, C_{CO,r_1} can be expressed as a function of C_{CO,r_p} as

$$C_{CO,r_1} = \frac{C_{CO,r_p}}{1 + \frac{k_1 \Omega_C \theta_{CZO_2} l_p r_p^2}{3D_{p,CO} r_1}}.$$
(A.6)

Also here is the relationship between site coverage of oxidized OSM CZO₂ (θ_{CZO_2}) and geometry parameters in CZO particle (r_1 and r_p). Assume the reduced CZO layer and oxidized CZO core (CZO₂ core and CZO_{1.85} shell) has the same molar density, the volume based site coverage can be defined by

$$\theta_1 = \frac{V_{oxidized \ OSM}}{V_{total \ OSM}} = \frac{\frac{4}{3}\pi r_1^3}{\frac{4}{3}\pi r_p^3} = \frac{r_1^3}{r_p^3}.$$
(A.7)

Correspondingly, length parameters r_1 and l_p can be expressed as a function of θ_{CZO_2} , that is:

$$r_1 = r_p \theta_{CZO_2}^{1/3} \tag{A.8}$$

and
$$l_p = r_p (1 - \theta_{CZO_2}^{1/3}).$$
 (A.9)

Substituting Eqns. A.6, A.8, A.9 into Eqn. A.1, the overall reaction rate of CO is given by

$$R_{CO} = k_1 \frac{c_{CO,r_p}}{1 + \frac{k_1 \Omega_C \theta_{CZO_2} l_p r_p^2}{3Dr_1}} \Omega_C \theta_{CZO_2}$$
(A.10)

and
$$R_{CO} = k_1 \frac{C_{CO,r_p}}{1 + k_1 \Omega_C \frac{r_p^2 (1 - \theta_{CZO_2}^{1/3}) \theta_{CZO_2}^{2/3}}{_{3D_{p,CO}}} \Omega_C \theta_{CZO_2}.$$
 (A.11)

Here the modified rate constant k_{mod} is defined as

$$k_{mod,CO} = \frac{k_1}{1 + k_1 \Omega_C} \frac{r_p^{2(1-\theta_{CZO_2}^{1/3})\theta_{CZO_2}^{2/3}}}{{}_{3D_{p,CO}}}.$$
(A.12)

Thus, the rate of CO consumption is first-order in the CO concentration at the surface with the modified rate constant which contains the diffusional impacts.

Similar to the reduction process, the oxidation of reduced CZO (CZO_{1.85}) is also assumed to occur only at the interface between the reduced OSM (CZO_{1.85}) layer and oxidized OSM core (CZO₂). During oxidation, the oxidized core increases and the reduced OSM layer thickness decreases. Following the same procedure and notation, the reaction and diffusion rate can be written as Eqns. A.13 and A.14,

$$R_{rxn.\ surface,O_2} = \frac{4}{3} (\pi r_p^3) k_2 C_{o_2,r_1} \Omega_{\rm C} \theta_{CZO_{1.85}} \qquad at\ r = r_1 \tag{A.13}$$

and
$$R_{diff. shell, O_2} = \frac{4\pi D_{p, O_2}}{l_p} (C_{O_2, r_p} - C_{O_2, r_1}) r_p r_1 \qquad r_1 < r < r_p.$$
 (A.14)

Here r_{O_2} is the reaction rate of O₂ based on OSM volume and has the unit of mol/(s•m³), k_2 is the rate constant of O₂ oxidation, $\theta_{CZO_{1.85}}$ is the site (or volume) fraction of reduced OSM in total OSM (i.e., $\theta_{CZO_{1.85}}$ for CZO).

The correlation between θ_1 and θ_2 is expresses as

$$\theta_{CZO_2} + \theta_{CZO_{1.85}} = 1.$$
 (A.15)

Finally, the modified oxidation rate can be written as Eqns. A.16 and A.17, with the modified rate constant as Eqn. A.18:

$$R_{O_2} = k_2 \frac{c_{O_2, r_p}}{1 + \frac{k_1 \Omega \theta_2 l_p r_p^2}{3D_{p, O_2} r_1}} \Omega \theta_2,$$
(A.16)

$$R_{O_2} = k_2 \frac{c_{O_2, r_p}}{1 + k_2 \Omega \frac{r_p^2 (1 - \theta_1^{1/3}) (1 - \theta_1)}{3D_{p, O_2} \theta_1^{1/3}}} \Omega(1 - \theta_1),$$
(A.17)

and
$$k_{mod,O_2} = \frac{k_1}{1 + k_2 \Omega \frac{r_p^2 (1 - \theta_1^{1/3})(1 - \vartheta_1)}{3D_{p,O_2} \theta_1^{1/3}}}.$$
 (A.18)