

REACTION AND TRANSPORT COUPLING IN MULTI-FUNCTIONAL
CATALYSTS FOR SELECTIVE OXIDATION OF AMMONIA TO NITROGEN

by
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ABSTRACT

A multi-functional catalytic reactor (popularly known as “Ammonia Slip Catalyst (ASC)” or “AMOX”) comprising Pt/Al₂O₃ and Cu or Fe-exchanged zeolite is utilized for selective oxidization of NH₃ to N₂ in the diesel engine emission control system. Pt catalyzes the oxidation of NH₃ to four products (N₂, N₂O, NO, NO₂) while the metal-exchanged zeolite concurrently catalyzes the selective catalytic reduction of NO/NO₂ with NH₃, directing the product mixture towards N₂. The state-of-the-art ASC has a dual-layer washcoat architecture with a bottom layer of Pt/Al₂O₃ and a top layer of Cu/SSZ-13. As emission control catalysts experience degradation under the severe operating conditions which can negatively impact the product distribution and conversion. The first part of this dissertation study elucidates the effect of hydrothermal aging on the performance of a Pt/ γ -Al₂O₃, Cu/SSZ-13 and dual-layer washcoated monolith used for oxidation of ammonia. The catalysts was subjected to a feed stream containing H₂O at 550 °C for over 250 hours and performance was measured at discrete intervals as it was progressively aged.

In the next part of this study, the enhanced mass transport phenomenon coupled with multi-functional catalytic reactions in ASC is investigated. Earlier works have shown that pore diffusion can be limiting in ASC. we used sacrificial agents (polymer, yeast) to increase the porosity of washcoat for ASC. The sacrificial agents are removed by oxidation generating pores to increase the washcoat macroporosity. Steady state reaction experiments showed a noted increase in NH₃ conversion while testing NH₃ oxidation the dual-layer ASC with negligible change in N₂ selectivity. Modeling and analysis of ASC catalysts is presented using 1 + 1 dimensional reactor model containing

tuned multi-step kinetic formulations to simulate ASC performance for understanding and optimization. We also describe a systematic study to identify the ASC architecture and composition that optimize the trade-off between conversion and selectivity. The in-house synthesized ASC samples span the single layer Pt/Al₂O₃, conventional dual-layer Pt/Al₂O₃ + Cu/SSZ-13, uniform single layer of mixed Pt/Al₂O₃ + Cu/SSZ-13, and a hybrid design comprising a bottom layer of mixed Pt/Al₂O₃ + Cu/SSZ-13 and a thin top layer of Cu/SSZ-13.

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Chapter 1. Introduction

1.1 Emissions Overview

Exponential growth of industries in last century is a huge step in human advancement but at same time put a major threat to environment. It could be dangerous solid waste from nuclear energy plants, harmful liquid waste from chemical plants or gaseous emissions from combustion engines and industries. Techniques to minimize the negative industrial impact on environment plays an important role for sustainability of the planet earth. Here, we focus on gaseous emission from combustion engines and chemical engineering approaches for ecological endurance. Gaseous emissions source can either be stationary or non-stationary. Chemical plants including refineries, stationary combustion engines, steel or coal plants are all categorized under stationary sources of emissions. On the other hand, non-stationary sources are such as vehicles, ships, planes or movable machines. This study specifically focused eliminating emissions from combustion engines especially diesel fuel engines, stationary or non-stationary.

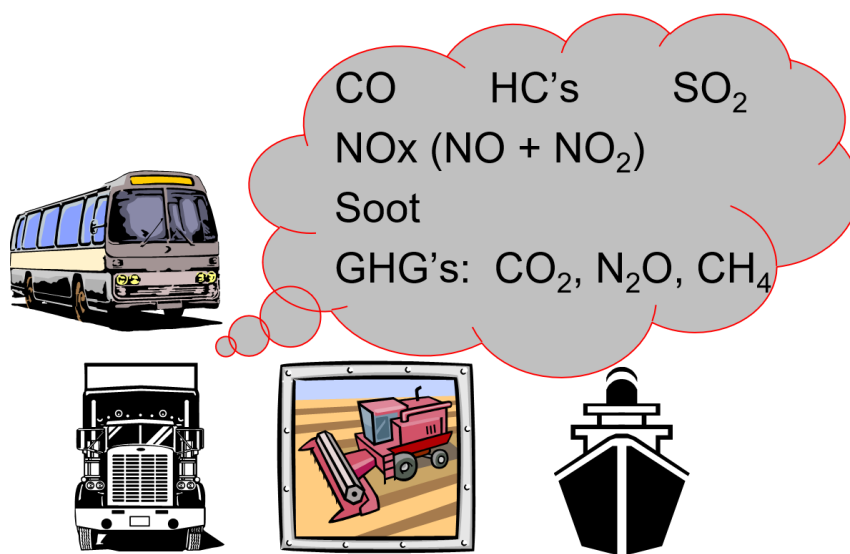


Figure 1.1 Schematic diagram representing gaseous emission from various sources.

Diesel engines are pervasively used throughout the world to generate power. Unlike spark ignition engines, the diesel engines work on principle of injecting fuel into cylinders comprising high temperature and high pressure. The diesel fuel combusts and convert fuel's chemical energy into mechanical power. The combustion reaction of fuel and air mainly produce CO_2 and H_2O , and exhaust comprises four main components CO_2 (2-12%), H_2O (2-12%), O_2 (3-17%) and balance N_2 [1]. In addition to main combustion reaction, some non-ideal by-product reactions such as partial or no oxidation of hydrocarbons, nitrogen oxidation to form NO_x at high temperature and high pressure, oxidation of sulfur present in diesel fuel or engine/lube oil etc. [2]. These undesired side reactions add harmful and toxic pollutants to diesel engine exhaust. The pollutants are particulate matter, unburnt HCs, CO, NO_x , N_2O and SO_x (Fig. 1.1).

Particulate matter is the black smoke present in diesel engine exhaust. There is no defined chemical species details for the elements present in the particulate matter. It composes mainly of solid fraction (elemental carbon and ash), soluble organic fraction (organic material derived from fuel and engine lubricating oil) and sulfate particulates (sulfuric acid and water) [1]. The elemental carbon, named as 'black carbon' or 'soot', is mainly generated in heterogeneous combustion in diesel engine. The black carbon sticks to the internal surfaces of exhaust pipes. The metals (Fe, CA, Zn, MG) present in lube oil or engine oil oxidize to form metal oxide and add up to the ash. The sulfates (SO_4) are sulfur compound mainly H_2SO_4 , produced from the sulfur compounds present in diesel fuel or lube oil. Diesel particulate filters (DPF) are installed in exhaust aftertreatment system to trap these particulate matters and prevent it from releasing into atmosphere.

Unburnt hydrocarbons are the hydrocarbon compounds that originate from fuel or the

lubricating oil and remain unreacted during the combustion reactions. These are termed as total hydrocarbons (THC) in emission regulations and has generic chemical formula of C_nH_m . Due to differential atmospheric effects of CH_4 , these days the hydrocarbons regulated in emissions are non-methane hydrocarbons (NMHC). Hydrocarbons in exhaust can be present in gaseous or particulate (liquid or adsorbed) form. These unburnt hydrocarbons are made to oxidize to CO_2 and H_2O with the application of diesel oxidation catalyst (DOC) in exhaust aftertreatment system.

Carbon monoxide (CO) is another odorless, colorless and a very toxic pollutant gas that forms in diesel combustion engine with partial oxidation of hydrocarbons. Excess O_2 is necessary for combustion reaction to produce CO_2 and H_2O , whereas limited O_2 supply move the reaction toward CO and H_2 formation during oxidation. In addition, the carbon present in soot oxidize to produce CO. CO is highly toxic and could be fatal if inhaled in excess quantity. CO in engine exhaust typically range from 10 to 500 ppm. CO is made to oxidize to CO_2 using DOC emission catalyst.

NO_x is one of the most critical emission associated with diesel engine exhaust. NO_x comprises mainly NO (~90%) and rest NO₂. N_2 and O_2 can react directly to form NO under high temperature and high pressure conditions in diesel engines. The NO_x emitted from engine range from 50 to 1000 ppm. NO is colorless, odorless and a highly active ozone precursor that could lead to smog formation. On the other hand, NO₂ is red-brown gas with irritating odor and is highly toxic. NO₂ is very reactive and exhibit strong oxidizing properties. Selective catalytic reduction is the catalysis approach in diesel aftertreatment system used to convert NO_x back into N_2 . In SCR, the NO_x is made to react with NH_3 which is supplied from outside source called urea dosing system in diesel aftertreatment

system. The aqueous urea thermally breaks down to form NH_3 and react with emitted NO_x over NO_x reduction catalysts to form N_2 . The reacting mixture require ideal inlet stoichiometric ratio of $\text{NH}_3:\text{NO}$ (1:1) and it is challenging to maintain this ratio during real-time road driving conditions. In addition, some NH_3 oxidize over SCR catalyst which rationale the injection of NH_3 in slight excess to the requisite ratio for complete conversion of NO_x . The excess injection of NH_3 contribute to NH_3 slippage, in other words unreacted NH_3 left after SCR. This add NH_3 to diesel engine emissions. In fact, the diesel vehicles are becoming major source of NH_3 emissions in urban cities [3]. Ammonia slip catalyst (ASC) is a catalytic reactor in aftertreatment system to convert ammonia selectively into N_2 . Apart from these nitrogen compounds, nitrous oxide (N_2O) is another emission associated with diesel engines. N_2O is laughing gas, not directly harmful but has potent greenhouse gas effects, several times more than CO_2 greenhouse effect.

1.2 Emissions Health Effects

Every emitted gas from diesel engine exhaust is detrimental to atmosphere and human health except O_2 and N_2 . Toxic compounds present in diesel engine exhaust are CO , NO_x , SO_x and NH_3 . Carbon monoxide is highly toxic and has strong affinity for hemoglobin, if inhaled displaces oxygen in blood and reduces oxygen supply to all the vital organs. It could be fatal if a person is exposed to CO for longer period of time. CO being colorless, odorless and non-irritating make it impossible to detect directly by human eye or nose, so a CO detector is always recommended while working in CO prone areas. [Remark: Room heating mechanisms such as firepots or similar in non-ventilating room can produce high amount of CO and could lead to fatality [99]].

NO_x gases are another major pollution concern of diesel engine exhaust. NO_x act as a

precursor for ground level ozone formation and cause smog. NO_x readily reacts with water to form nitric acid and lead to acid rain. On the other hand, NO₂ is toxic and directly affect respiratory tract inflammation. Similar to NO_x, the Sulphur oxides (SO_x) gases also cause respiratory tract irritation and contributes to the acid rain through formation of H₂SO₄ [4]. Current emission regulations mandate ultra-low sulfur content diesel, so the quantitative SO_x formation is significantly lower in comparison to other pollutants in exhaust.

On the other hand, CO₂ and N₂O are greenhouse gases contribute to global warming. N₂O is released in smaller fractions compared to CO₂ but has several times stronger greenhouse effect compare. Unburnt hydrocarbon ranging from CH₄ to higher HCs differentially impact human health. Methane exhibit greenhouse gas effect. The main harmful hydrocarbons are benzene and formaldehydes that are considered carcinogenic. The regulation for benzene is less than 1 ppm. Also, the pollutants like carbon soot cause smog formation and directly affect respiratory system.

Last but not the least, NH₃ emitted by diesel engines is corrosive, toxic and exhibit pungent odor. NH₃ led to respiratory tract inflammation and cause burning sensation in eyes if exposed. NH₃ does not form inherently in diesel engine, indeed the result of NH₃-SCR technology where the NH₃ is injected by outside source in diesel engine aftertreatment system to remove NO_x. This study has investigated catalytic technology called “ammonia slip catalyst or AMOx” to minimize NH₃ emissions.

1.3 Emission Regulations

Every country defines and continually update emission regulations within region correspond to each emission gas. Environmental agencies of the respective country administer the renewal and enforcement of emission regulations. EPA and CARB are two

agencies that operate in the USA. Upper limit of a emitted gas is defined for every different engine type such as light duty or heavy duty vehicles. The increasing number of automobiles every year necessitate revision and reduction in upper limits. Also, the emission testing protocols demonstrate significant variability under different circumstances. Vehicles show noticeable discrepancy between lab and real-time driving emissions test. On-board diagnosis (OBD) of vehicles has shown that gases emissions are significantly higher on road compared to lab test analysis.

Based on current emission regulations release, every country is expected to cut CO₂ by 3-4% per year [5]. For passenger vehicles, EU applied most strict CO₂ targets of 130 g/km in 2015 and reducing to 60 g/km in 2030. US announced CO₂ limit of 150 g/km (2015) with reduction to 90 g/km in 2025. In US, the NO_x regulations have been reduced exponentially from 10.7 g/(bhp-hr) in 1980s to 0.2 g/(bhp-hr) in 2007 for heavy duty engines [6]. Similarly, CO norms reduced from 40 (in 1970s) to 15.5 g/(bhp-hr) (in 2007).

The current European emission regulations for heavy duty compression engines (diesel engines with RM>1760 kg) as of 2017 are 740 mg/km CO, 125 mg/km NO_x, 215 mg/km THC+NO_x and 4.5 mg/km PM [7].

Johnson [5] has published review articles almost every year to summaries the most recent emission regulations from all over the world. His most recent article [5] states that India has published BS VI regulations and to be implemented in 2020 and has already started 10 ppm sulfur fuel with two years ahead of 2020 target. Brazil is implementing Proconve 8, similar to HD EURO VI in 2023. Mexico will have all new HD vehicles with US2010 and EURO VI regulations starting 2021. China VI HD was proposed in 2016 and to be implemented nationwide in 2020. Also, China introduced a policy to give incentive

to companies for making electric vehicles.

1.4 Diesel Engine Exhaust Aftertreatment System

Diesel engine exhaust aftertreatment is intended to eliminate and treat all the harmful gaseous of engine exhaust before releasing into atmosphere. An ideal eco-friendly exhaust should consist of O_2 , N_2 , CO_2 and H_2O . This is feasible with catalytic conversion of undesired carbon and nitrogen compounds into CO_2 and N_2 respectively. Multiple chemical reactions require complex aftertreatment system with several catalysts aligned in a systematic architecture. It consists of a chain of catalytic components starting from diesel oxidation catalyst (DOC), diesel particulate filter (DPF), selective catalytic reduction (SCR) to ammonia slip catalyst (ASC) (Fig. 1.2). In other words, an aftertreatment system is no less than a chemical plant on wheels. Each of the catalytic components are washcoated monolith, where the catalyst is coated over monolith core. Use of monolith type reactor is to minimize the back pressure effect on engine. Figure 1.2 display schematic of diesel engine aftertreatment system.

Diesel oxidation catalyst (DOC), first in chain, is applied to oxidize unburnt hydrocarbons and CO into CO_2 . The traditional DOC comprises of PGM (Pt and Pd) supported over Al_2O_3 . Since Pt surface get poisoned by CO, so Pd and Pt is used in combination to achieve high performance without catalyst poisoning [8]. Several recent studies investigated the effect of Pt-Pd composition, washcoat structure (layer or zone) for better performing DOC [9]. Alongside, DOC catalyzes NO oxidation and convert fraction of NO into NO_2 which indirectly benefit downstream SCR catalyst as NO_2 presence initiate fast SCR reaction over SCR catalyst. DOC is situated closest to the engine outlet and bear the heat of the engine, so thermal degradation is serious issue due to Pt or Pd sintering.

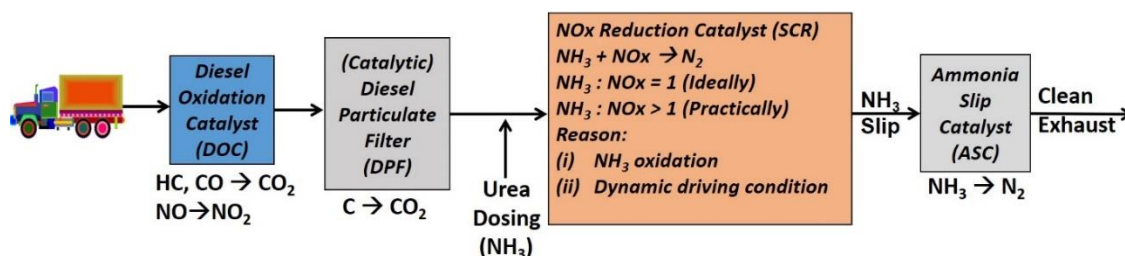


Figure 1.2 Schematic representation of diesel engine aftertreatment system.

Diesel particulate filter (DPF) is a catalytic reactor after DOC (Fig. 1.2). It is meant to filter out coke, soot and particulate matter. Currently, the commercial DPFs are being incorporated with active sites that oxidize coke into CO_2 and facilitate self-regeneration [10]. The filters are washcoated monolith reactor with alternate channels blocked, front or back cross section looks like a board of chess. The filtration prevents downstream catalytic reactors from getting poisoned by coke or soot. Research is underway to incorporate SCR catalytic sites onto DPF which will reduce the load over downstream SCR catalyst.

Selective catalytic reduction (SCR) technology is utilized to convert NO_x into N_2 . Since NO_x emissions is a big challenge associated with diesel channel, the SCR has been given special focus in the research. Till date, numerous catalysts have been investigated to combat NO_x emission. In 1990s, vanadium based SCR catalysts were extensively used to selectively reduce NO_x into N_2 by reacting it with hydrocarbon [11]. Vanadium SCR was profoundly popular in removing NO_x for industrial application attributed to its low cost. On the other hand, vanadium exhibits poor thermal properties that mandate frequent catalyst replacements for automobile exhaust cleaning applications. In early 2000s, Cu and Fe zeolites (beta, ZSM-5) were studied for removing NO_x by reducing it with NH_3 [12]. Cu exhibit extremely high activity and selectivity, notwithstanding, the thermal

degradation and catalyst poisoning remained a challenge. A chabazite structured zeolite (SSZ-13) discovered by Chevron in 1985 for application in methanol to olefins process. Recently, Cu-SSZ-13, Cu exchanged SSZ-13 is commercialized for SCR applications. The Cu resides inside the zeolite cage with cage's opening sufficiently small that it restricts HC entry and prevent Cu poisoning [13]. Hydrothermal aging study [14] showed that Cu-SSZ-13 catalyst has excellent resistance to thermal degradation. A dedicated on-board urea dosing system is required for generating NH_3 feed to SCR. To clean unreacted NH_3 leftover from SCR, an additional catalyst ammonia slip catalyst (ASC) is installed.

Ammonia slip catalyst (ASC) is the last catalytic step for selective oxidation of NH_3 to N_2 . NH_3 injected by on-board urea dosing system react with NO_x over SCR catalyst. The aqueous urea thermally breakdown to produce NH_3 and CO_2 . Urea dosing system is additional on-board system that add up cost and complexity to aftertreatment system. The refilling of aqueous urea (DEF) is required after certain mileage limit and is very uneconomical. It is also challenging to dose urea precisely as the depositions form inside the exhaust pipe surfaces during cool down. Another important factor is to precisely control urea dosing to attain requisite stoichiometric ratio of $\text{NH}_3:\text{NO}$ (1:1). To account for dynamic road driving conditions and NH_3 oxidation over SCR catalyst, the NH_3 is practically injected in slight excess that leads to ammonia slippage and hence the ammonia slip catalyst (ASC) become a necessity. The main research objective of our study is to improve the existing ammonia slip catalyst.

1.5 Ammonia Slip Catalyst

Several catalysts (Pt, Pd, Rh, Ru, Ag, Cu, Fe or V) have been studied till date for ammonia oxidation. Out of all the catalysts, Pt is highly active but at same time poorly

selective toward N_2 formation. Ag produce N_2 as main product but its productivity is extremely low compared to Pt, tremendously low space velocities would be an operating constraint to attain full conversion. Cu also facilitate selective oxidation of NH_3 to N_2 but activation energy for reaction is very high, a temperature above 400 °C is required to light-off the reaction [15]. On the other hand, a highly diluted Pt catalyst (0.1 wt% in Al_2O_3 or $\sim 1 \text{ g/ft}^3$ washcoat loading) demonstrate complete NH_3 conversion even at extreme operating conditions of high space velocity $250,000 \text{ h}^{-1}$ and low temperature 250 °C.

Apart from active sites, the choice of support also affect conversion and product selectivity. In this study, Pt supported over $\gamma-Al_2O_3$ was used in all of the experiments. The high activity of Pt makes it favorable for NH_3 oxidation but formation of NO as major product at high temperatures disapprove it for environmental catalysis purpose. Fig. 1.3 show typical Pt catalyzed NH_3 oxidation results, producing mainly NO in high temperature regime. The poor N_2 selectivity necessitate the addition of Cu active sites and introducing bi-functional catalyst for NH_3 -SCO.

Incorporating Cu-SSZ-13 significantly increase N_2 selectivity whereas commercially applied ASC is dual-layer washcoated reactor comprising base Pt/ Al_2O_3 and top Cu-SSZ-13 layer (Fig. 1.4). NH_3 present in fluid phase along with O_2 travel through top SCR layer and oxidize to form several different product over base PGM layer. The NOx produced in base layer diffuse back to fluid phase through SCR layer where it reacts with part of incoming NH_3 or stored NH_3 inside SCR layer, to form N_2 . Thus, an application of bifunctional dual-layer structured catalyst converts NH_3 selectively into N_2 .

Even though the dual-layer ASC is commercialized but it is not considered as best solutions. It has several drawbacks that are discussed throughout this study and systematic

set of studies were performed in an attempt to find best solution. This study encapsulates the conjunction of ASC fundamentals research on par with frontline industrial applications.

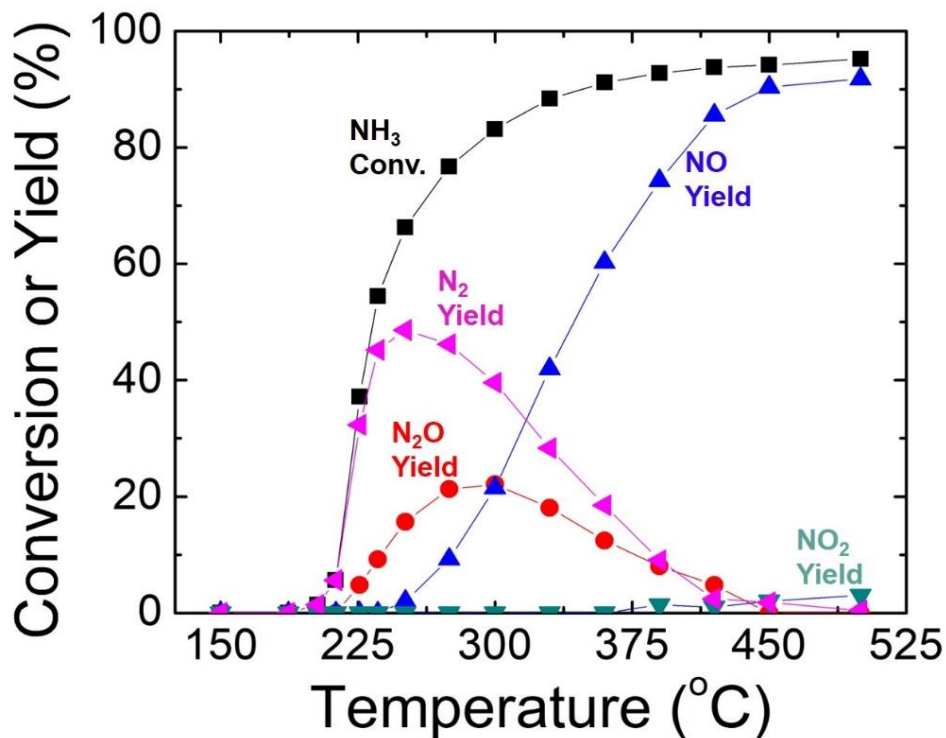


Figure 1.3 Steady state NH₃ conversion and product yields over Pt/γ-Al₂O₃. Feed: 500 ppm NH₃, 5% O₂ and balance Ar at 265k h⁻¹ space velocity.

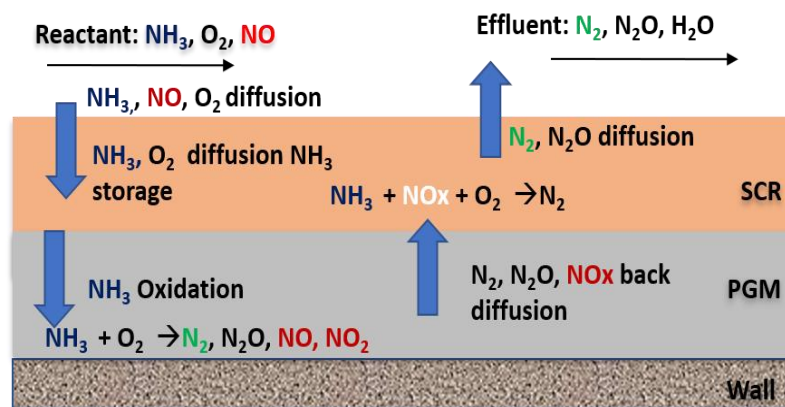


Figure 1.4 Schematic representation of dual-layer ASC comprising top SCR (Cu-SSZ-13) and base PGM (Pt/Al₂O₃) layer.

1.6 Outline

The dissertation study is mainly focused on ammonia slip catalyst (ASC) and its auxiliaries. The dual-layer ASC was already being used as a commercial catalyst when this research began in 2016. The major challenge in using dual-layer morphology was that the application of top SCR layer increases N_2 selectivity but at same time act as a diffusion barrier and restrict NH_3 to reach the base $\text{Pt}/\text{Al}_2\text{O}_3$ layer and decrease NH_3 conversion. The experimental work on an innovative and economical approach to enhance mass transport through SCR layer was just about to kick-off while at same time our collaborators and sponsors (Cummins Inc.) encountered a real world problem of pre-mature catalyst deactivation for SCR and ASC with speculations of hydrothermal aging or catalyst poisoning. This immediately diverted our research focus to investigate the root cause for ASC catalyst performance degradation over longer period of time.

The chapter 2 describe hydrothermal aging study over $\text{Pt}/\text{Al}_2\text{O}_3$, Cu-SSZ-13 and dual-layer ASC. The objective was to disintegrate both layer and study the effect of aging over each layer separately followed by combined dual-layer, starting with base $\text{Pt}/\text{Al}_2\text{O}_3$ layer. Systematic set of reaction experiments followed by catalyst characterization and mathematical modeling was performed to uncover hydrothermal aging effects over $\text{Pt}/\text{Al}_2\text{O}_3$. Accelerated catalyst aging was done at 550 °C in flowing atmosphere consisting 5% O_2 , 5% H_2O , 4% CO_2 and balance Ar. These aging conditions were decided in agreement with Cummins Inc. to mimic the real-time road driving conditions. The catalyst performance was evaluated at different aged levels by running NH_3 oxidation. Reaction experiments showed monotonic decline in NH_3 conversion with aging time at high temperatures. Surprisingly, the light-off temperature did not change, anticipating negligible

change in Pt activity. Catalyst characterizations including BET, chemisorption and SEM showed that mass transport being the underlying mechanism affecting NH_3 conversion. A 1+1 dimensional mathematical model was developed that accurately predicted experiment results and found the absolute change in λ (tortuosity/porosity) value with aging time. In addition, the C_3H_6 oxidation experiments were performed over fresh and aged Pt/ Al_2O_3 which further corroborate the finding of mass transfer limitations. It was found that prolonged hydrothermal aging transform $\gamma\text{-Al}_2\text{O}_3$ into $\text{Al}(\text{OH})_3$. The evidence of $\text{Al}(\text{OH})_3$ formation was confirmed using DRIFTS characterization. After studying Pt/ Al_2O_3 layer in detail, the hydrothermal aging was then conducted over single layered Cu-SSZ-13 sample followed by combined dual-layer ASC. The reaction testing were performed at different aged levels for Cu-SSZ-13 and dual-layer ASC.

The aging study answered many questions for ASC. The research focus was once again shifted back to the diffusion problem in dual-layer ASC. The top SCR layer was extremely beneficial in increasing N_2 selectivity while it simultaneously reduced NH_3 conversion due to diffusion limitations at high space velocities. The chapter 3 explain the diffusion challenges associated with dual-layer and pore-forming approach to enhance mass transport through top SCR layer. The diffusion limitations in SCR washcoat was earlier reported by Metkar et al. [16] and has been further confirmed in this study. The objective was to increase the NH_3 conversion by increasing porosity of top SCR layer with the application of economical sacrificial agents such as yeast or polymer. These sacrificial agents burn away at high temperature and generate holes inside the washcoat. The modified washcoat with calcined holes can be visualize as a slice of swiss cheese. The washcoat modification increased macroporosity of top SCR layer and resulted in 15% increase in

NH₃ conversion compared to conventional dual layer sample. Surprisingly, the N₂ selectivity remain unaffected. Along with ASC, the single layer modified and unmodified Cu-SSZ-13 (SCR) samples were synthesized and tested for standard SCR conditions. Similar conversion improvements were noticed for single Cu-SSZ-13 layer. Also, the transient experiment including NH₃ adsorption and temperature programmed desorption were run to understand enhanced washcoat diffusion through the SCR layer.

The chapter 4 describe a mathematical model developed on basis of the experimental study of enhanced transport. A 1+1 dimensional model was prepared by discretizing the differential transport equations for fluid phase, solid phase and surface species balance. Two kinetic models, each for Pt and Cu are described. The Pt kinetic model is dual-site microkinetic model developed from first principle DFT study of Pt(111). Two sites include top and hollow sites, where the top sites facilitate NH₃ adsorption and desorption while rest of the reaction steps catalyzed over hollow sites. The model satisfactorily predicted Pt catalyzed ammonia oxidation with minor discrepancies at low temperature. An ongoing kinetic study is being conducted to investigate the further improvements in the Pt model. On the other hand, Cu model was developed on the line of models reported in literature and by performing kinetic experiments over powder Cu-SSZ-13. The developed model very well predicted experiment results for single layer Cu-SSZ-13 and dual-layer ASC. It was found that effective diffusion inside Cu-SSZ-13 washcoat almost doubles with washcoat modification. The model also showed good accuracy in predicting transient NH₃ adsorption and temperature programmed desorption behavior.

The chapter 5 describe a detailed study of various washcoat structures and their impact on conversion and product selectivities. An attempt was made to investigate the washcoat

architectures for optimum conversion and selectivity. Apart from conventional dual layer or uniform mixture of Pt/Al₂O₃ and Cu-SSZ-13, a hybrid layer design with base layer mixed (Cu+Pt) and sufficiently thick top SCR layer were synthesized and evaluated. The samples show dissimilar trend for change in conversion and selectivity with varied washcoat structures. The conversion drops linearly when transiting from mixed layer to dual layer while N₂ selectivity increases logarithmically. The above explained model was then used and it very well predicts the experiment results for all samples including hybrid layer.

The chapter 6 conclude the research study and show the finding along with future directions of the project. An ongoing sulfur poisoning study of dual-layer ASC is explained with various aspects of catalyst deactivation. The chapter also discuss the future aspects of sulfur poisoning study.

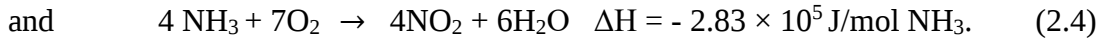
Chapter 2. Hydrothermal aging of ASC

2.1 Introduction

In recent years increasing attention has been on fuel efficient diesel vehicles which are being outfitted with increasingly advanced emission after-treatment systems. Extensive research has been done on ammonia-based Selective Catalytic Reduction (SCR), which has emerged as the technology of choice for abating NO_x (NO + NO₂) from heavy duty diesel vehicles. The NH₃ is generated by an on-board aqueous urea dosing system. The NH₃ reacts with NO_x on a metal-exchanged zeolite catalyst (e.g. Cu/Chabazite) through a set of reactions that ideally requires a 1:1 (NH₃: NO_x) ratio, generating N₂ in high selectivity [17-22]. One of the challenges with SCR is the unavoidable “slip” of NH₃ from the SCR unit as a slight excess of NH₃ is often used to achieve optimal NO_x reduction performance [23]. Moreover, the transient nature of the vehicle operation complicates the achievement of a high NO_x conversion while minimizing the NH₃ slip. Indeed, diesel vehicles are becoming a major source of ammonia emissions [3]. Ammonia is both toxic and corrosive, justifying Industry standards to maintain ammonia concentration below 10 ppm emission during normal engine operation [24,25].

Current Ammonia Slip Catalyst (ASC) technology comprises an additional catalytic reactor positioned downstream of the SCR reactor. The function of the ASC is to reliably convert slipped NH₃ at high conversion to N₂. While not nearly as extensive as SCR, research on the ASC communicated in patents and open literature describes ASC characteristics needed to accomplish this function. The state-of-the-art ASC has a dual-layer architecture consisting of a bottom precious group metal (PGM; usually Pt) and top SCR layer. This design has emerged as the most effective one for selective oxidation of

NH₃. In the dual-layer ASC, the NH₃ oxidizes to NO over a base Pt/Al₂O₃ layer, with the generated NO reacting with part of incoming NH₃ in the top SCR layer, forming N₂. The following reactions occur during Pt-catalyzed ammonia oxidation:



The dual-layer ASC concept and performance features are described in more detail by Scheuer et al. [26], Shrestha et al. [27], Colombo et al. [28, 29] and Nova et al. [30]. Both high NH₃ conversion and N₂ selectivity have been demonstrated over a range of operating conditions [26,27].

While considerable progress has been made on the ASC, challenges remain. In particular, the ASC volume and precious metal loading should be minimized to reduce its footprint and cost. In addition, the ASC, like the SCR, must be durable during extended operation and associated exposure to high temperatures. Like all supported metal catalysts, it may be susceptible to hydrothermal aging. Literature has suggested that hydrothermal aging of the SCR catalyst leads to the degradation of Cu active sites of Cu/SSZ-13 for (NO_x + NH₃) reaction [17,31,32]. This may lead to increase NO selectivity in dual-layer ASC, adversely affecting N₂ selectivity. Degradation may also occur in the upstream diesel oxidation catalyst (DOC).

In order to understand the hydrothermal aging effects on the ASC and DOC, we have conducted a systematic aging study on the base PGM layer only, as the first step towards understanding the overall ASC and DOC aging performance. The first objective of this

study is to investigate long-term hydrothermal aging of Pt/Al₂O₃ and how it affects ammonia conversion and product distribution. A second study of propylene oxidation is also conducted. Steady-state ammonia or propylene oxidation is described in which the catalyst performance is quantified at different aging levels, accompanied by catalyst characterization to interpret the trends. A monolith reactor model including an established ammonia oxidation kinetic scheme is applied to interpret experimental results and quantify aging effects. The approach identifies washcoat morphology changes and effects on transport as the root cause for the activity decline. The propylene oxidation experiments and modeling independently validate the findings. Further, the hydrothermal aging was briefly studied over single layered Cu-SSZ-13 catalyst, and dual-layer ASC consisting base Pt/Al₂O₃ and top Cu-SSZ-13 layer.

2.2 Experimental

The experimental system and procedures generally follow those described by Shrestha et al. [27, 33]. More details are provided here on the aging and certain characterization protocols.

2.2.1 Catalyst synthesis and slurry preparation

The Pt/Al₂O₃ catalyst powder was synthesized by incipient wetness impregnation method using chloroplatinic acid hexahydrate as a Pt precursor. The γ -alumina powder was dispersed over a quartz glass boat and aqueous solution of Pt precursor was added drop-wise and uniformly to impregnate Pt into the alumina. The volume of deionized water for aqueous solution was calculated based on the pore volume of alumina powder. The impregnated powder was dried overnight in an oven at 120 °C, followed by calcination at 550 °C for 5 h with a slow temperature ramp rate of 0.5 °C/min. The Pt/Al₂O₃ slurry was

prepared by adding deionized water and boehmite solution to Pt/Al₂O₃ catalyst powder (mass ratio Pt/Al₂O₃:water:boehmite = 8:15:2). The pH of the slurry was adjusted to 3.5-4.0 using acetic acid and ammonium hydroxide. The prepared slurry was then ball-milled for 20 h to reduce alumina particle size in the range of 1-3 μ m. For Cu-SSZ-13 slurry, the powdered Cu-SSZ-13 (provided by Johnson Matthey Inc.) was mixed with water and boehmite in same ratio of 8:15:2 and the pH value was tuned at around 4, followed by 20 h of ball milling.

2.2.2 Monolith coating

The cordierite monolith (400 cpsi) was cut into 0.5 cm length and 0.8 cm diameter comprising 28 channels. The blank monolith was dipped into prepared Pt/Al₂O₃ slurry for 30 s and excess slurry was blown with air for 10 s. Subsequently, the monolith was dried in an oven at 120 °C for 2 h and the same dipping procedure was repeated to get the required loading. Finally, the coated monolith was dried overnight in an oven at 120 °C, followed by calcinations at 550 °C for 5 h with a temperature ramp rate of 0.5 °C/min. The freshly prepared monolith was then reduced with 2% H₂ and balance Argon for 1 h at 500 °C to eliminate any chlorine, followed by degreening with 5% O₂ and balance Argon at 500 °C for 6 h. The monolith was kept in an oxidizing atmosphere containing 5% O₂ and balance Ar at 650 °C for 30 min before starting reaction testing. The prepared samples had Pt/Al₂O₃ loading of 1.5 g/(in³ of monolith) which has Pt loading of 3.2 g/(ft³ of monolith). Similar procedure was used for single layered Cu-SSZ-13 samples, and the catalyst with 1.5 g/in³ loading was prepared. For dual-layer ASC, first Pt/Al₂O₃ was coated over blank monolith followed by coating of Cu-SSZ-13 over already coated Pt/Al₂O₃ monolith. Dual-layer has loadings of 1 g/in³ Pt/Al₂O₃ (1 g/ft³ Pt) in base and 3 g/in³ Cu-SSZ-13 in top layer.

2.2.3 Bench scale reactor set up

The full schematic diagram of reactor set up is reported by Kabin et al. [34]. The coated monolith was wrapped in Fiberfrax ceramic paper and fitted inside a quartz tube (O.D. 1.27 cm and I.D. 0.81 cm). The tube was then placed into furnace in such a way that the thermocouple end-point was at the middle of the monolith, axially as well as radially. The feed gas flows were metered by MKS mass flow controllers, and the gases used in our work were from Matheson Inc. The concentrations of outlet gases from the reactor were analyzed by FTIR and OMNIC software. The nitrogen reported in this paper is calculated by difference using an overall N balance. The pressure inside the flow lines was maintained at 880 Torr by using globe valve downstream of the FTIR.

2.2.4 Steady state reaction experiments

All flow lines were heated to 150 °C using electrical heating tape before starting reaction experiments to prevent condensation of water vapor and ammonia. All lines were flushed with Ar for 1 h before collecting background spectra. After taking the background spectra, 500 ppm NH₃, 5% O₂ and balance argon were directed through a reactor bypass line to measure inlet concentration of NH₃ for reference. The performance was tested at steady state in the temperature range from 150 to 400 °C. When the gas concentrations do not change for almost 30 min, the steady state data was collected for certain temperature. Generally, for temperatures below 250 °C, it took few hours to reach steady state whereas at temperature > 250 °C, steady state was reached within 30 mins.

The complete oxidation of propylene was conducted in a set of experiments to complement the NH₃ oxidation results. A catalyst sample of similar size and composition used with feed gas consisting of excess O₂ (5%) and balance Ar to maintain total flow of

1000 sccm. In most experiments, the C_3H_6 concentration was held at 250 ppm with a similar temperature sweep spanning 150 to 400 °C conducted. Experiments were conducted to estimate the activation energy of C_3H_6 oxidation by flowing constant concentration of 250 ppm and varying the temperature from 216 °C to 229 °C, the corresponding measured conversion ranged from 5% to 14%. For the reaction order, the concentration was varied from 186 to 280 ppm with the conversion ranging from 16% to 6% at a constant catalyst temperature of 223 °C. After kinetic analysis, the steady state reaction testing was done for complete temperature regime, followed by aging. For testing single layered Cu-SSZ-13 samples at different aged level, the SCR feed consisting of 500 ppm each of NO and NH_3 , 5% O_2 and balance Ar at 66 k h^{-1} GHSV was also used along with NH_3 oxidation.

2.2.5 Aging

The Pt/ Al_2O_3 and Cu-SSZ-13 monolith sample was aged at 550 °C while dual-layer ASC at 650 °C, with a gas flow mixture consisting of 5% O_2 , 5% H_2O , 4% CO_2 and balance Ar to maintain total flow of 1000 sccm. The catalyst reaction testing was done at different aging levels. For post-reaction catalyst characterization, a powdered Pt/ Al_2O_3 and γ -alumina samples were aged in similar manner.

2.2.6 Catalyst characterization

To evaluate the fresh and aged catalyst, SEM, BET surface area, DRIFTS and Chemisorption were used. To measure the change in Pt dispersion, the CO Chemisorption test was performed in Micromeritics Accelerated Surface and Porosity System (ASAP2020). The same equipment was used to measure BET surface area for powder Pt/ Al_2O_3 catalyst. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was done using Thermo-Scientific Nicolet 6700 FT-IR, in order to characterize the surface

elements on alumina particles. The SEM images taken with Leo 1525 Gemini FEG (Manufacturer: Zeiss) showed the physical change on the surface of alumina particles with aging. Also, Hg porosimetry was performed by Core Laboratories Inc. (Houston, TX) which measured the mesopore radius $r_{p,meso}$ and mesoporosity of fresh alumina particles as 5 nm and 0.59, respectively.

2.3 Model Description

2.3.1 Reactor model

A single channel washcoated monolith model adopted from earlier work [35] was used to simulate catalyst performance for both Pt-catalyzed ammonia and propylene oxidation. The 1D + 1D model was previously developed to understand the ammonia oxidation reaction over single layered Pt/Al₂O₃ in monolithic reactor [26, 33]. The model is framed based on assumption of laminar flow through the channel with no axial dispersion and constant physical properties with isothermal conditions. Even though the ammonia oxidation over Pt is exothermic but due to small sample size and limited reactant ammonia concentration, the difference in temperature at inlet and outlet of monolith is very small and can be neglected. Isothermal conditions preclude the need for energy balance.

The developed microkinetic model consist three sets of transport equations (i) fluid phase mass balance, (ii) solid phase mass balance and (iii) surface species balance. The mass balance of species ‘j’ in fluid phase is given by

$$\frac{\partial x_{f,j}}{\partial t} = -\langle u \rangle \frac{\partial x_{f,j}}{\partial z} - \frac{K_{me,j}(Z)}{R_{\Omega 1}} (x_{f,j} - x_{s,j}). \quad (2.5)$$

It comprises convective mass transfer in axial direction and external mass transfer from fluid phase to washcoat.

The mass balance of species ‘j’ inside the washcoat is equated following solid phase equation

$$\varepsilon_{wc} \frac{\partial x_{wc,j}}{\partial t} = D_{e,j} \frac{\partial^2 x_{wc,j}}{\partial y^2} + \frac{1}{C_{Tm}} (\sum_{r=1}^{n_r} \vartheta_{jr} R_r(T, \theta, x_{wc,j})). \quad (2.6)$$

The mass transfer in radial direction due to diffusion and consumption/generation by chemical reaction. The rate of change of surface species concentration can be calculated using

$$\frac{\partial \theta_k}{\partial t} = \frac{1}{C_{pt}} (\sum_{r=1}^{n_r} \vartheta_{kr} R_r(T, \theta, x_{wc,j})). \quad (2.7)$$

Here, $x_{f,j}$ and $x_{wc,j}$ are cup-mixing mole fraction of species ‘j’ in fluid and solid phase respectively. $x_{s,j}$ is mole fraction of species ‘j’ at fluid-washcoat interface. $k_{me,j}(Z)$ is external mass transfer coefficient. ε_{wc} , $D_{e,j}$, $R_{\Omega 1}$ and $R_{\Omega 2}$ are washcoat porosity, effective diffusivity through washcoat, hydraulic radius (ratio of cross-sectional area to parameter) and effective washcoat thickness. $\langle u \rangle$ is average velocity through monolith channel. R_r and ϑ_{jr} are reaction rate and stoichiometric coefficient of species ‘j’. C_{pt} is the total active site density ($\text{mol/m}^3_{\text{washcoat}}$) of platinum in the washcoat and C_{Tm} is total molar concentration. θ_k is fraction of surface species ‘k’.

The boundary conditions for the monolith reactor model are:

$$x_{f,j}(t) = x_{f,j}^{in}(t) \quad \text{at } z = 0 \quad , \quad (2.8)$$

$$k_{me,j}(z)(x_{f,j} - x_{s,j}) = -D_{e,j} \frac{\partial x_{wc,j}}{\partial y} \Big|_{x_{wc,j}=x_{s,j}} \quad \text{at } y = 0 \quad , \quad (2.9)$$

$$\frac{\partial x_{wc,j}}{\partial y} = 0 \quad \text{at } y = R_{\Omega 2} \quad , \quad (2.10)$$

and
$$k_{me,j} = \frac{Sh_e D_{f,j}}{4R_{\Omega 1}}. \quad (2.11)$$

Here $D_{f,j}$ is the diffusivity of the species ' j ' in the fluid phase, calculated as a function of temperature using the Lennard-jones formulation, $D_{f,j} = aT^b$. The diffusivities values of all the species are listed in Table 2.2. The ratio of the fluid and effective diffusivity for each species is given by

$$\frac{D_{f,j}}{D_{e,j}} = \tau/\varepsilon_{wc}. \quad (2.12)$$

Table 2.1 Parameter values

Parameter	Value
a	1.1e -3m
$R_{\Omega 1}$	0.268e-3m
$R_{\Omega 2}$	15e-6m
$\langle u \rangle$	$0.49\left(\frac{T}{273.15}\right)\left(\frac{a}{a-2R_{\Omega 2}}\right)$ (m/s)
ε_{wc}	0.4
τ	10.5
L	0.5e-2m
C_{Tm}	$(12187.3/T)$ mol/m ³
C_{pt}	3.2 mol exposed Pt/(m ³ of washcoat)
Sh_e	3.608

Table 2.2. Diffusivities values in fluid phase (m²/s)

$D_{f,NH3}$	$1.2*10^{-9} T^{1.75}$
$D_{f,NO}$	$1.2*10^{-9} T^{1.75}$
$D_{f,N2O}$	$0.8*10^{-9} T^{1.75}$
$D_{f,N2}$	$1.3*10^{-9} T^{1.75}$
$D_{f,NO2}$	$0.8*10^{-9} T^{1.75}$
$D_{f,O2}$	$1.1*10^{-9} T^{1.75}$

Where τ is tortuosity of washcoat and ε_{wc} is washcoat porosity. The effective diffusivity estimation using eq. (2.12) is ascribed to simple transport model based on average porosity and tortuosity of washcoat, whereas a more advanced model involving pore-size distribution is defined in next section of this paper. The diffusion regime (bulk, Knudsen

or both) decides the order of temperature dependence of effective diffusivity, 1.75 for bulk and 0.5 for Knudsen. Here in eq. (2.12), $D_{f,j}$ is calculated using bulk diffusivity formula assuming species ' j ' diluted in argon, therefore $D_{e,j}$ temperature dependence is of the order of 1.75. The flow through channel develops fully within 5% length of the monolith, therefore, the value of Sh_e , external Sherwood number for a square channel, is taken as position independent.

The finite difference method has been applied to solve discretized equations. The equations were discretized into m axial and n radial mesh points. We used 27 axial and 10 radial mesh points, above which the simulation results are mesh invariant. The MATLAB solver Odes15 is used to simulate data using given initial conditions and based on our understanding the time 2000 s was enough to get steady state results.

2.3.2 Kinetic model and parameter estimation

The kinetic model incorporated with the reactor model follows from already applied successfully by Scheuer et al. [26] and Shrestha et al. [33] to interpret ammonia oxidation over fresh Pt/Al₂O₃ catalyst. In the current study, the model is extended to that of an aged catalyst. Two different type of active sites are defined in the reaction mechanism, the active sites on the top of Pt surface 'site b ' is responsible for adsorption/desorption of ammonia, whereas, hollow active 'site a ' is responsible for the rest of reaction steps. The reaction rate is defined by

$$R_r = C_{pt} k_r \prod \theta_k^{\vartheta_{kr}} \prod (C_{Tm} x_{wc,j})^{\vartheta_{jr}} \quad (2.13)$$

and
$$k_r = A_r \exp\left(-\frac{E_r}{RT}\right). \quad (2.14)$$

For kinetic parameter estimation, the pre-exponential factor ' A_r ' and activation energy ' E_r ' were varied to fit simulation results with our experimental data. The kinetic

parameter values reported in Shrestha et al. [33] were taken as the initial guess and then adjusted to fit the experimental data from the current study. The reaction schemes along with kinetic parameters are listed in Table 2.3.

Table 2.3. Ammonia oxidation kinetic model and parameter values.

No.	Reaction Step	Parameter	Parameter Values	Rate Expression (R_r)
P1	$\text{NH}_3 + b \rightarrow \text{NH}_3 - b$	A_1 E_1	1.25e1 0	$k_1 C_{pt} X_{\text{NH}_3} \theta_b C_{Tm} T$
P2	$\text{NH}_3 - b \rightarrow \text{NH}_3 + b$	A_2 E_2	2e4 106.16	$k_2 C_{pt} \theta_{\text{NH}_3}$
P3	$\text{O}_2 + 2a \rightarrow 2\text{O} - a$	A_3 E_3	2.6e1 0	$k_3 C_{pt}^2 X_{\text{O}_2} \theta_a^2 C_{Tm} T$
P4	$2\text{O} - a \rightarrow \text{O}_2 + 2a$	A_4 E_4	1.2e11 125.02	$k_4 C_{pt}^2 \theta_{\text{O}}^2$
P5	$\text{NH}_3 - b + 1.5\text{O} - a$ $\rightarrow \text{N} - a$ $+ 1.5\text{H}_2\text{O}$ $+ 0.5a + b$	A_5 E_5	2.7e15 140.70	$k_5 C_{pt}^2 \theta_{\text{NH}_3} \theta_{\text{O}}$
P6	$\text{NO} - a \rightarrow \text{NO} + a$	A_6 E_6	1.9e17 117.44	$k_6 C_{pt} \theta_{\text{NO}}$
P7	$\text{NO} + a \rightarrow \text{NO} - a$	A_7 E_7	0.9e2 0	$k_7 C_{pt} X_{\text{NO}} \theta_a C_{Tm} T$
P8	$2\text{N} - a \rightarrow \text{N}_2 + 2a$	A_8 E_8	1.9e18 174	$k_8 C_{pt}^2 \theta_{\text{N}}^2$
P9	$\text{N} - a + \text{O} - a$ $\rightarrow \text{NO} - a$ $+ a$	A_9 E_9	2.2e12 120.32	$k_9 C_{pt}^2 \theta_{\text{N}} \theta_{\text{O}}$
P10	$\text{NO} - a + \text{N} - a$ $\rightarrow \text{N}_2\text{O}$ $+ 2a$	A_{10} E_{10}	7.3e18 130.5	$k_{10} C_{pt}^2 \theta_{\text{NO}} \theta_{\text{N}}$
P11	$\text{NO} - a + \text{O} - a$ $\rightarrow \text{NO}_2 - a$ $+ a$	A_{11} E_{11}	6.4e13 103.4	$k_{11} C_{pt}^2 \theta_{\text{NO}} \theta_{\text{O}}$
P12	$\text{NO}_2 - a + a \rightarrow \text{NO} - a$ $+ \text{O} - a$	A_{12} E_{12}	9.0e8 77.12	$k_{12} C_{pt}^2 \theta_{\text{NO}_2} \theta_a$
P13	$\text{NO}_2 - a \rightarrow \text{NO}_2 + a$	A_{13} E_{13}	0.4e14 120	$k_{13} C_{pt} \theta_{\text{NO}_2}$
P14	$\text{NO}_2 + a \rightarrow \text{NO}_2 - a$	A_{14} E_{14}	1.5e4 0	$k_{14} C_{pt} X_{\text{NO}_2} \theta_a C_{Tm} T$

E_r is reported in kJ mol^{-1}

While varying activation energies and pre-exponential factor, it is noted that some reactions are almost insensitive whereas some show significant change in result even with small variation in reaction parameter. NH_3 adsorption over Pt is assumed temperature independent. The reaction (P5) is the most important; even a small variation in its activation energy showed noticeable change in light-off of NH_3 . NO desorption is described by (P6), this reaction step dominates at high temperature.

2.3.3 Meso-macro transport model (Wakao Smith model)

As shown later, the reaction experiments and post-reaction characterization indicate that washcoat transport effects are primarily responsible for the observed catalyst deactivation which elevates the need of using a more sophisticated and physically meaningful transport model. Mass transport through the particle-based alumina washcoat is modeled using meso-macro transport formulation developed by Wakao et al. [36]. Other more sophisticated pore-scale models have been developed for predicting the transport properties of washcoat [37, 38]. However, their implementation is computationally cumbersome, so for the purpose of the current study the meso-macro model should suffice.

The meso-macro formulation defines two types of void regions in the washcoat. One is the macro voids, which comprise the pores between the alumina crystals while the other is meso voids, which comprise the pores inside the alumina particle. The transport rate through both regions are different and based on the diffusivity value in the respective region. This diffusion model formulates effective diffusivity as a function of four variables, porosities and diffusivities in the respective region, as follows:

$$D_e = \varepsilon_a^2 D_{\text{mac}} + \frac{\varepsilon_i^2(1+3\varepsilon_a)}{(1-\varepsilon_a)} D_{\text{meso}} \quad , \quad (2.15)$$

$$(\varepsilon_a + \varepsilon_i + \varepsilon_s = 1) \quad , \quad (2.16)$$

$$\frac{1}{D_{\text{mac}}} = \frac{1}{D_f} + \frac{1}{D_{K,\text{mac}}} \quad \frac{1}{D_{\text{meso}}} = \frac{1}{D_f} + \frac{1}{D_{K,\text{meso}}} \quad , \quad (2.17)$$

$$\text{and} \quad D_{K,\text{mac}} = \left(\frac{2r_{p,\text{mac}}}{3}\right) \sqrt{\frac{8RT}{M_w\pi}} \quad D_{K,\text{meso}} = \left(\frac{2r_{p,\text{meso}}}{3}\right) \sqrt{\frac{8RT}{M_w\pi}} \quad . \quad (2.18)$$

Here D_{mac} and D_{meso} are diffusivities through macro and meso void region, respectively. Depending upon pore size and pressure, diffusion through macro and meso region can be bulk, Knudsen or a combination of both. The D_{mac} and D_{meso} can be estimated for each region. Similarly, ε_a and ε_i are the washcoat macro and mesoporosity, respectively, while ε_s is the solid volume fraction of washcoat. Finally, $r_{p,\text{mac}}$ and $r_{p,\text{meso}}$ are the macro and mesopore size, respectively. Using this formulation, an approach described below is used to predict a decline in the overall washcoat porosity with age and to quantify the effect of this decline on catalyst performance.

2.4 Results and Discussion

2.4.1 Steady state ammonia oxidation over unaged Pt/Al₂O₃

A freshly-prepared monolith sample (Pt/Al₂O₃, single layer) was tested in a quartz tube reactor by running NH₃ oxidation reaction using 500 ppm NH₃, 5% O₂ and balance Ar. A high space velocity of 265k h⁻¹ was used by design to make catalyst more sensitive towards aging effects. Pt supported on Al₂O₃ is highly active for NH₃ conversion but poorly selective for N₂ yield. Light-off (defined as the temperature giving 50% conversion) for the 500 ppm NH₃ feed occurred at ~210 °C while 90% conversion was achieved at ~250 °C (Fig. 2.1). Complete NH₃ conversion was not achieved even at higher temperature due to mass transfer limitations. The upper bound limiting conversion was estimated as 98%, using flat velocity profile and finite axial Peclet number expression from Balakotaiah et al. [39]. The transverse Peclet number ($Pe_t = R_{\Omega 1}^2 \frac{\langle u \rangle}{D_f L}$) and axial Peclet number ($Pe_a = \frac{\langle u \rangle L}{D_f}$)

were calculated as 0.18 and 62 for given set of values in Table 2.1 at 350 °C. N_2 was the only reaction product detected up to 210 °C. With increasing temperature; its yield achieved a maximum at 225 °C and tended to approach zero by 400 °C. Rebrov et al. [40] and Gland et al. [41] have given detailed explanation for N_2 formation mechanism and reaction pathways involved. At low temperature, the Pt surface is largely covered by N-adspecies, whereas adsorbed oxygen coverage dominates at high temperature. The reaction product N_2O yield displayed a similar trend in N_2 with a maximum yield for N_2O of ~30% achieved at ~270 °C (Fig. 2.1). NO is an intermediate for N_2O formation and for temperatures exceeding ~300 °C the NO desorption rate increases relative to its reaction with O adatoms, leading to a decreasing (increasing) N_2O (NO) yield. At higher temperatures, NO is the major product of ammonia oxidation over Pt. The NO_2 measured was less than 1% in the whole temperature regime.

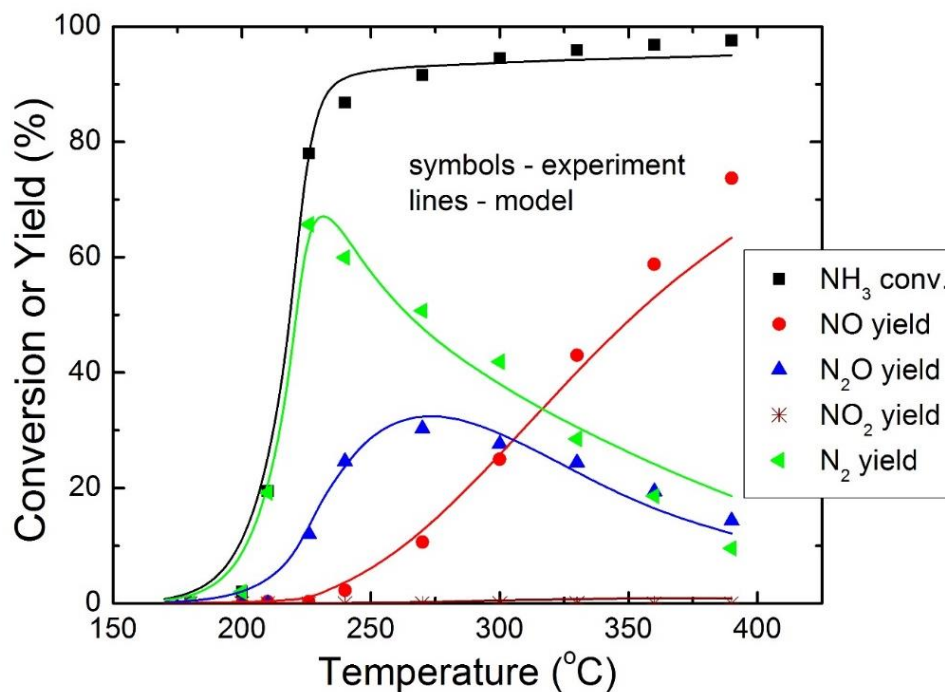


Figure 2.1 Steady state NH_3 oxidation over Pt/Al_2O_3 as a function of temperature, NH_3 = 500 ppm, O_2 = 5%, Balance gas: Ar.

2.4.2 Aging effects on ammonia oxidation

The Pt/Al₂O₃ monolith was aged hydrothermally within the reactor at a temperature of 550 °C in the presence of 5% O₂, 5% H₂O, 4% CO₂ and balance Argon, maintaining total flow of 1000 sccm. At discrete aging times of 0 (post de-greening), 122 h and 253 h, the catalyst performance was evaluated over the 150 to 400 °C temperature range. Fig. 2.2 reports the NH₃ conversion (2.2(a)) and yields of N₂O (2.2(b)), NO (2.2(c)), and N₂ (2.2(d)). The activity testing revealed little change in the NH₃ conversion in the lower temperature regime (up to 210 °C) with almost no change in light-off temperature. In contrast, a noted decrease in ammonia conversion occurred in the higher temperature regime (Fig. 2.2(a)). The conversion data show a monotonic decline in catalyst activity in this regime.

In general, exposure of a supported metal catalyst to high temperature is detrimental to catalytic activity due to a loss of exposed metal surface area by sintering. This would translate into an increase in the light-off temperature. However, clearly this trend is not evident in the data and suggests that the aging conditions are not sufficiently severe as to sinter the Pt [42-44]. The combination of the negligible lower temperature conversion change and high temperature conversion decrease suggests a cause rooted in a change in the washcoat morphology that impacts the mass transport but not the intrinsic activity. We expand on this conjecture later.

The reaction testing data also reveal a decrease in the NO and N₂O yields with age, along with the decrease in NH₃ conversion (Figs. 2.2(b) - (d)). However, the data indicate a negligible change in the product selectivities. A negligible change in the selectivity again reflects that the intrinsic rates of reaction are minimally affected by age. Finally, the N₂

yield also decreased nearly with age, although a subtle increasing trend above 360 °C. This trend may be attributed to reaction between NH_3 and NO at temperature above 360 °C, as more NH_3 is available [45].

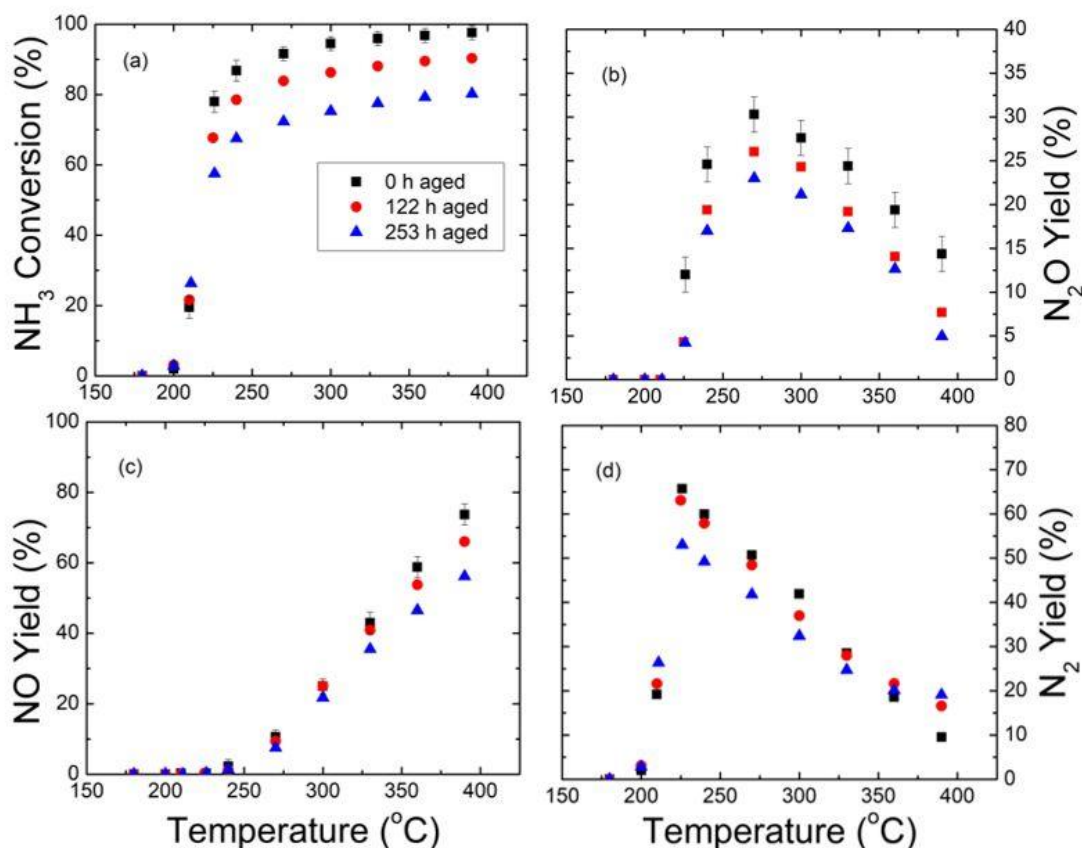


Figure 2.2 Experiment results of steady state (a) NH_3 conversion, (b) N_2O yield, (c) NO yield and (d) N_2 yield as a function of temperature at different aging time, NH_3 = 500 ppm, O_2 = 5%, Balance gas: Ar.

2.4.3 Chemisorption

Chemisorption measurements were conducted to directly check if Pt sintering occurred. In order to make these measurements, $\text{Pt}/\text{Al}_2\text{O}_3$ powder catalyst having a similar loading as the monolith washcoat was subjected to the same aging protocol. The degreened, unaged catalyst had a Pt dispersion of 13.6% and an estimated Pt particle size of

8.3 nm. After 120 h of aging, the Pt dispersion measured was 12.8 % and particle size 8.8 nm. The 240 h aged catalyst had a 12.7 % dispersion and 8.8 nm particle size. These results reveal that Pt particle sintering was not occurring beyond a negligible level under these aging conditions. The Chemisorption result is consistent with the lack of any shift in the light-off temperature, and further substantiates our suspicion that the metallic Pt remains unaffected with aging. The results are consistent with those of Fiedorow et al. [46], who have reported the Pt dispersion with Al₂O₃ support is nearly insensitive to aging time in the presence of O₂ for temperatures ≤ 550 °C.

2.4.4 BET analysis

The BET surface area was measured at different aging durations to assess any change in the washcoat morphology. The BET surface area test was carried out on both the monolith and powder samples. The BET surface area of the monolith sample decreased from 34.6 to 26.3 m²/(g of monolith sample) over 210 h of aging. The powder catalyst showed a similar drop in surface area as the monolith. The de-greened, unaged catalyst powder had a BET surface area of 157 m²/(g of catalyst) and pore volume of 0.49 cc/g. After aging the catalyst for 144 h, the surface area dropped to 132 m²/(g of catalyst), and further decreased to 126 m²/(g of catalyst) after 176 h of aging. The pore volume dropped to 0.45 cc/g with 176 h of aging. The rates of decrease in BET surface area with age for the monolith and powder samples were nearly identical, and essentially showed a linear trend with aging time. These results are consistent with an apparent morphology change during the aging protocol. To uncover the reason behind surface area drop, we performed additional experiments and characterization followed by modeling to quantify the aging effects. These are presented next.

2.4.5 Aging without water

The decrease in BET area indicates a change in the alumina morphology with exposure to the hydrothermal, 550 °C conditions. We conducted additional aging experiments to uncover further evidence for the suspected alumina morphology change. In one of the experiments we aged the catalyst sample without water to determine if water plays a role. In this experiment, the monolith sample was aged at the same temperature of 550 °C, in a flowing stream of 5% O₂, 4% CO₂ and balance Argon for 96 h. This aging process was followed by the same reaction testing. The same sample was then further aged for another 72 h at same temperature 550 °C in presence of 5% O₂, 4% CO₂, 5% H₂O and balance Argon. The results show (Fig. 2.3) that aging without water resulted in a negligible change in catalyst activity even after 96 h, whereas 72 h of aging with water showed similar decline in activity as in previous aging experiment.

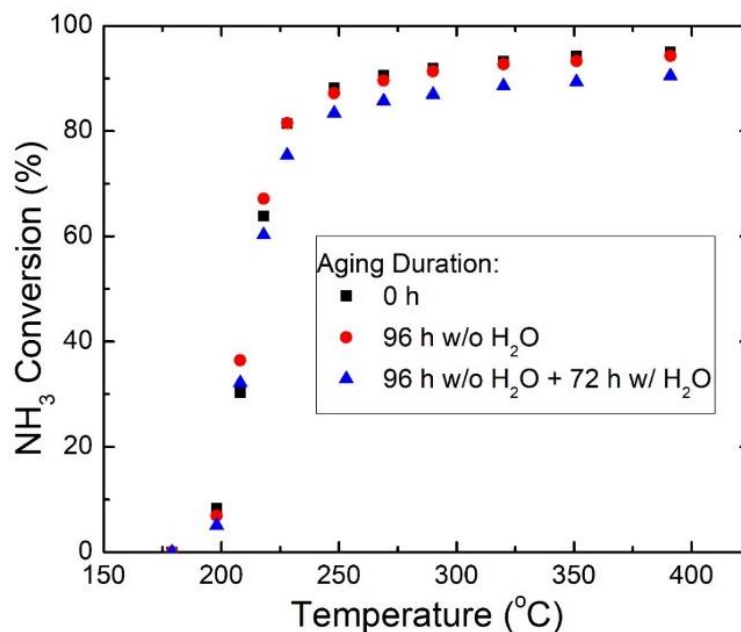


Figure 2.3 Experiment results of steady state NH₃ conversions as a function of temperature at different aging time/conditions, NH₃ = 500 ppm, O₂ = 5%, Balance gas: Ar. 96 h aging without H₂O and further 72 h of aging with H₂O.

This experimental finding suggests that water plays an important role during the of catalyst exposure to 550 °C. Brey et al. [47] reported that alumina aging at temperature ≥ 500 °C in presence of water vapor start the growth of alumina crystallites composing of solid. Lefevre et al. [48] performed aging of alumina in water at room temperature for longer period and claimed the formation of oxi-hydroxide (AlOOH) and tri-hydroxide (Al(OH)₃) over alumina surface. Our findings together with these earlier studies prompted a deeper investigation which we discuss next.

2.4.6 DRIFTS analysis

The literature suggests that alumina can react with water to form aluminum hydroxide. To confirm the formation of hydroxyl group over alumina surface, DRIFTS analysis was conducted on powdered γ -Al₂O₃ aged in similar manner. The absorbance spectra of unaged and aged γ -Al₂O₃ were collected at 400 °C and in flowing helium, using the absorbance spectra of α -Al₂O₃ as background (Fig. 2.4). The absorbance bands match those of Al(OH)₃, gibbsite as well as bayerite, and also show the presence of a small amount of boehmite [49, 50].

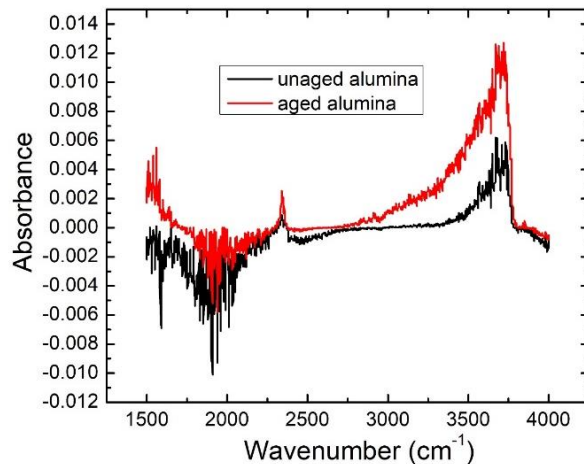


Figure 2.4 Absorbance of aged alumina, using unaged alumina as background spectra.

2.4.7 SEM analysis

Alumina powder was sieved and bigger crystals with size range of 50 μm separated to clearly observe the change on the particle surface with aging. The surfaces of unaged alumina particles seem to be smoother whereas the aged particles have rugged surfaces (Fig. 2.5). It can be visually observed from SEM images that aged particles have solid depositions formed over the surface which is expected to be aluminum hydroxyl groups. This aluminum hydroxyl is less dense than alumina and expands to occupy more volume which results in decline in porosity of alumina.

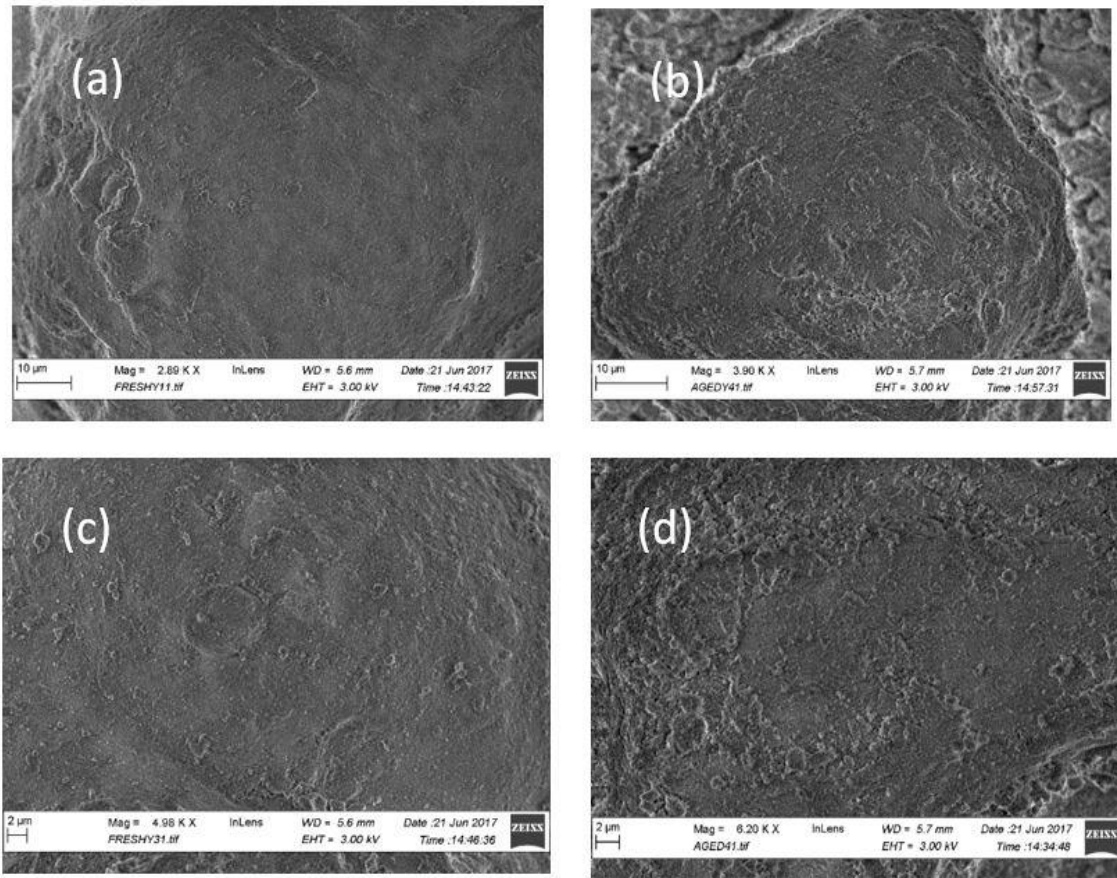


Figure 2.5 SEM images of unaged alumina surface (a and c) and aged alumina surface (b and d), top: 10 μm scale and bottom: 2 μm scale

2.4.8 Quantification of aging effects using simple transport model

After completing reaction experiments and post-reaction catalyst characterizations, the reactor model was used to simulate the experiments. For the unaged catalyst, the model gave a reasonable fit of the experimental data (Fig. 2.1). At low temperature, the model somewhat over-predicts ammonia conversion while at high temperature the model under-predicts (over-predicts) the NO (N₂) yields. Despite these deviations, the model captures the overall trends of the oxidation reaction system, and to proceed to apply the model as a tool for interpreting the aging results.

The approach is to follow the premise dictated by the experiments that the catalytic activity and Pt dispersion was negligibly affected by the hydrothermal aging, while the washcoat morphology was impacted. Specifically, with catalyst age the ammonia conversion in the mass transport regime shows a decrease in conversion, BET shows a loss in surface area, while DRIFTS show a change in the support composition.

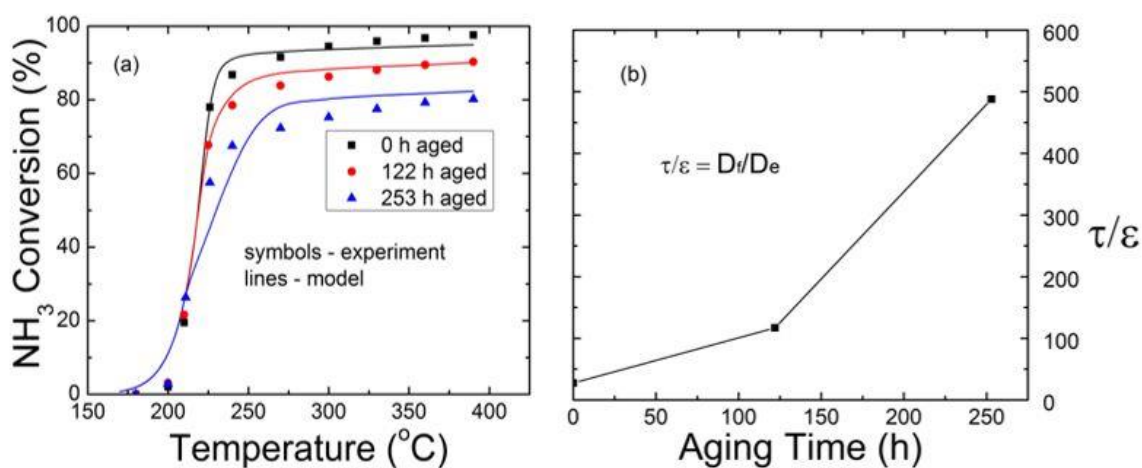


Figure 2.6 (a) Steady state NH₃ conversions as a function of temperature at different aging time, NH₃ = 500 ppm, O₂ = 5%, Balance gas: Ar, (b) shows the variation of tortuosity/porosity with aging time

As the first step, the kinetic parameters were tuned for the fresh, de-greened catalyst, shown in Fig. 2.1. The kinetic parameters were kept constant with subsequent simulation of the aged catalyst. The simple transport model was then applied; i.e., $D_e = \frac{\varepsilon}{\tau} D_f$, with the τ/ε ratio used a fitting parameter for the data and for detailed study, a meso-macro transport model given by Wakao et al. [36] was adopted to calculate D_e .

Fig. 2.6(b) shows the τ/ε is plotted as a function of aging time using 27.5 for the fresh catalyst (following Shrestha et al. [33]). The model predicts that a significant increase in τ/ε with age is needed to predict the declining high temperature ammonia conversion. For example, $\tau/\varepsilon \sim 100$ at for the 122 h aged catalyst and ~ 500 for the 253 h aged catalyst. Notwithstanding these rather high estimates for τ/ε , the model predicts reasonably well the conversion in the high temperature transport limited regime. Moreover, as expected, there is a negligible variation in the conversion in the low temperature kinetic regime. The physical interpretation is that the diffusive transport through the washcoat is restricted in the aged catalyst.

2.4.9 Quantification of aging effects using meso-macro model

To expand on this finding, the meso-macropore transport model was applied to establish a clearer physical picture of the aging effect on the morphology. As described earlier, the meso-macro model includes five input parameters; namely, ε_a , ε_i , ε_s , $D_{K,mac}$ ($r_{p,mac}$), and $D_{K,meso}$ ($r_{p,meso}$). This number can be reduced by experimental measurements and judicious simplifying assumptions. The mesopore radius $r_{p,meso}$ of the unaged catalyst is 5 nm as measured with Hg porosimetry. For this pore size transport through the mesopores is assumed to be dominated by Knudsen diffusion; i.e., $D_{meso} = D_{K,meso}$. In addition, SEM measurements reveal the crystallite size of alumina is in the range of 1-3

μm after ball milling for 20 h. We therefore assume that the average macropore radius $r_{p,\text{mac}}$ is ~ 500 nm, corresponding to a gap size of $1 \mu\text{m}$. The macropore size assumption is based on the SEM measurements of washcoat cross-section and the washcoat does contain few cracks and cavities, which add up to macro space and enhance diffusivity [51]. For this macropore size, Knudsen diffusion may be neglected; i.e., $D_{\text{mac}} = D_f$. This leaves three remaining unknowns; namely, ε_a , ε_i and ε_s . One of these (ε_a) was iteratively guessed while the other two (ε_i and ε_s) were calculated with Eq. 2.16 using a mesoporosity value of 0.59 for the alumina particles, as measured by Hg porosimetry. A ε_a value of 0.3 for the unaged catalyst gave a good fit of the experimental results; this ε_a estimate is consistent with the pore size estimates, as the macropore size (diameter) is approximately half the size of particle (Fig. 2.7). We conjecture that the chemical impact of the hydrothermal aging produces a surface layer forms on the $\gamma\text{-Al}_2\text{O}_3$ crystallites, likely in the form of $\text{Al}(\text{OH})_3$ based on DRIFTS and SEM analyses. The formation of this layer reduces the pore size, resulting in a decrease in the macroporosity and mesoporosity. To quantify this effect, it is assumed that layer forms uniformly on all the alumina surfaces in both the macro and meso space regions. We define the thickness of this layer to be y_1 (nm) and y_2 (nm) in these regions (Fig. 2.7). The new layer formed is assumed to have comparable mesoporosity as alumina particles.

The decline in the mesoporosity of alumina particles with catalyst aging is assumed proportional to pore volume decrease, which was evaluated using BET. It is further assumed that area void fractions are same as volume void fractions as mentioned in Wakao et al. [36]. Thus, the reduced mesopore size and value of y_2 can be estimated using the mesoporosity of alumina particle. Iterative model fitting with experimental results was

performed to find y_1 while calculating corresponding $\varepsilon_{a,aged}$ and $\varepsilon_{i,aged}$ from equations (2.18 & 2.19). The macro (ε_a) and meso (ε_i) porosity of the washcoat after aging can be estimated using following formulae:

$$\varepsilon_{a,aged} = \varepsilon_{a,unaged} * \left(1 - \frac{y_1}{r_{p,mac}}\right) \quad (2.18)$$

and
$$\varepsilon_{i,aged} = (1 - \varepsilon_{a,aged}) * \varepsilon_{i,unaged} * \left(1 - \frac{y_2}{r_{p,meso}}\right). \quad (2.19)$$

Here y_1 , y_2 , $r_{p,mac}$ and $r_{p,meso}$ are in nm while the unaged particle porosity is given by $\varepsilon_{i,unaged} = 0.59$.

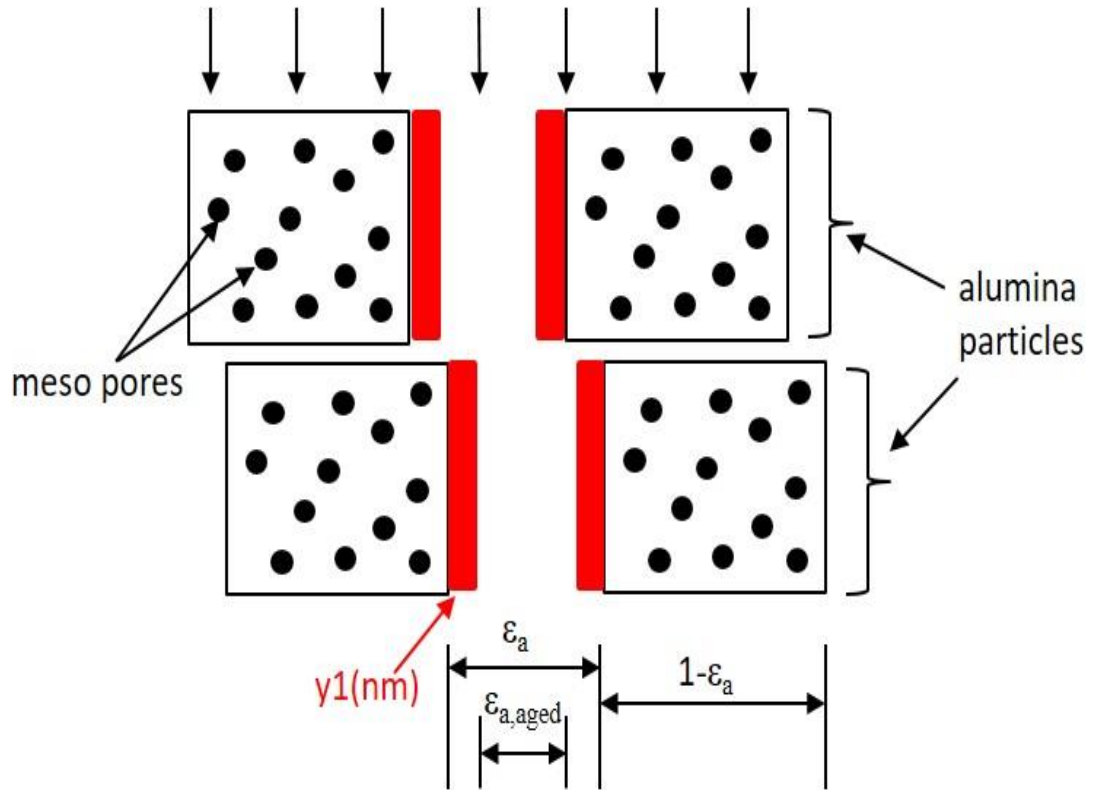


Figure 2.7 Diffusion mechanism in bi-disperse porous material incorporating aging

The transition from bulk-only diffusion to bulk and Knudsen occurs at a pore size (diameter) somewhat below 1000 nm at 880 Torr [52]. To this end, bulk diffusion in the

macro region is replaced with a combination of bulk and Knudsen diffusion after aging. A reasonable estimate between experimental and simulation results (Fig. 2.8a) gives the y_1 as a function of aging time. Fig. 2.8b shows the variation in macro/mesoporosity and solid volume fraction with aging while the corresponding values for $r_{p,mac}$ and $r_{p,meso}$ are shown in Fig. 2.10. The results suggest that the solid volume fraction ε_s is an increasing function of hydrothermal aging while decline in macroporosity from 0.30 to 0.15 is slightly higher. SEM imaging of washcoat cross-section was carried out in an attempt to visualize the decline in macroporosity (Fig. 2.9).

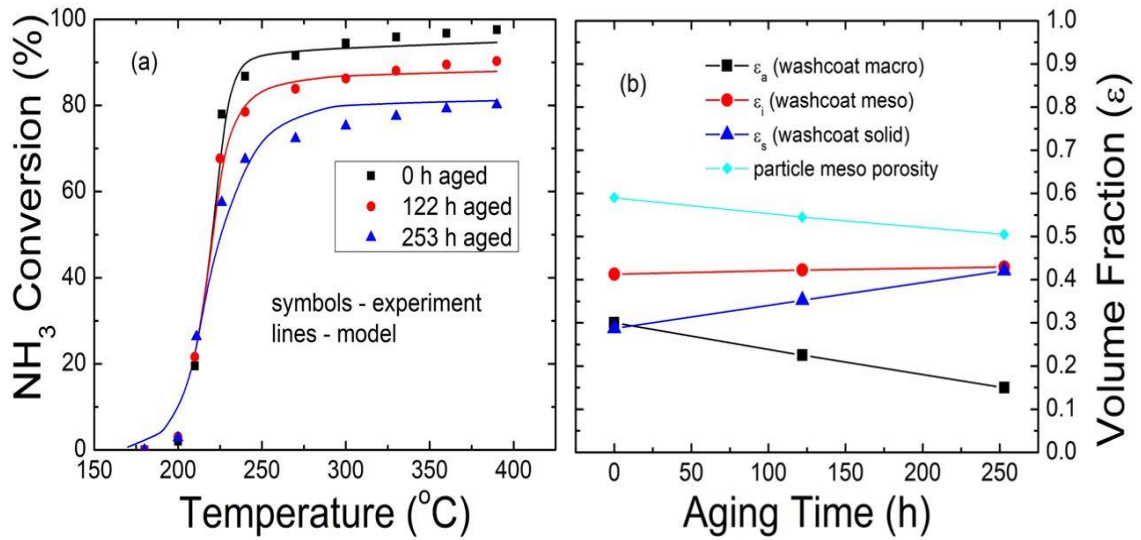


Figure 2.8 (a) Steady state NH_3 conversions as a function of temperature at different aging time, $NH_3 = 500$ ppm, $O_2 = 5\%$, Balance gas: Ar, (b) variation in macro void/meso void /solid volume fraction of washcoat with aging time

Also, mesoporous region of washcoat increases since the new layer is assumed non-porous. Thus, the model predicts a negligible change in the mesoporosity of washcoat despite the fact that mesopores are constricting. The model quantitatively explains growth of alumina particles through reaction with H_2O during with aging. This is consistent with

the surface growth that is inferred from SEM and DRIFTS analyses. The overlayer formed on the alumina crystals is responsible for the decrease in macroporosity. While not captured in the model, the layer formation might block a fraction of the mesopores.

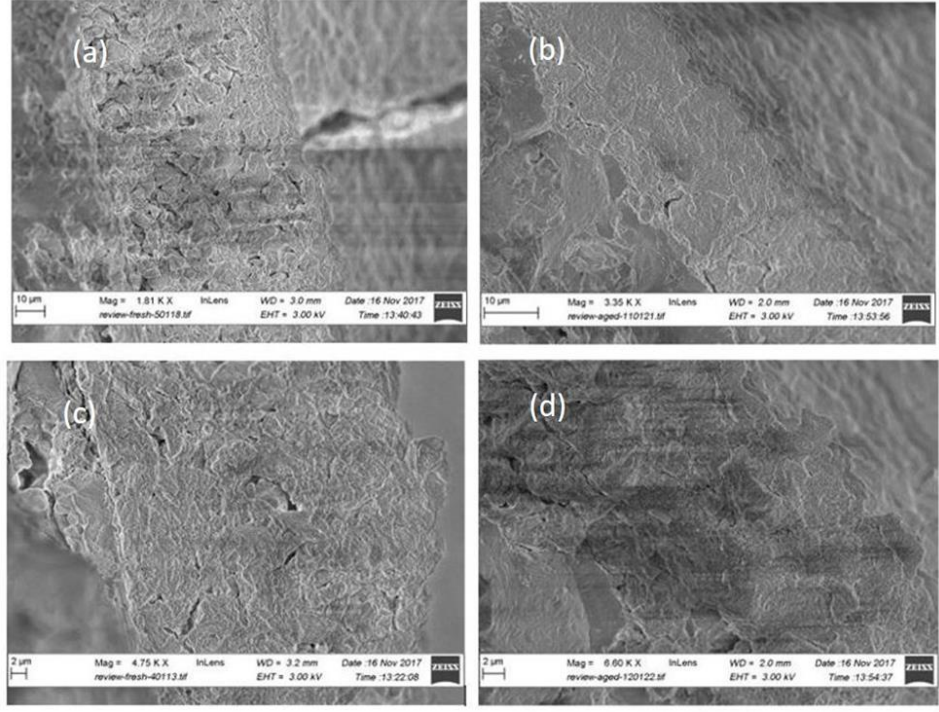


Figure 2.9 Washcoat cross-section SEM images of unaged (a and c) and aged (b and d), top: 10 µm scale and bottom: 2 µm scale

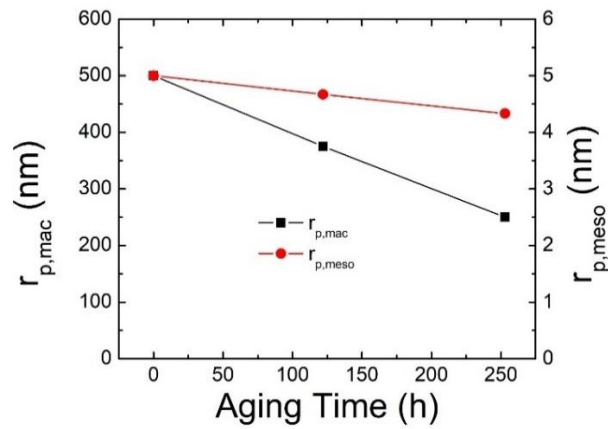


Figure 2.10 Variation in $r_{p,mac}$ and $r_{p,meso}$ with aging using meso macro model

2.4.10 Propylene oxidation – kinetics and aging analysis

In order to examine the generality of the findings, propylene oxidation was carried out on the same catalyst aged by the same protocol. A global kinetic model for propylene oxidation was prepared considering single overall reaction. The independently measured kinetics of C_3H_6 oxidation over Pt/Al_2O_3 were incorporated into the same monolith reactor model described in section (2.3). The overall activation energy was estimated from the steady state conversion measured at varied temperatures using a fixed feed concentration of 250 ppm. The temperatures were low enough that the C_3H_6 conversions were less than 15%. A plot $\ln(\text{rate})$ vs $1000/T$ gives a line with a slope of -16.73 (Fig. 2.11b), corresponding to a E_a of 139.1 kJ. The activation energy of 139.1 kJ is on par with literature reports [53,54]. To determine the reaction order, the conversion was measured at varied reactant concentration at a constant catalyst temperature (in the kinetic regime) of 223 °C. It was noted that conversion decreases with the increase in inlet concentration, which means that it lies in negative order regime. A plot of $\ln(\text{rate})$ vs. $\ln(C_{\text{avg}})$ gives a reaction order of -1.12 (Fig.2.11). The following rate expression was used

$$R = \frac{kY_{C_3H_6}}{(1+KY_{C_3H_6})^2} \quad , \quad (2.20)$$

$$k = A_1 \exp\left(-\frac{E_a}{RT}\right) \quad , \quad (2.21)$$

and

$$K = A_2 \exp\left(-\frac{\Delta H}{RT}\right). \quad (2.22)$$

Here, $Y_{C_3H_6}$ is cup-mixing mole fraction of C_3H_6 . E_a is activation energy of 139.1 kJ/mol, as found in kinetic experiments. The parameter value of A_2 and $-\frac{\Delta H}{R}$ was estimated as 2500 (moles/m³ of wc/s) and 117 K, respectively, these values are consistent with reported values of Raj et al. [55]. A_1 was estimated as 1.4×10^{19} (moles/m³ of wc/s).

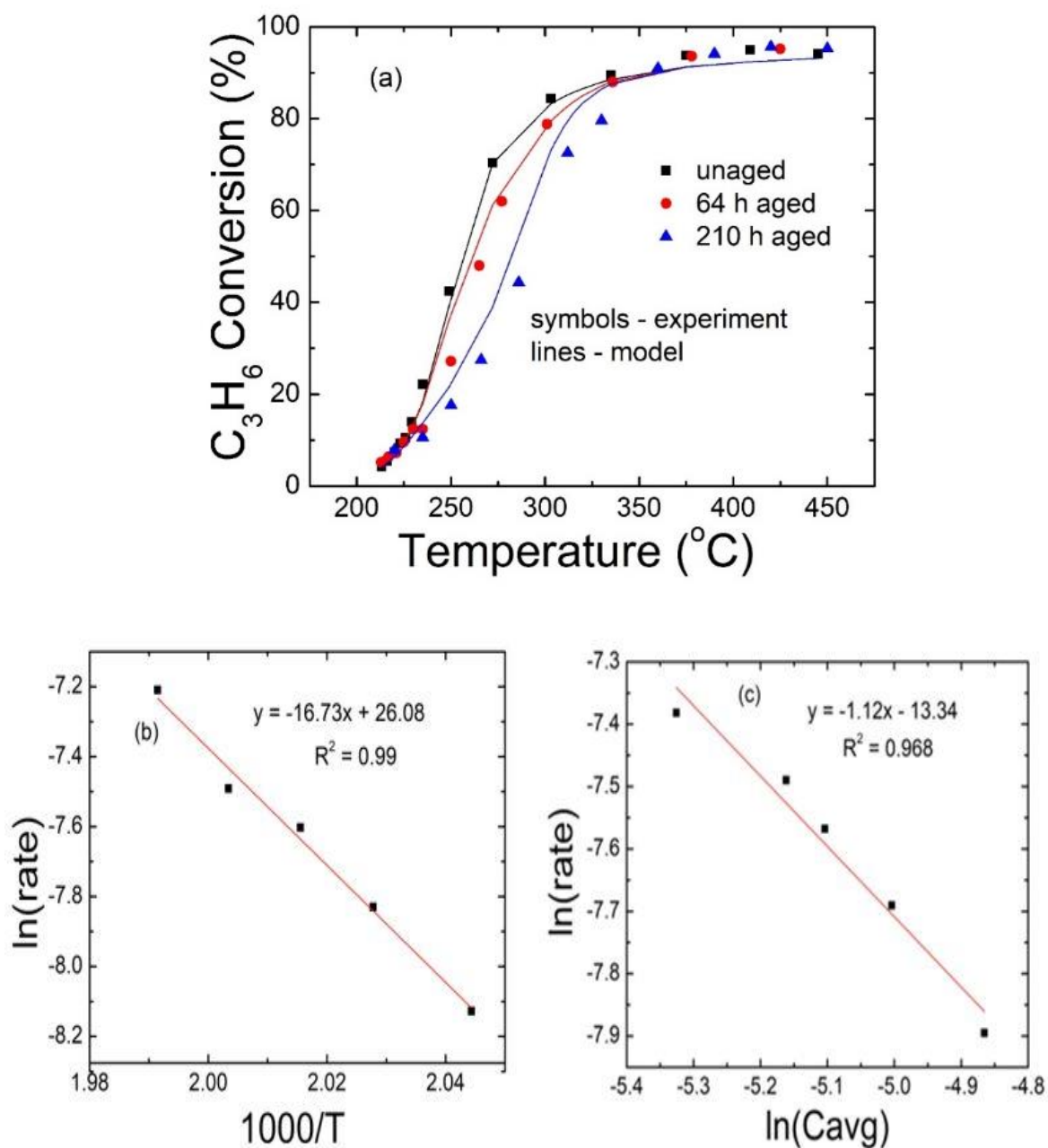


Figure 2.11 (a) C_3H_6 conversion as a function of temperature at different aged time using reactant condition of 250 ppm propylene, 5% O_2 and balance Argon at GHSV of $265k\ h^{-1}$, (b) & (c) for kinetic analysis of C_3H_6 oxidation.

The propylene kinetics were incorporated into the monolith reactor model, which resulted in a good fit with the data. An approach similar to that of the ammonia oxidation

simulation was followed. The tortuosity/porosity ratio (τ/ε) was adjusted from the initial value (27.5) to 75 and 500, to fit respectively the conversion data for the catalyst aged for 64 and 210 h. There are a few points below 250 °C which show some discrepancy from the model predictions, but overall the model captures the data trends (Fig. 2.11a). In comparison, for the earlier presented ammonia oxidation results, we found that the tortuosity/porosity ratio of 60 and 400 was needed to predict catalyst performance at 64 and 210 h of aging, respectively. While the ammonia and propylene models do not predict the exact values, the trends are quite comparable. Finally, the propylene oxidation results were also simulated using meso-macro model approach, which predicts an approximate 75 and 260 nm (y_1) layer forms over alumina particles in the macro void region after 64 and 210 h of aging, respectively. In comparison, the ammonia oxidation model predicted values of 50 and 200 nm for the same aging time. Thus, the two different studies are consistent, strengthening the findings.

2.4.11 Aging of single layered Cu-SSZ-13

To Further investigate the hydrothermal aging of ASC, the top SCR layer was aged in similar aging conditions. The single layered Cu-SSZ-13 catalyst was hydrothermally aged and tested at different aged level using SCR and NH₃ oxidation reactions. Fig. 2.12 show results when Catalyst was tested using SCR feed. It can be seen that catalyst activity noticeably drop from unaged to 110 h aged level but no further degradations was observed from 110 to 210 h aging. The drop in activity could be attributed to the initial transformation or degreening of the catalyst. After, there is very minor drop in activity. Similar results are noticed for NH₃ oxidation feed conditions (Fig. 2.13). It is evident that first 110 h drop in activity show that active sites could be stabilizing during this aging.

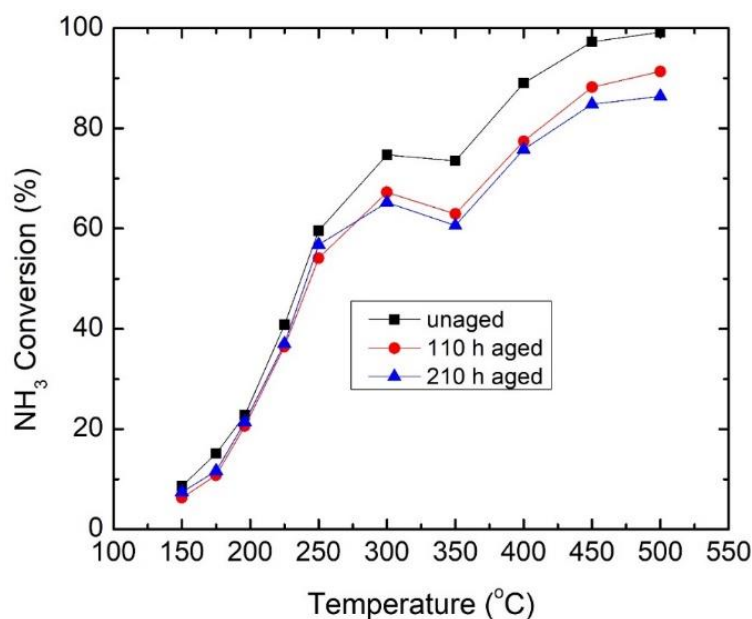


Figure 2.12 Steady state NH_3 conversion as a function of temperature ($^{\circ}\text{C}$) for unaged and aged single layered Cu-SSZ-13 sample. Feed conditions: 500 ppm NO and NH_3 each, 5% O_2 and balance Ar, 66k h⁻¹ GHSV.

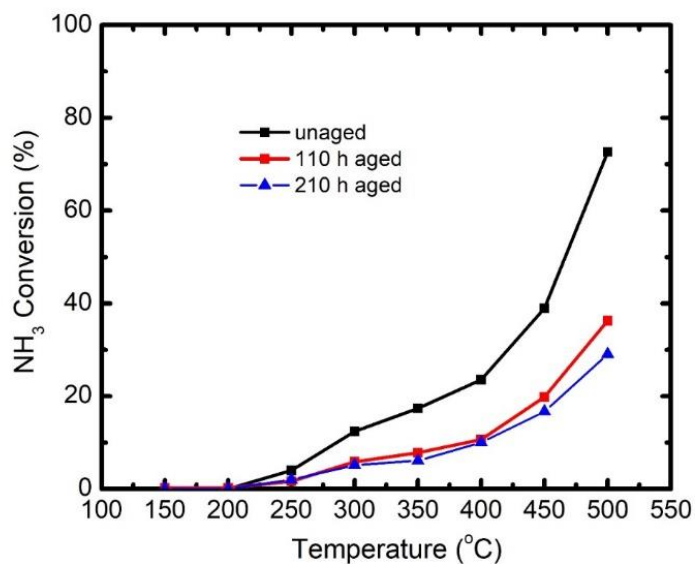


Figure 2.13 Steady state NH_3 conversion as a function of temperature ($^{\circ}\text{C}$) for unaged and aged single layered Cu-SSZ-13 sample. Feed conditions: 500 ppm NH_3 , 5% O_2 and balance Ar, 66k h⁻¹ GHSV.

2.4.12 Aging of dual-layer ASC

Once the hydrothermal aging was separately studied over bottom and top layer of dual-layer ASC. Experiments performed to study HT aging effect on dual-layer combined. The aging temperature used here is 650 °C while the aging time is reduced to one-fourth. Fig 2.14 show that even for unaged sample the top layer provide diffusion barrier and restrict the NH₃ conversion to ~80% at high temperature. Thus, the slight decline in activity of bottom Pt layer with aging is not reflected in dual-layer sample results because the conversion is already transport limited by top layer. On the other hand, as we see decline in SCR activity of top layer (Fig. 2.12) from unaged to 110 h, the NO yield in dual-layer increase significantly from unaged to 25 h aged. There is negligible change in NO yield after further 25 h aging. This is consistent with results of single layer Cu-SSZ-13 sample (Fig. 2.13) that also show negligible change from 110 to 210 h aging.

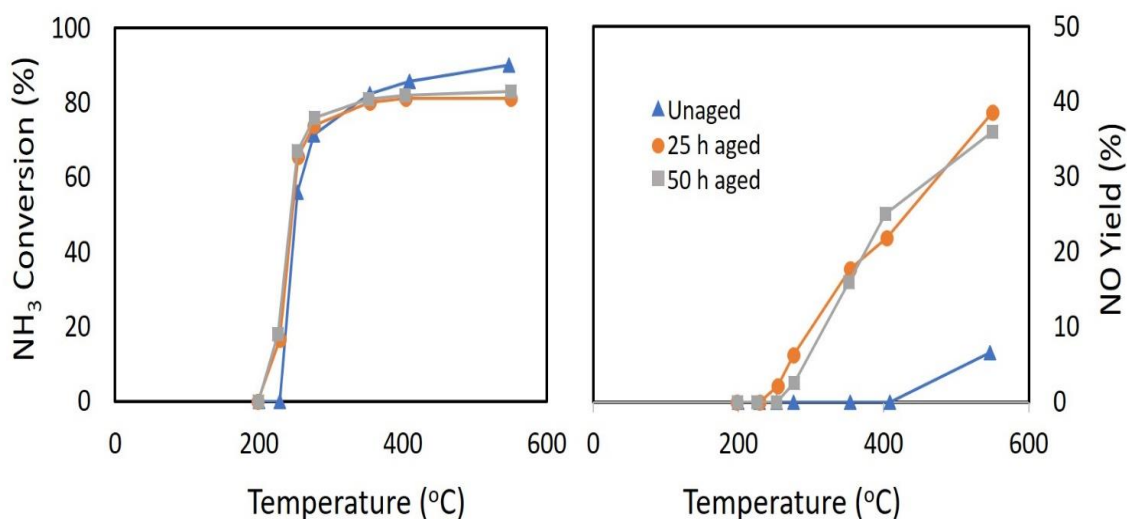


Figure 2.14 Steady state NH₃ conversion as a function of temperature (°C) for unaged and aged over dual-layer ASC sample. Feed conditions: 500 ppm NH₃, 5% O₂ and balance Ar, 150k h⁻¹ GHSV.

2.5 Conclusions

In this study, systematic aging of a Pt/Al₂O₃ washcoated monolith was conducted to understand and quantify the impact of aging on catalyst performance for the oxidations of ammonia and propylene. The findings show that moderate hydrothermal aging has the effect of reducing the pore size in the washcoat, which in turn reduces the diffusional flux and the high temperature conversion while the conversion at lower temperature is negligibly affected. For ammonia oxidation, the NH₃ conversion and N₂ yield decrease with aging but product selectivity remains the same. It is shown that water plays a major role in altering the morphology of alumina through a gas-solid reaction. The formation of hydroxyl groups over alumina surface has been observed. While the study involved the oxidations of ammonia and propylene probe reactions, the findings are applicable to other catalytic reactions carried out over Pt/Al₂O₃ catalyst that undergoes a similar hydrothermal aging protocol. Also, the hydrothermal aging over single Cu-SSZ-13 layer and dual-layer ASC was briefly studied using reaction experiments.

Chapter 3. Enhanced mass transport through ASC

3.1 Introduction

NO_x (nitric oxide and nitrogen dioxide) is a major pollutant in internal combustion engine exhaust. Emerging emission standards demand increasingly innovative and efficient catalyst aftertreatment technologies [56]. Several catalysts have been studied and developed for NO_x removal including V₂O₅-WO₃/TiO₂ [57,58], Pt/BaO/Al₂O₃ [59,60] and Cu-/Fe-zeolite [17-22]. Urea-based Selective Catalytic Reduction (SCR) is the technology of choice to reduce NO_x from heavy-duty diesel vehicle exhaust. Recent research has shown that Cu-SSZ-13 is highly active, selective and hydrothermally stable [14,21], and, as a result, has become the most popular SCR catalyst for (NO_x + NH₃) reaction. While the performance of Cu-SSZ-13 has been studied extensively, the impact and mitigation of washcoat diffusion limitations associated with Cu-SSZ-13 has seen less attention.

NH₃ is generated by on-board urea dosing system [22]. In practice, NH₃ is injected in slight excess of the requisite 1:1 stoichiometry to account for undesired NH₃ oxidation and the inevitable NH₃ slippage during the transient operation. This can result in the release of NH₃ to the environment. In fact, modern vehicles have become a major source of NH₃ [16]. To this point, Ammonia Slip Catalyst (ASC) is required downstream to convert unreacted NH₃, hopefully to N₂. As described in recent works [26,27,33], the dual-layer ASC comprising a base PGM layer and top SCR layer is an effective design to achieve high N₂ selectivity and NH₃ conversion. Scheuer et al. [26] and Shrestha et al. [27,33] studied the functionality of dual layer ASC. Colombo et al. [28,29] and Nova et al. [30] reported kinetic features of the dual layer ASC. It is by now understood that with the dual layer ASC, NH₃ is oxidized to NO by the base PGM layer (usually Pt/Al₂O₃) at high

temperature, and the NO formed reacts with a portion of the incoming NH_3 in top SCR layer, forming N_2 .

For both Cu-SSZ-13 SCR and PGM-based ASC monoliths, mass transfer limitations in the washcoat have been shown to be limiting at moderate to high temperatures. Metkar et al. [16] showed the presence of washcoat diffusion limitations for Cu- and Fe-ZSM-5 catalytic monoliths for both standard and fast SCR. Similarly, while evaluating selective oxidation of NH_3 over the dual-layer ASC comprising base $\text{Pt}/\text{Al}_2\text{O}_3$ and top Cu-SSZ-13 layer, Shrestha et al. [27] reported a monotonic decline in NH_3 conversion with increased thickness of the top Cu-SSZ-13 layer, attributed to diffusional barrier provided by top layer. A simulation study by Scheuer et al. [26] highlighted the importance of diffusion through top SCR layer in dual-layer ASC. Collectively, these observations indicate that under certain conditions washcoated SCR catalyst is diffusion limited by itself and also when used as top layer in dual-layer ASC.

There have been several studies of diffusion in SCR and ASC monoliths. Tronconi et al. [61] studied mass transfer limitations in vanadium-based SCR catalyst, Metkar et al. [16] reported washcoat diffusion limitations for Cu- and Fe-ZSM-5. The effective diffusivity of NO ($D_{e,\text{NO}}$) is a crucial parameter that is a function of catalyst particle size, washcoat architecture, porosity and pore-size distribution. Several studies have estimated $D_{e,\text{NO}}$ for washcoated SCR catalysts. The $D_{e,\text{NO}}$ value of $\sim 10^{-7} \text{ m}^2/\text{s}$ is reported in the modeling studies of Metkar et al. [19], Olsson et al. [62] and Colombo et al. [63], indicating a rather high ratio of $D_{f,\text{NO}}/D_{e,\text{NO}}$ of 80-100. On the other hand, Joshi et al. [64] has found $D_{f,\text{NO}}/D_{e,\text{NO}}$ around 10 for a commercial Cu-SAPO-34 catalyst, potentially pointing to the importance of the washcoat preparation. Beeckman et al. [65] claimed 50% increase in NO

conversion with optimized and reconfigured pore structured SCR catalyst. A modeling study by Scheuer et al. [26] emphasized that NH_3 conversion may be increased without affecting the product selectivity by improving diffusion through top SCR layer in dual-layer ASC. It is of interest to exploit the diffusion impact in order to design the catalyst architecture for enhanced performance. This is an objective of the study.

The ca. 0.38 nm pores of the eight-member ring SSZ-13 zeolite prevent active site poisoning from hydrocarbons. On the other hand, the catalyst is susceptible to local micropore diffusion limitations inside the zeolite. Increasing the intercrystallite macroporosity could enhance the mass transport properties without impacting the intrinsic zeolite unit cell structure. Dudak et al. [66] has also reported macro-porosity as a major contributing factor for overall mass transport through coated zeolite washcoat in his study of intra-/inter-particle diffusion. One of the methods of achieving this enhancement is through the addition of sacrificial agents that would occupy inter-particle space in washcoat and generate calcined holes when consumed by calcination during the catalyst preparation [67-70].

In this study, we attempt to mitigate washcoat diffusional limitations using sacrificial agents to create additional porosity for diffusion. Vaclavik et. al. [67] incorporated yeast as a sacrificial agent in $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ washcoat to enhance effective diffusivity and showed improved reaction results for CO oxidation. Industries use various pore formers such as polymer, organic or carbohydrate etc. to enhance washcoat porosity and to make more porous ceramic substrates for filtrations, which has been communicated through the patents [68-70]. To our knowledge the concept of macro scale pore-formation has not been reported for Cu-SSZ-13 for SCR and ASC to date. In this study we use two

different sacrificial agents (yeast or poly-tert-butyl acrylate) during the Cu-SSZ-13 washcoat synthesis for both single-layer SCR and dual-layer ASC monoliths. Figure 3.1 display a schematic depiction of unmodified and modified washcoat for SCR and ASC samples prepared. Due to volume occupied by the agents, the modified washcoat may be slightly thicker. Monolith reactor experiments show that modified samples prepared using sacrificial agents outperform unmodified samples with increase in NO_x/NH₃ conversions for SCR and ASC. Implications for both SCR and ASC catalyst design and performance are discussed.

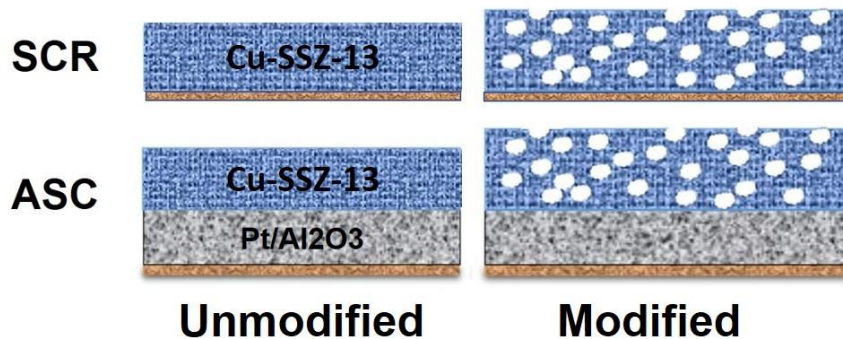


Figure 3.1 Schematic diagram of washcoated monolith, top: SCR and bottom: dual-layer ASC; left: unmodified and right: modified.

3.2 Experimental Methods

3.2.1 Catalyst synthesis and slurry preparation

The Cu-SSZ-13 powder catalyst was provided by Johnson Matthey; composition provided in Table 3.1. Three batches of Cu-SSZ-13 slurry were prepared by physically mixing Cu-SSZ-13 powder, water and boehmite (20 wt.% AlOOH) in a mass ratio of 4:8:5. The alumina serves as a binder for the washcoat. The pH of the slurries was adjusted to 3.5-4.0 using ammonium hydroxide and/or acetic acid. The slurries were then ball milled for

20 h following a procedure developed in previous studies [19,27]. The ball milling step leads to a modest reduction in the zeolite crystal size without adversely impacting the pore structure based on comparisons of the catalytic activity of ball milled samples to unmilled samples. One batch of slurry was kept as such for unmodified SCR (Cu-slurry-1) while active dry yeast was added and physically mixed to the second (Cu-slurry-2) and poly (tert-butyl acrylate) was added to the third (Cu-slurry-3). The yeast particles had a uniform size distribution in the range of 1-3 μm whereas poly-tert-butyl-acrylate particles were mostly in the range of 2-5 μm with some larger particles ($\sim 10 \mu\text{m}$). The amount of yeast or polymer added correspond to 10% of the volume of Cu-SSZ-13; estimates were based on the loose bulk density of Cu-SSZ-13 (0.39 g/cm³). Poly-(tert-butyl acrylate), also referred as “polymer” for brevity, was synthesized by the Prof. Megan Robertson lab at the University of Houston; its synthesis recipe can be found in Yadav et al. [71].

Table 3.1 Cu-SSZ-13 powder catalyst description

Parameter	Value
Si/Al (atomic)	12.3
Cu/Al (atomic)	0.35
Cu (wt. %)	3.4

For dual-layer ASC, Pt/Al₂O₃ catalyst powder was synthesized using wetness impregnation method with precursor hexahydrate chloroplatinic acid followed by slurry preparation. The procedure is described in detail in chapter 2.

3.2.2 Monolith coating

The blank monoliths of cell density 400 cpsi comprising 28 channels were cut into ~ 0.4 cm or ~ 2 cm in length for catalyst coating. To prepare a single-layer unmodified SCR sample, the 2 cm long blank monolith was dipped in the Cu-slurry-1, Cu-slurry-2 or

Cu-slurry-3 were used for the modified SCR samples. Dipping and air blowing times were 30 and 10 s, respectively. After dipping, the unmodified sample was dried in an oven at 120 °C for 2 h while the modified samples were kept at room temperature for drying. The dipping and drying procedure was repeated to achieve the requisite loading. The unmodified sample was calcined at 500 °C in air for 5 h while the modified samples were calcined at 500 °C in controlled medium with a stream containing 5% O₂ and balance Argon for 2 h. This treatment avoided any undesirable local temperature rise while the sacrificial agents were oxidized. We do not believe that the difference in O₂ concentration between the unmodified and modified samples during calcination had any effect on the resulting catalytic activity.

Table 3.2 Sample nomenclature and loading details

Sample	Length (cm)	Pt/Al₂O₃ base layer loading (g/in³)	Pt loading (g/ft³)	Cu-SSZ-13 loading (g/in³)	Type	Sacrificial Agent used
Cu(2.1)	2	-	-	2.1	unmodified	-
Cu(2.1)y	2	-	-	2.1	modified	yeast
Cu(2.1)p	2	-	-	2.1	modified	polymer
Cu(3.2)	2	-	-	3.2	unmodified	-
0.4Pt(1.45)	0.4	1.45	1.45	-	unmodified	-
Pt(1.46)Cu(2.90)	0.4	1.46	1.46	2.90	unmodified	-
Pt(1.47)Cu(2.90)y	0.4	1.47	1.47	2.90	modified	yeast
Pt(1.20)Cu(3.20)p	0.4	1.20	1.20	3.20	modified	polymer
Pt(4.80)Cu(2.75)	0.4	1.60	4.80	2.75	unmodified	-

For the dual-layer ASC, a base Pt/Al₂O₃ layer was deposited over the blank monolith following the dipping procedure described in our previous work. Once the base Pt/Al₂O₃ layer was applied, the dipping-drying-calcination procedure described above was followed to deposit top layer of unmodified or modified washcoat. The description of prepared samples with final catalyst loadings is given in Table 3.2. Freshly prepared dual-

layer monolith samples were reduced at 500 °C in 2% H₂ for 30 min and then kept in an oxidative environment comprising 5% O₂ for 2 h at 500 °C. Before every reaction experiment, the sample was pre-treated in 5% O₂ and balance Argon at 500 °C for 2 h.

3.2.3 Bench scale reactor set-up

The bench scale reactor set up is explained in detail by Kabin et al. [34]. The monolith sample wrapped in ceramic fiber was fixed inside a quartz tube (I.D. 0.81 cm and O.D. 1.27 cm) and positioned in a furnace. A fine thermocouple (K-type from Omega Engineering) was positioned in the center of the monolith (axially and radially). The inlet gas flows were metered by MKS mass flow controllers while the outlet gas component measurements were accomplished with a Thermo-Nicolet FTIR with OMNIC software. N₂ was estimated by an overall N balance. The flow lines were pre-heated to 150 °C to avoid NH₃ or H₂O condensation and the pressure through flow lines was maintained at 880 Torr.

3.2.4 Steady state reaction experiments

Single-layer SCR (Cu-SSZ-13) samples were tested at steady state using standard SCR (NH₃ + NO, 500 ppm each) and NH₃ oxidation (500 ppm) with feed conditions including 5% O₂, balance Ar and a feed temperature range of 150-500 °C, increments of 25 or 50 °C were taken. Steady state SCR reaction experiments were repeated by adding 2% water in the feed. Dual-layer ASC samples were tested using NH₃ oxidation (500 ppm) with 5% O₂. The total flow through the reactor tube was maintained at 1 L/min using Ar as inert; at this volumetric flow, the space velocity for 0.4 and 2 cm long samples was estimated as 332,000 and 66,000 h⁻¹. The steady state is considered when outlet concentration remained steady for a minimum of 30 min.

3.2.5 NH₃ adsorption and temperature programmed desorption (TPD)

Transient adsorption and temperature programmed desorption of NH₃ were carried out on prepared SCR samples to quantify NH₃ storage and to further assess washcoat diffusion impact. The samples were first pre-treated in an oxidative environment of 5% O₂ and balance Ar at 500 °C for 2 h. The experiment protocols followed similar approach as Joshi et al. [64], the steps included:

Step 1: At 0 min, only Ar flowing at 149 °C.

Step 2: At 10 min, inlet NH₃ (220 ppm) started, fixing temperature at 149 °C.

Step 3: At 130 min, inlet NH₃ turned-off and temperature maintained at 149 °C.

Step 4: At 140 min, inlet NH₃ remained off and temperature ramped-up to 550 °C with 10 °C/min.

The inlet NH₃ of 220 ppm diluted with balance argon and the space velocity was maintained at 40k h⁻¹ for these transient experiments. The time lag between inlet flow controller and outlet FTIR has been measured by running experiment through blank tube, which is subtracted while doing quantification. The TPD results reported in Fig. 3.6 and Fig. 3.10 are discussed in later section of this paper.

3.3 Catalyst Characterization

3.3.1 Thermogravimetric analysis (TGA) of yeast and poly (tert-butyl acrylate)

Thermogravimetric analysis (Instrument: 2050 TGA V5.3C) was performed to study the combustion behavior of sacrificial agents. The temperature was increased to 500 °C at a ramp rate of 1 °C/min under ambient air atmosphere. Fig. 3.2 represents the mass loss as a function of temperature. The polymer sample started to combust at ~200 °C while the yeast commenced at the lower temperature of 50 °C. Although the polymer combustion

started later it was completely consumed by 500 °C, while the yeast had some unconsumed material (~10% of initial) at high 500 °C. The ash was analyzed using XPS (PHI Model 5700 X-Ray Photoelectron Spectrometer).

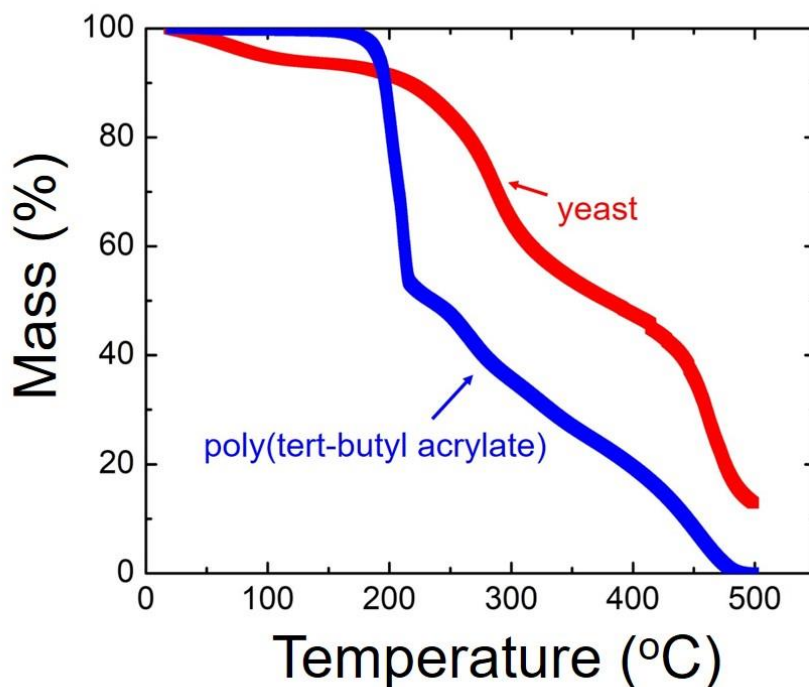


Figure 3.2 Thermogravimetric analysis (TGA): The change in mass (%) of sacrificial agents as a function of temperature with thermal gradient of 1 °C/min.

3.3.2 Scanning electron microscopy (SEM)

The morphology of the modified washcoats were evaluated using scanning electron microscopy (SEM). SEM images were obtained using Leo 1525 Gemini FEG (Manufacturer: Zeiss) in an attempt to visualize structural changes that result from washcoat modification. Figs. 3.3(a)-(c) show SEM micrographs of washcoat cross-sections for both unmodified (3.3a) and modified samples (3.3(b), 3.3(c)) at a scale of ~10 μm. The micrographs reveal the appearance of larger pores that forms due to sacrificial agents in the yeast- and polymer-modified washcoats. The sample modified with polymer (Fig.

3.3(c)) exhibits few larger holes of size 5-10 μm , indicating non-uniformity in the polymer particles size. The yeast-modified sample (Fig. 3.3(b)) shows evidence of increased pore size but without the large holes. In comparison, the unmodified washcoat shows no evidence of these larger pores (Fig. 3.3(a)). The unmodified washcoat SEM image at a zoomed scale of $\sim 2 \mu\text{m}$ show interparticle pores in the range of around 0.1 to 0.5 μm . These smaller interparticle pores occurs in both unmodified and modified samples.

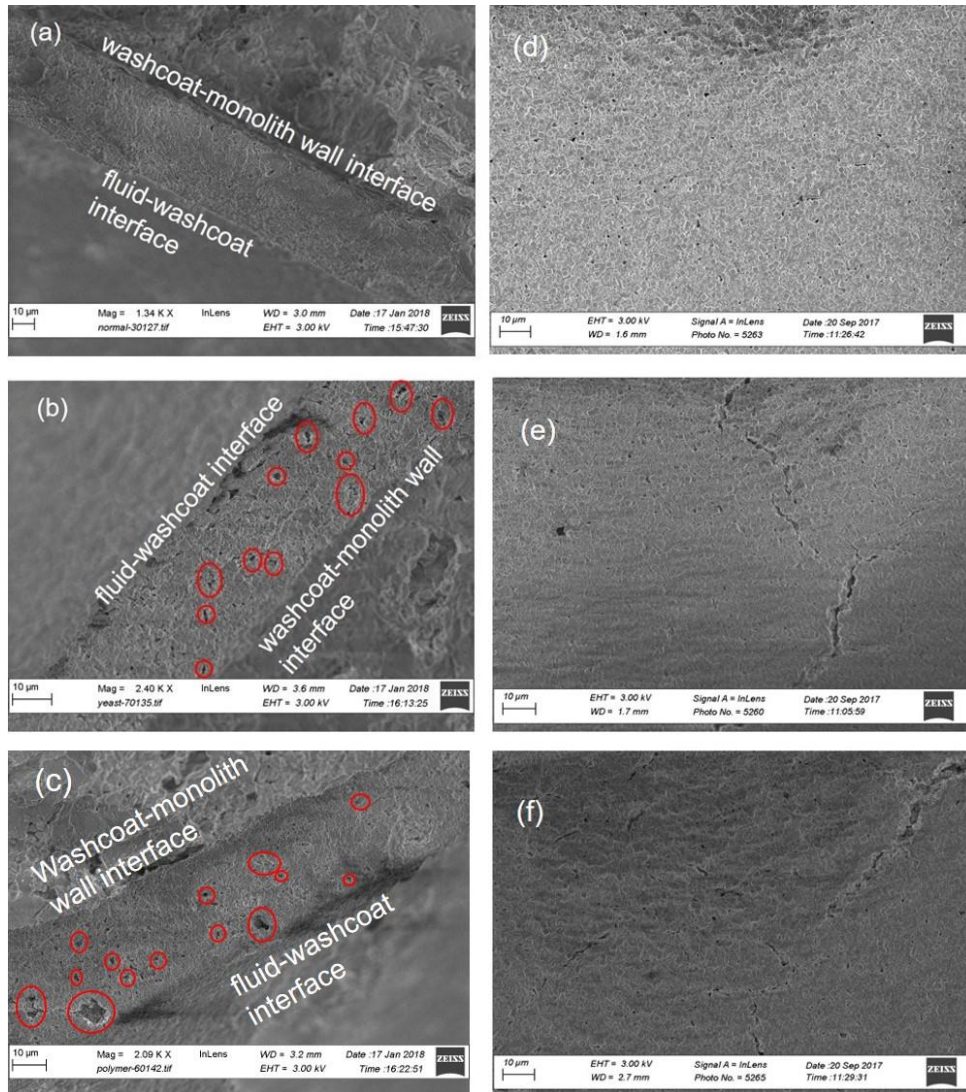


Figure 3.3 SEM micrographs showing unmodified sample (a: washcoat cross-section, d: washcoat surface) and modified samples prepared using yeast (b and e) and poly-tert-butyl acrylate (c and f).

In addition, micrographs of the washcoat surface (Figs. 3.3(d)-(f)) reveal the existence of cracks and cavities which might negatively impact mechanical integration of washcoat. Sacrificial agents improved the washcoat transport properties but simultaneously may affect their mechanical strength. Few cracks/cavities can be seen in modified samples which are inconspicuous in unmodified samples. On the other hand, Novak et al. [51] reported that cracks play an important role in enhancing washcoat transport. Thus, these cracks likely contribute to an increase in porosity along with generated isolated pores.

More work is needed to optimize the washcoat modification procedure. Since we used in-house synthesized polymer, the commercial polymer with uniform particle sizes could prevent formation of non-uniform large pores to some extent.

3.4 Results and Discussion

3.4.1 Steady state SCR ($\text{NH}_3 + \text{NO} + \text{O}_2$) reaction testing

Fig. 3.4 shows the dependence of the NO_x conversion on catalyst temperature for several samples. Single-layer Cu-SSZ-13 monolith samples were evaluated under steady state conditions using an anhydrous feed of 500 ppm NO and NH₃, 5% O₂ and balance argon (Fig. 3.4(a), 3.4(b)) at a space velocity of 66,000 h⁻¹ (@ STP). For comparison, a feed containing 2% H₂O was also used (Fig. 3.4(c), 3.4(d)). For the catalyst geometry and flowrate, the transverse Peclet number ($\text{Pe}_t = \frac{R_{01}^2 \langle u \rangle}{LD_f}$) and axial Peclet number ($\text{Pe} = \frac{L \langle u \rangle}{D_f}$) are estimated to be 0.04 and 240 at 350 °C, respectively. $\text{Pe}_t \ll 1$ indicates that the transverse diffusion time is small compared to the convective mass transfer time, and therefore conversion should approach 100% at high temperature. $\text{Pe} \gg 10$ indicates that

the overall transport in axial direction is expectedly dominated by convection. This leaves the reaction and washcoat diffusion as the presiding rate controlling processes.

A comparison of the unmodified and modified SCR samples without and with water show enhancement in NO_x conversion for an intermediate range of temperature. Specifically, in the intermediate temperature window of 250-450 °C, the modified samples (Cu(2.1)y, Cu(2.1)p) exhibit a ~10% (absolute) higher NO conversion compared to the unmodified sample with the same washcoat loading Cu(2.1). Notably, the modified samples with Cu loading of 2.1 g/in³ give a conversion similar to that of an unmodified sample with higher washcoat loading of 3.2 g/in³. This finding indicates that the amount of catalyst required could be reduced with optimized washcoat architecture. On the other hand, at lower temperature (T < ~225 °C) the NO_x conversions for samples with the same Cu loading, (Cu(2.1), Cu(2.1)y and Cu(2.1)p) are nearly identical. This is attributed to the overall rate being kinetically controlled. The modified sample Cu(2.1)y prepared using yeast has a slightly lower conversion compared to the polymer-modified sample; this could be possibly due to the detrimental impact of the residual ash in the washcoat. Finally, all samples have nearly the same NO_x conversion at high temperature (T ≥ 450 °C). The measurement error for NO conversion is within 2%.

The Weisz-Prater modulus ($\Psi = \frac{R_{\text{O}_2}^2 R_{\text{obs}}}{D_e C_i}$) is a dimensionless parameter for assessing the importance of internal diffusion limitations. Specifically, for $\Psi > 1$ washcoat diffusion limitations are likely. We estimated Ψ for washcoat diffusion limitation at various temperatures from 150 to 450 °C; these estimates are reported in table 3.3. The analysis revealed $\Psi > 1$ for temperatures exceeding ~250 °C, this result is consistent with the difference in conversion for the samples in Fig. 3.4.

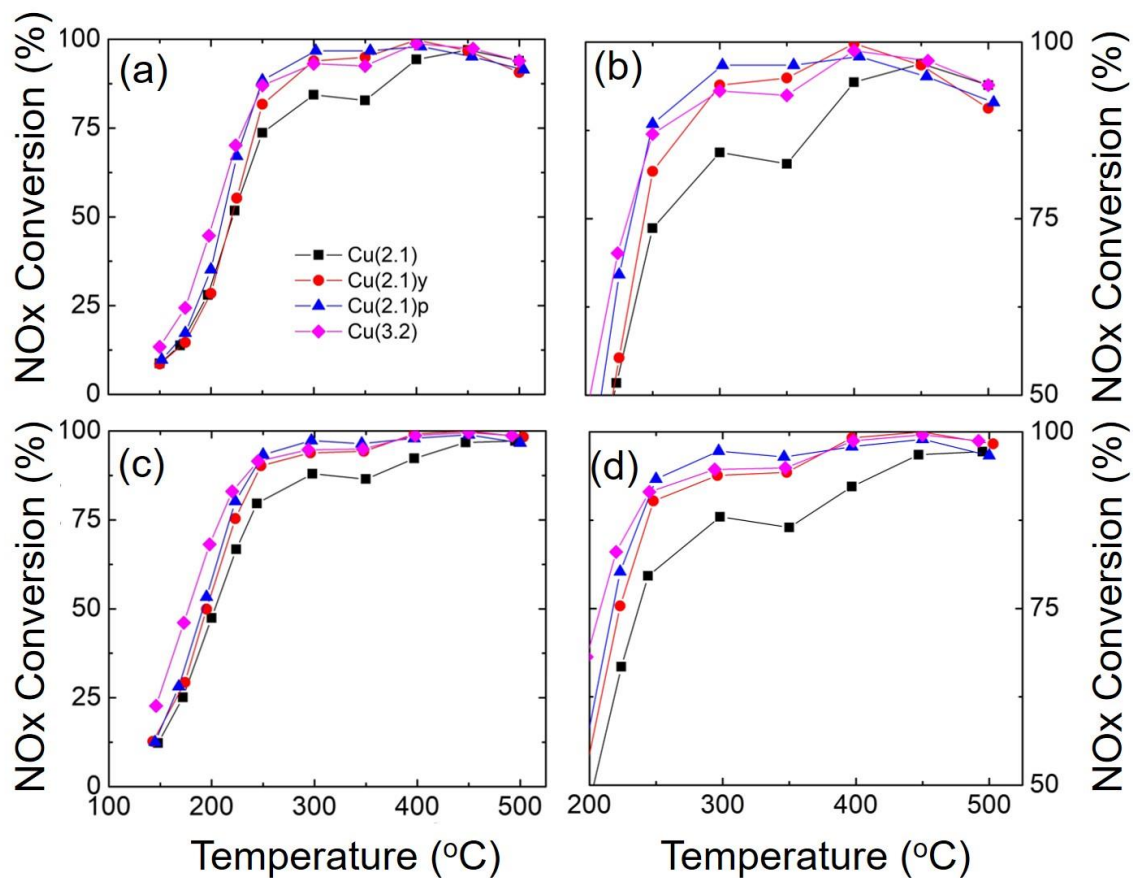


Figure 3.4 Steady state NO_x conversion with temperature over Cu-SSZ-13 samples. (a) Feed: 500 ppm NO and NH₃, 5% O₂ and balance Ar, GHSV 66k h⁻¹ and (c) with 2% H₂O in feed, the results are magnified in (b) and (d).

Table 3.3 Weisz-prater modulus ($\frac{R_{\Omega 2}^2 R_{obs}}{D_e C_i}$)

Temperature (°C)	Value
150	0.19
200	0.43
250	2.23
300	2.63
350	2.63
400	3.22
450	3.50

* $R_{\Omega 2} = 25 \mu\text{m}$, $D_e = 10^{-7} \text{ m}^2/\text{s}$

In a forthcoming modeling study, we use a controlling regime analysis and intrinsic kinetic measurements to definitively identify the rate controlling processes. That study confirms the reaction resistance is largest at low temperatures ($< 200\text{ }^{\circ}\text{C}$) while the role of internal and external mass transport becomes important at higher temperature. These findings are consistent with the appearance of conversion enhancement in the $250 - 450\text{ }^{\circ}\text{C}$ temperature window (Fig. 3.4).

While comparing the anhydrous and hydrous feeds, it is observed that H_2O enhances the conversion over the entire temperature range. Moreover, the modified samples exhibit higher conversion over the same intermediate temperature range. This result follows from previous works that have proposed that hydration of Cu-SSZ-13 make Cu^{2+} more mobile and readily reducible to Cu^+ at low temperature, leading to a faster SCR reaction [36]. Several studies have characterized Cu^{2+} active sites although the Cu^{2+} position inside Cu-SSZ-13 is under debate. Gao et al. [13] reported that Cu^{2+} resides in 6-member ring (MR) of dehydrated Cu-SSZ-13 whereas the Cu^{2+} moves to the 8-member ring in hydrated Cu-SSZ-13. The coordination number of Cu^{2+} in dehydrated and hydrated Cu-SSZ-13 is 3 and 4, respectively. The Cu^{2+} located at 8 MR has more mobility and easily accessible to reactants. Also, the reduction of Cu^{2+} to Cu^+ speed-up in presence of OH^- ligand.

3.4.2 Steady state NH_3 oxidation on Cu-SSZ-13

Steady state NH_3 oxidation reaction was conducted over the same Cu-SSZ-13 samples using 500 ppm NH_3 , 5% O_2 and balance argon while maintaining the same GHSV of $66,000\text{ h}^{-1}$. NH_3 oxidizes selectively to N_2 over Cu-SSZ-13 with a drawback of a higher activation barrier (typically $\sim 180\text{ kJ/mol}$) than standard SCR; a temperature well in excess

of 300 °C is needed to initiate the reaction [12,62]. Fig. 3.5 shows that NH₃ oxidation commences at ~250 °C, gradually increasing up to 350 °C, followed by a sharp increase to ~90% at 500 °C. The NH₃ oxidation light-off behavior is attributed to the presence of two types of active sites with a probable shift in the rate limiting step. (We expand on the dual site issue in the next section.) Despite the difference in temperature range compared to standard SCR, the washcoat modification results in conversion enhancement. The enhancement for NH₃ oxidation is absolute 15-20% increase in the temperature window of 300-500 °C. This further validates the role of internal diffusion limitations which could be improved using sacrificial agents in washcoat. Moreover, the modified samples Cu(2.1)y and Cu(2.1)p have comparable or slightly higher activity compared to the higher loading unmodified sample Cu(3.2).

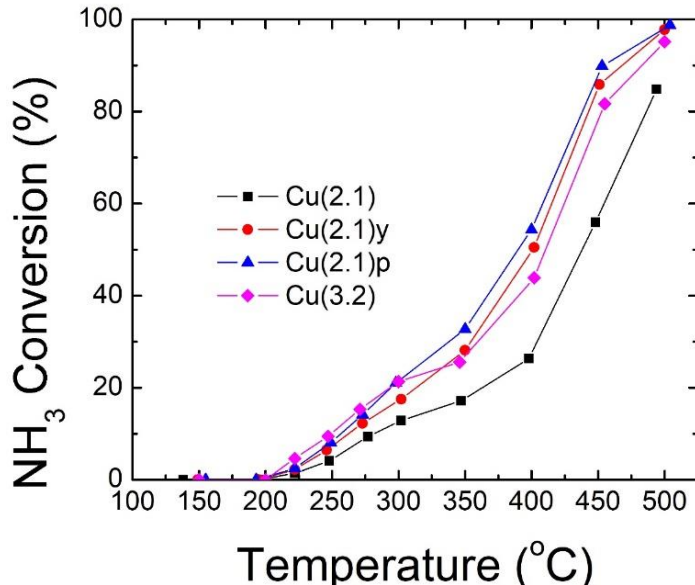


Figure 3.5 Steady state NH₃ conversion as function of temperature over single layered Cu-SSZ-13 samples. Feed composition: 500 ppm NH₃, 5% O₂ and balance Argon, GHSV 66k h⁻¹.

The reaction is presumably kinetic limited when the conversion is below 15% (i.e., for $T < \sim 275$ °C). In the kinetic controlled regime the data show a slightly higher NH_3 conversion for the modified samples Cu(2.1)y and Cu(2.1)p compared to unmodified Cu(2.1) sample. This indicates some change in the kinetic activity with washcoat modification. We suspect that this may be due to a local temperature rise during the sacrificial agent combustion that led to Cu active site transformation or redistribution, similar to enhanced overall performance after high temperature hydrothermal aging (explained in section 4.6). Washcoat modification effects on the kinetics is expected to be small compared to mass transport; the magnitude of which is to be investigated and will be reported in our forthcoming modeling study.

3.4.3 NH_3 temperature programmed desorption (TPD) on Cu-SSZ-13

Both SCR and ammonia oxidation results suggest the existence of at least two types of active sites on the Cu-SSZ-13. Transient NH_3 storage experiments were conducted to examine this issue and NH_3 uptake along with the impact of washcoat diffusion and the efficacy of washcoat porosity modification. Fig. 3.6 shows the temporal feed and effluent NH_3 concentration spanning the constant temperature uptake and temperature-programmed desorption. The feed NH_3 (220 ppm) was turned on at 600 s with inert argon and a space velocity of 40 k h^{-1} for each of the four samples.

Each of the four samples displayed similar NH_3 breakthrough curves. For each sample the effluent NH_3 does not appear until ~ 600 s after NH_3 introduction with some minor differences for the Cu(2.1) loading samples. The main differences between these three Cu(2.1), Cu(2.1)y and Cu(2.1)p samples are the steepness of the breakthrough curves. As expected, the higher catalyst loading sample Cu(3.2) adsorb comparatively more NH_3

than the rest of the samples.

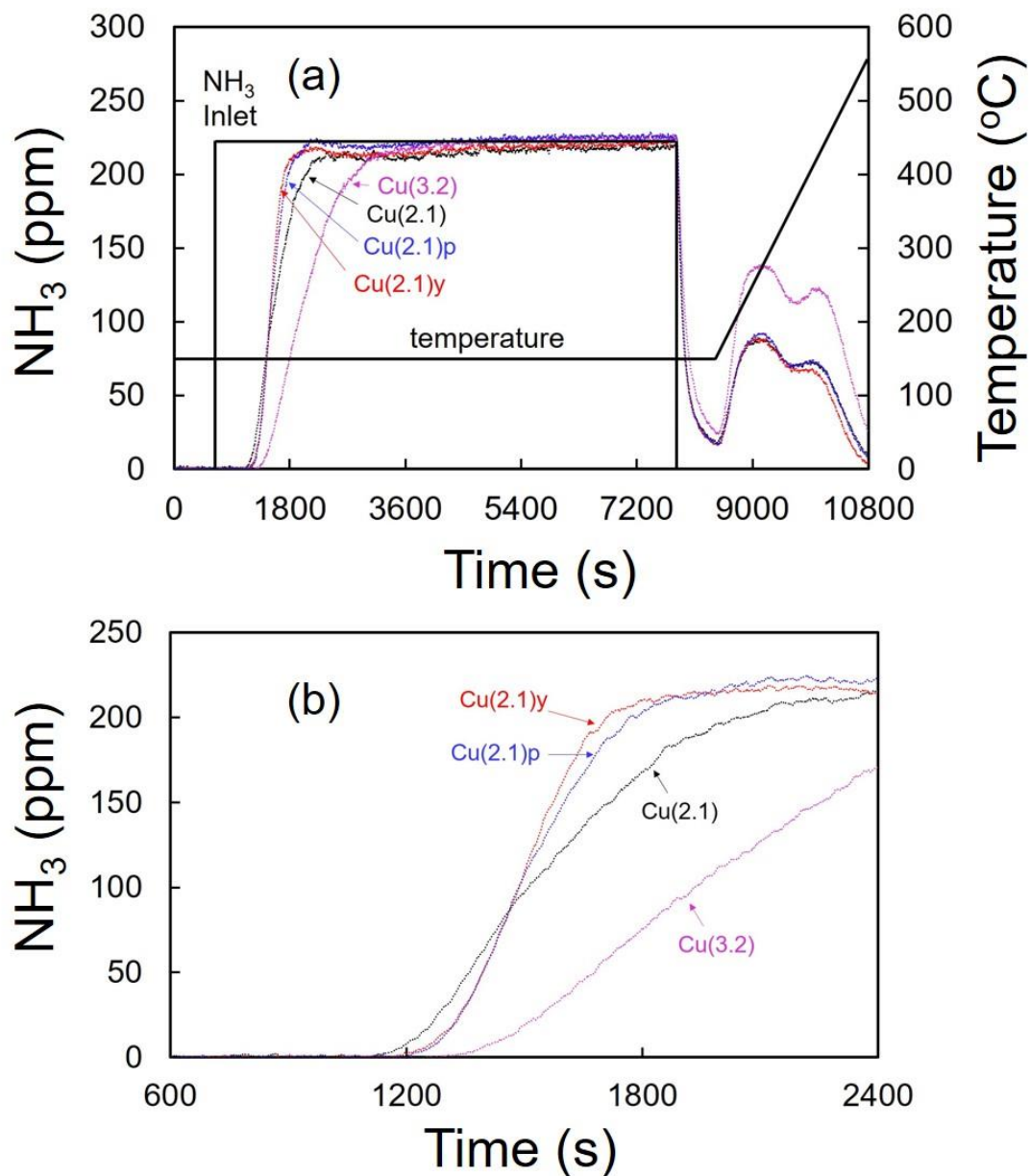


Figure 3.6 (a) Transient NH_3 evolution as a function of time during temperature programmed desorption study. For clear distinction in breakthrough, bottom plot (b) is shown on cropped time scale

The modified sample Cu(2.1)y has a slightly lower uptake compared to the unmodified Cu(2.1) and polymer-modified Cu(2.1)p. This finding suggests possible active site blockage by the residual ash from the yeast combustion. Recall that similar results were

observed in the reaction experiments (Fig. 3.4 and Fig. 3.5) where Cu(2.1)y exhibit slightly less NO_x and NH₃ conversion as compared to Cu(2.1)p. The estimated NH₃ storage was somewhat higher than that of the Cu loading. This suggests that multiple NH₃ molecules adsorb on a single Cu species and/or uptake on Bronsted sites or physical adsorption at low temperature.

Temperature programmed desorption curve display two peaks, one at a ~250 °C and other at ~400 °C. This is direct evidence of two chemisorption sites, along with a physical adsorption site evidenced by the NH₃ elution immediately after turning the feed NH₃ off. Although the amount of NH₃ stored in Cu(2.1), Cu(2.1)y and Cu(2.1)p is approximately the same, it is evident that the washcoat modification impact the transient features. Unmodified Cu(2.1) exhibits a more gradual adsorption breakthrough than the modified Cu(2.1)y and Cu(2.1)p. A washcoat with no diffusion limitation would have a step increase in outlet NH₃; breakthrough tends to be more gradual when diffusion is present. The washcoat diffusion characteristic time depends inversely on effective diffusivity, therefore more porous modified washcoat has a shorter diffusion time than the unmodified sample. In a forthcoming modeling study, these data are modeled to extract both NH₃ adsorption and diffusivity parameters.

3.4.4 Steady state NH₃ conversion over dual-layer ASC

The Ammonia Slip Catalyst (ASC) is the last catalytic component in the modern diesel engine exhaust treatment system. The role of the ASC is to convert leftover NH₃ coming from SCR into N₂. The dual-layer ASC architecture comprising a Pt-containing base layer and a lean NO_x reduction top layer has emerged as the best design for selectively oxidizing NH₃ to N₂. The base Pt/Al₂O₃ is highly active but poorly selective toward N₂,

with N_2O , NO , and NO_2 being undesired byproducts of the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst [17]. Deposition of a SCR (Cu-SSZ-13) layer over the $\text{Pt}/\text{Al}_2\text{O}_3$ increases the N_2 selectivity at the expense of NH_3 conversion. On the one hand, the SCR layer catalyzes the selective lean reduction of NO_x produced in the bottom layer by NH_3 to N_2 . On the other hand, the top layer introduces an additional diffusional barrier to diffusion of reacting species from the feed gas.

In the current study, ASC samples were evaluated under steady state conditions using 500 ppm NH_3 , 5% O_2 and balance argon at $332,000 \text{ h}^{-1}$ GHSV as the feed gas. The space velocity was kept intentionally high to sensitize the catalyst towards washcoat diffusion limitations. Thus, samples with a fixed Pt loading (1.5 g/ft^3) have comparable NH_3 oxidation so that deviations signal the onset of washcoat diffusion limitations.

Fig. 3.7 compares the NH_3 conversion as a function of temperature for four samples; an uncoated $\text{Pt}/\text{Al}_2\text{O}_3$ sample [Pt(1.45)], three samples with nearly the same Pt loading and coated with different unmodified and modified top layers [Pt(1.46)Cu(2.90), Pt(1.47)Cu(2.90)y, Pt(1.20)Cu(3.20)p], and one sample with a higher Pt loading and unmodified Cu-SSZ-13 top layer [Pt(4.80)Cu(2.75)]. Indeed, above 250°C the modified samples show a 10% (absolute) higher NH_3 conversion compared to the unmodified dual-layer sample (Fig. 3.7). The NH_3 conversion over the single-layer $\text{Pt}/\text{Al}_2\text{O}_3$ is shown for reference; it is clearly much more active but much less selective than the dual-layer samples. In contrast to the SCR results shown earlier, the modified and unmodified samples give a NH_3 conversion that do not converge at high temperature of $\sim 500^\circ\text{C}$ which suggests that external mass transfer limitations are not encountered for these conditions. The modified sample Pt(1.2)Cu(3.20)p gives a slightly lower conversion than

Pt(1.47)Cu(2.90)y due to a slightly lower Pt loading in the base layer and slightly thicker top layer (Fig. 3.7).

The unmodified, higher Pt loading (4.8 g/ft³) sample exhibits a slightly lower light-off temperature reflecting the higher concentration of PGM sites (Fig. 3.7). Interestingly, at higher temperatures, the modified samples having lower Pt loading give a moderately higher NH₃ conversion than the higher Pt loading sample. This illustrates the point that enhanced diffusion through the top SCR layer is key controlling process in the dual-layer ASC. Importantly, the higher porosity can result in better performance with lower precious metal content.

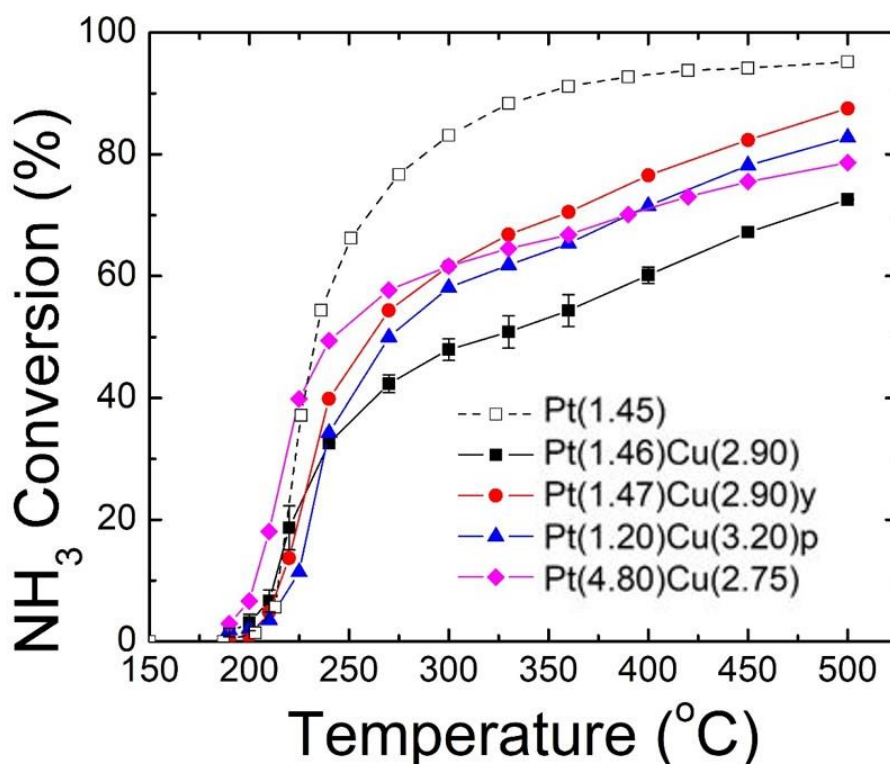


Figure 3.7 Steady state NH₃ conversion as function of temperature over dual-layer ASC samples. Feed composition: 500 ppm NH₃, 5% O₂ and balance Argon, GHSV 332k h⁻¹

In another set of dual-layer ASC experiments (Fig 3.8), the space velocity was lowered to 66,000 h⁻¹ with longer monoliths (length = 2 cm). Two sets of dual-layer samples were prepared, one with low (1 g/ft³) and other with high (3 g/ft³) Pt loading in the base layer; sample details are provided in Table 3.4 of the Supplementary Material section. When comparing modified and unmodified samples with essentially the same Pt loading, no measurable change in the NH₃ conversions was observed. Thus, at the lower space velocity of 66,000 h⁻¹ the reactants have sufficient time to diffuse through the top layer.

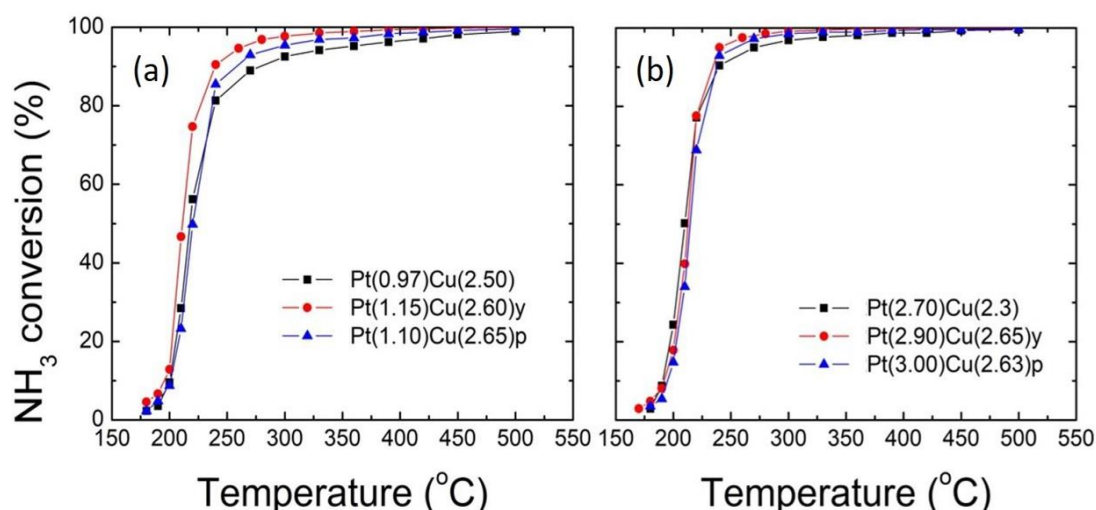


Figure 3.8 Steady state NH₃ conversion as function of temperature over dual-layer ASC at low space velocity. Feed composition: 500 ppm NH₃, 5% O₂ and balance Argon, GHSV 66k h⁻¹.

Table 3.4 Sample details

Sample	Length (cm)	Pt/Al ₂ O ₃ base layer loading (g/in ³)	Pt loading (g/ft ³)	Cu-SSZ-13 loading (g/in ³)	Type	Sacrificial Agent used
Pt(0.97)Cu(2.50)	2	0.97	0.97	2.50	unmodified	-
Pt(1.15)Cu(2.60)y	2	1.15	1.15	2.60	modified	yeast
Pt(1.10)Cu(2.65)p	2	1.10	1.10	2.65	modified	polymer
Pt(2.70)Cu(2.3)	2	0.90	2.70	2.30	unmodified	-
Pt(2.90)Cu(2.65)y	2	0.97	2.90	2.65	modified	yeast
Pt(3.00)Cu(2.63)p	2	1.00	3.00	2.63	modified	polymer

3.4.5 ASC selectivity to N_2

The product distribution over the single-layer washcoated Pt/Al₂O₃ monolith has been discussed in detail in chapter 2. The Pt/Al₂O₃ is highly active for NH₃ oxidation but poorly selective to N₂. Fig. 3.9(a) shows a dramatic reduction in the N₂ selectivity, decreasing from ~100% at ~200 °C to 0% at ~500 °C. Incorporation of the top SCR layer significantly improves the N₂ selectivity (Fig. 3.9(a)), demonstrating the working principle of the dual layer ASC in converting NO_x produced by the Pt-based bottom layer to N₂ through lean, NH₃-based NO_x reduction.

A key question with the washcoat modification is whether the gain in NH₃ conversion efficiency come at the expense of a loss in N₂ selectivity. N₂ is the major product of NH₃ oxidation over dual-layer ASC with selectivity of 80% or higher throughout the temperature range (Fig. 3.9(a)). A point of fact seen in Fig. 3.9(a) is that the N₂ selectivity is maintained at a high level during the gain in NH₃ conversion. Fig. 3.9(b) shows that at intermediate temperature the main selectivity loss is to N₂O while Fig. 3.9(c) and Fig. 3.9(d) respectively show that the production of NO at moderate to high temperature and NO₂ at high temperature are the main undesired byproducts. The high Pt loading sample [Pt(4.80)Cu(2.75)] has a comparatively lower N₂ selectivity due to the Pt loading and slightly lower SCR loading. However, N₂ selectivity remains relatively unaffected or within the measurement error with washcoat modification.

N₂O is an undesired reaction product at intermediate temperature regime with maximum yield around 270 °C (Fig. 3.9(b)) shows that N₂O selectivity in the dual-layer samples is notably lower than that of the single-layer Pt/Al₂O₃ for similar Pt loading. While testing (NH₃ + NO + O₂) reaction over Cu-SSZ-13, the maximum N₂O was ~ 5-10 ppm

which precludes the formation of N_2O in top layer of dual-layer ASC. Thus, the $\text{Pt}/\text{Al}_2\text{O}_3$ layer is responsible for formation of N_2O in the dual-layer ASC. The presence of the SCR top layer leads to some of the NH_3 reacting with counter-diffusing NO which results in a lower N_2O selectivity. The polymer-modified dual-layer has a somewhat lower N_2O selectivity than the yeast-modified sample (Fig. 3.9(b)). This may be due in part to the slightly lower Pt loading for the polymer-modified sample. A detrimental impact of residual ash with the yeast-modified layer cannot be ruled out, however.

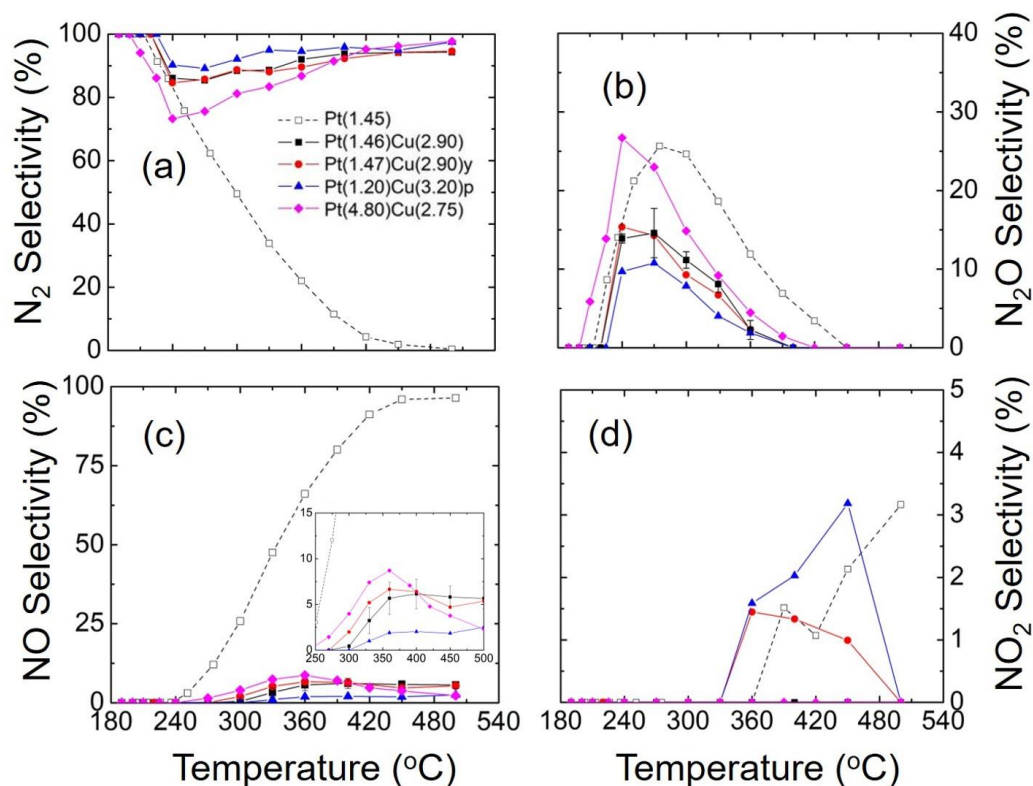


Figure 3.9 Steady state N_2 (a), N_2O (b), NO (c) and NO_2 (d) selectivity as a function of temperature over dual-layer ASC samples. Feed composition: 500 ppm NH_3 , 5% O_2 and balance Argon, GHSV 332 k h^{-1}

The single layer $\text{Pt}/\text{Al}_2\text{O}_3$ has a much higher NO selectivity compared to the dual-layer ASC since the NO produced in base Pt layer reacts with fraction of incoming NH_3 in

top Cu-SSZ-13. The pore structure changes in the top layer do not appreciably impact the NO selectivity (Fig. 3.9(c)). Finally, the NO₂ was measured to be in the 5-10 ppm at temperatures above 350 °C. No NO₂ was detected in unmodified dual-layer samples.

3.4.6 High temperature hydrothermal aging of SCR samples

It is of interest to determine whether the washcoat modifications impact is sustained for aged catalyst. To probe this issue, all four Cu-SSZ-13 samples were systematically aged at 800 °C in flowing medium consist of 5% O₂, 5% H₂O and balance argon for 4 h. After aging, standard SCR was carried out for a range of temperatures. The measured trends shown in Fig. 3.10 show the elimination of the “sea gull” shape of the unmodified sample (Fig. 3.10) which is consistent with Luo et al. [17,72] studies which mentioned elimination of the high temperature active site with hydrothermal aging. The overall activity of all the samples increased with aging, attributed to the Cu ion redistribution phenomena [73,74].

In relevance to our diffusion study, after aging the increase in NO_x conversion with washcoat modification persist and this further substantiate our claim of enhanced diffusion with modified washcoat. Above 250 °C, the NO_x conversion of the modified samples (Cu(2.1)y, Cu(2.1)p) is ~10% higher than unmodified sample Cu(2.1). Both Cu(2.1)y and Cu(2.1)p exhibit NO_x conversions comparable to that of the unmodified sample of high Cu loading Cu(3.2) for temperatures above ~250 °C. Unlike the unaged SCR catalyst behavior (Fig. 3.4), the NO_x conversion curves (Fig. 3.10) do not converge at high temperature. This underscores the importance of washcoat diffusion even at very high temperature. The analysis of controlling regimes will be reported in our forthcoming modeling study.

Finally, the washcoat properties of aged samples were also studied by performing

transient NH_3 TPD experiments as explained in previous section. The TPD results of aged samples (Fig. 3.11) showed only one desorption peak unlike the unaged samples (Fig. 3.6) due to elimination of second site. To our point of interest, the NH_3 breakthrough curves are consistent as unaged samples, steeper in case of modified samples $\text{Cu}(2.1)\text{y}$ and $\text{Cu}(2.1)\text{p}$ as compared to gradual breakthrough of unmodified sample $\text{Cu}(2.1)$ (Fig. 10). This further validate our point that mass transport limitation exists in SCR washcoat and same can be improved by modifying washcoat architecture. Also, the total NH_3 storage was approximately the same as the baseline sample before and after aging, demonstrating that the sacrificial agents do not alter hydrothermal stability of the $\text{Cu}\text{-SSZ-13}$.

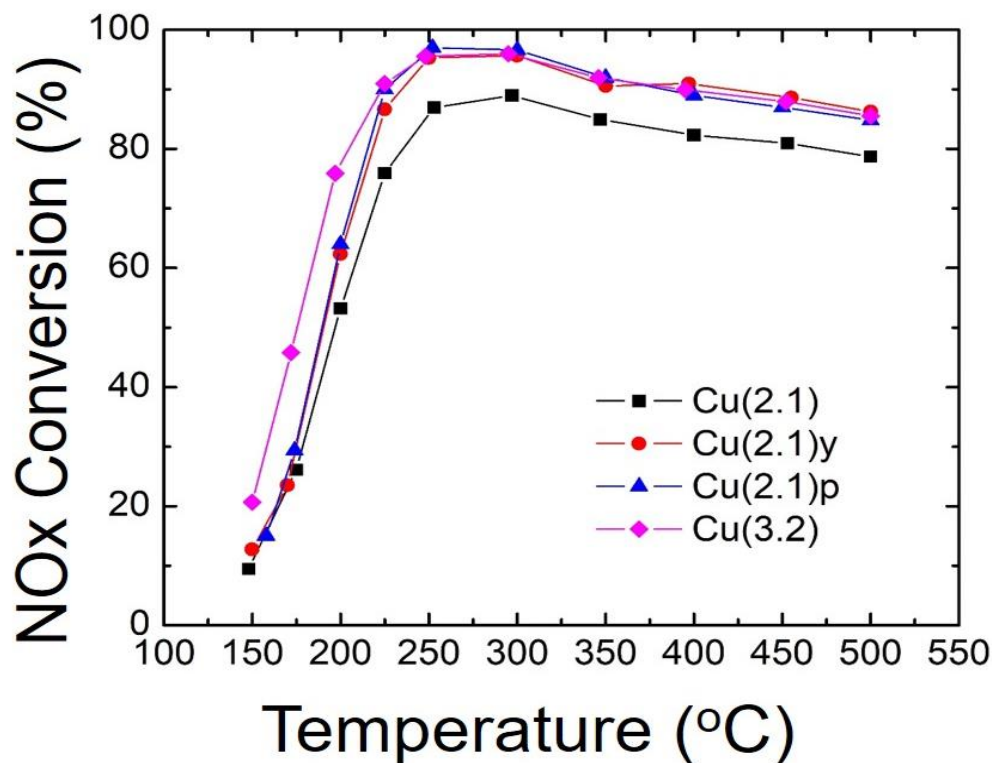


Figure 3.10 Steady state NO_x conversion as a function of temperature over single layered $\text{Cu}\text{-SSZ-13}$ samples after hydrothermal aging. Feed composition: 500 ppm NO , 500 ppm NH_3 , 5% O_2 and balance Argon, GHSV 66 k h^{-1}

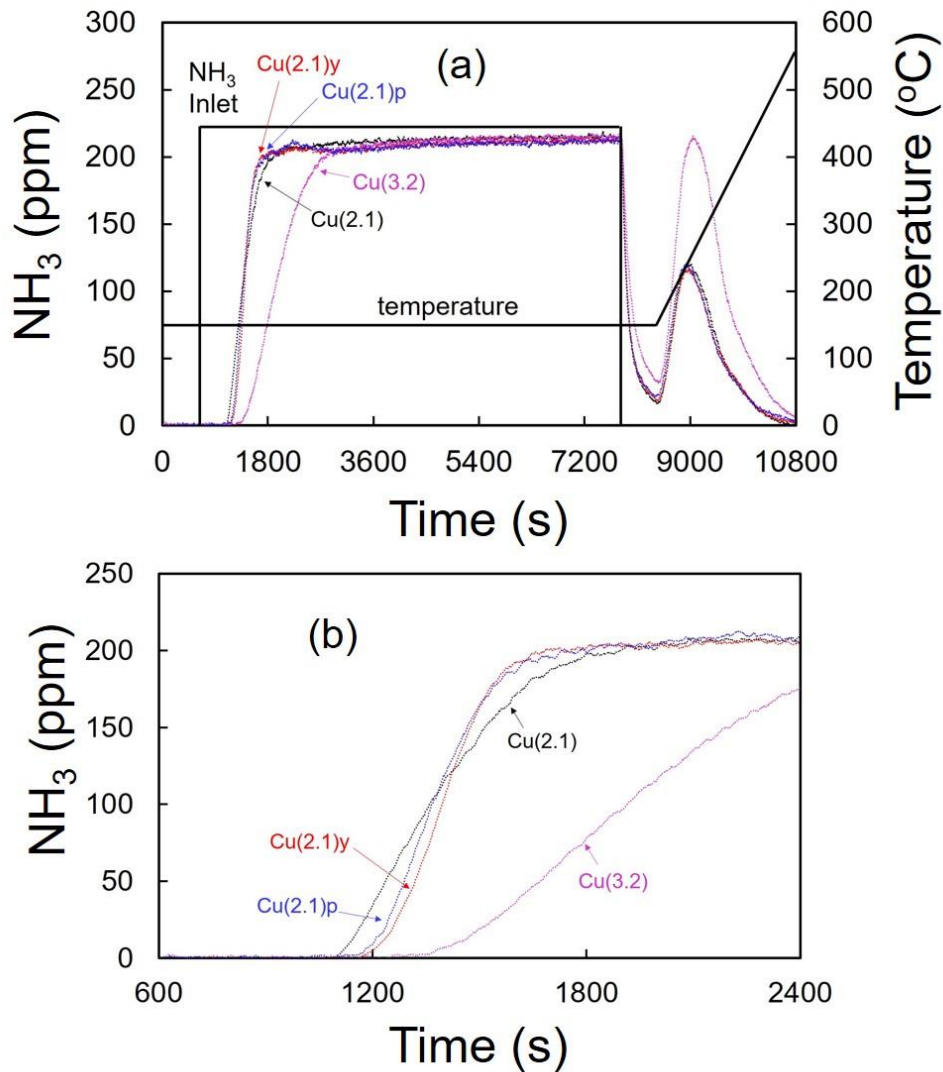


Figure 3.11 (a) Transient NH_3 evolution as a function of time during temperature programmed desorption study after hydrothermal aging. For clear distinction in breakthrough, bottom plot (b) is shown on cropped time scale.

3.5 Conclusions

Single-layer Cu-SSZ-13 and dual-layer ASC washcoats modified using sacrificial agents were systematically evaluated under standard SCR and NH_3 oxidation reaction conditions and compared to unmodified samples. The performance studies confirm that

washcoat diffusion in Cu-SSZ-13 is rate controlling over a range of conditions. The creation of macroporosity with sacrificial agents demonstrates a promising and economical way to enhance catalyst performance. Steady state reaction experiments performed on unmodified and modified Cu-SSZ-13 coated monoliths show a noted increase (~10% absolute) in NO_x/NH₃ conversions during standard SCR and NH₃ oxidation. Experiments with modified dual-layer ASC samples show a similar enhancement in the NH₃ conversion compared to the unmodified catalyst. The creation of macropores is found to be an economic way of increasing the monolith catalyst productivity. For both SCR and ASC, the requisite loading of active ingredients (Cu for SCR, Pt for ASC) may be lowered while maintaining the same productivity. The washcoat modification procedure creates some cracks and cavities which may negatively impact washcoat mechanical integration but that could be improved with revised catalyst synthesis procedure.

Chapter 4. Modeling and analysis of enhanced mass transport

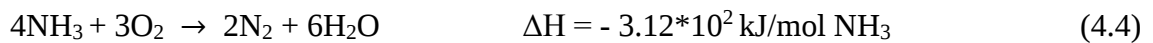
4.1 Introduction

Ammonia (NH₃) based selective catalytic reduction (SCR) has emerged as the technology of choice to eliminate NO_x from lean burn engine exhaust. NH₃ reacts selectively with NO_x over Cu- and Fe-exchanged zeolites to form N₂ through both standard, fast, and NO₂ SCR:



Cu- exchanged SSZ-13 exhibits excellent activity, selectivity and thermal stability for SCR (Kwak et al. [21, 32], Metkar et al. [19], Paolucci et al. [75, 76] & Gao et al. [13]).

The main side reaction is NH₃ oxidation by O₂:



which becomes important at high temperature (~400 °C).

To make up for undesired NH₃ oxidation (4.4), NH₃ is supplied in slight excess of the 1:1 (NH₃: NO_x) stoichiometry required by reactions (4.1) and (4.2). Despite sophisticated aqueous urea dosing strategies, unreacted NH₃ slip occurs. To mitigate NH₃ release to the atmosphere, the slipped NH₃ is oxidized to N₂ in the downstream Ammonia Slip Catalyst (ASC). State-of-the-art ASC comprises a bottom PGM (usually: Pt/Al₂O₃)

layer and a top SCR (Cu-SSZ-13 in this study) layer. The workings of the dual-layer ASC are described in detail elsewhere (Scheuer et al. [26]; Shrestha et al. [33]). The main challenge is to achieve high ammonia conversion and N_2 selectivity while minimizing ASC cost and volume.

The high activity of Cu-SSZ-13 leads to transport limitations within the porous washcoat, resulting in incomplete utilization of active sites. Achieving a high N_2 selectivity in the dual-layer ASC requires a thicker top SCR layer, however, this negatively impacts the NH_3 conversion as it poses a diffusion barrier (Shrestha et al. [27]). In chapter 3, it is showed that the effective SCR and ASC catalytic activity may be enhanced through the use of sacrificial pore-forming agents that increase the macroporosity of the Cu-SSZ-13 layer. An increase in the NH_3 conversion may be achieved without compromising the N_2 selectivity by modifying the morphology of top SCR layer.

The objective of this study is to predict the improved performance of single layer SCR and dual-layer ASC samples that have been modified with the pore forming. A systematic approach is followed by combining independently developed SCR and ammonia oxidation kinetic models. The model shows the impact of the porosity modification on the catalyst performance over a wide range of conditions for both SCR and ASC. New insights are provided for both SCR and ASC. The study has been published [111] and is reproduced with a permission from the Royal Society of Chemistry.

4.2 Literature review

Many researchers have studied SCR over Cu- and Fe-zeolites, some of which have developed predictive kinetic models, although there have been far fewer monolith reactor models for SCR. Metkar et al. [19] developed global kinetic models for Fe- and Cu-ZSM-

5 washcoated monoliths, showing good agreement with transient NH_3 uptake and TPD along with steady-state reaction spanning kinetic to transport controlled regimes. Olsson et al. [12,62] reported a multi-site kinetic model for Cu-SSZ-13 that captures transient NH_3 TPD and reaction results along with interpretation of SO_2 poisoning and regeneration. In these studies, a fixed value of effective diffusivity is used over a range of operating conditions. Joshi et al. [64] modeled bi-modal NO_x conversion for SCR over Cu-SAPO-34. The presence of two types of active sites is not uncommon in Cu-CHA; Gao et al. [77] has observed the same. More recently the homogeneous nature of Cu active site in Cu-SSZ-13 was reported by Paolucci et al. [76] and Gao et al. [77] questioning the fundamental definition of Cu-SSZ-13 as a heterogeneous catalyst. Joshi et al. [78] reported a negative activation energy for SCR reaction over Cu-SSZ-13 at high temperatures attributed to NH_3 desorption. Sjoval et al. [79,80] and Olsson et al. [12] reported a kinetic model for Fe- and Cu-zeolite while assuming negligible mass transfer limitation through washcoat. Similarly, Bendrich et al. [81] has reported a detailed kinetic model for Cu-SSZ-13 investigating nitrate formation while neglecting internal washcoat diffusion that might lead to incorrect estimation of kinetic parameters. The assumption of negligible internal diffusion also leads to the unrealistic step increase in NH_3 uptake for transient adsorption modeling (Bendrich et al. [81]).

Few modeling studies have appeared for dual-layer washcoated ASC monoliths. Scheuer et al. [26] developed a detailed microkinetic reaction mechanism for NH_3 oxidation over Pt that has been used in this study. A dual-layer model reported by Scheuer et al. [26] showed some discrepancy in predicting light-off temperature. Shrestha et al. [33] modeled a dual-layer ASC with Fe-ZSM-5 as top SCR layer. Colombo et al. [28,29] and

Nova et al. [30] reported a detailed kinetic model for dual-layer ASC. To reduce computational efforts, a low dimensional modeling approach has been reported by Mozaffari et al. [82] based on the work of Joshi et al. [83] for single layer. To date, there have been no model of an ASC having Cu-SSZ-13 as the top SCR layer.

4.3 Model Description

4.3.1 Monolith Reactor Model

The reactor model is developed on a single washcoated channel with a square cross-section. Figure 4.1 illustrates the side and the front cross-sectional view of the channel. Most of the model assumptions follow from the works of previous reported models. The physical properties (such as viscosity or density etc.) are assumed constant based on the highly diluted feed mixture. The laminar flow ($Re \sim 60$) is assumed to be fully developed. Axial dispersion is neglected due to high axial Peclet number (50 or 300 for 0.4 or 2 cm long samples, respectively). Finally, the pressure drop along the channel is assumed negligible.

The 1 + 1 dimensional monolith model consist of species fluid phase balances that include axial convection and radial diffusion:

$$\frac{\partial x_{f,j}}{\partial t} = -\langle u \rangle \frac{\partial x_{f,j}}{\partial z} - \frac{k_{me,j}(Z)}{R_{\Omega 1}} (x_{f,j} - x_{s,j}). \quad (4.5)$$

The external mass transfer coefficient $k_{me,j}(Z)$ is calculated using the external Sherwood number Sh_e :

$$k_{me,j}(Z) = \frac{Sh_e(z)D_{f,j}}{4R_{\Omega 1}}. \quad (4.6)$$

A position independent Sh_e is used as reported in Joshi et al. [83] and Ramanathan et al. [84]. The fluid phase species diffusivities values, taken from our previous study, chapter 2.

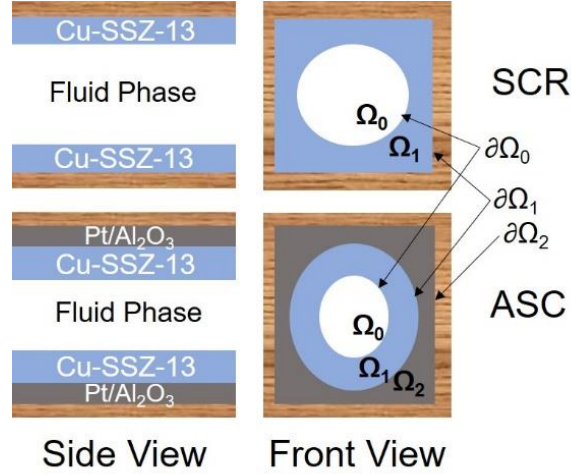


Figure 4.1 Schematic representation of side view (left) and front cross-sectional view (right) for washcoated monolithic channel, single layer SCR (top) and dual-layer ASC (bottom)

The 1+1 D model includes radial (transverse) diffusion along with reaction. For the single layer SCR, transport and reaction within the washcoat is described by the following species balances:

$$\varepsilon_{wc,scr} \frac{\partial x_{wc,scr,j}}{\partial t} = D_{e,scr,j} \frac{\partial^2 x_{wc,scr,j}}{\partial y^2} + \frac{1}{c_{Tm}} (\sum_{r=1}^{n_r} \vartheta_{jr} R_r(T, \theta, x_{wc,scr,j})). \quad (4.7)$$

Following previous studies, the boundary conditions for the single layer monolith is as follows:

$$x_{f,j}(t) = x_{f,j}^{in}(t) \quad \text{at } z = 0 \quad , \quad (4.8)$$

$$k_{me,j}(z)(x_{f,j} - x_{s,j}) = -D_{e,scr,j} \frac{\partial x_{wc,scr,j}}{\partial y} \Big|_{x_{wc,scr,j}=x_{s,j}} \quad \text{at } y = 0 \quad , \quad (4.9)$$

$$\text{and} \quad \frac{\partial x_{wc,scr,j}}{\partial y} = 0 \quad \text{at } y = R_{\Omega_2}. \quad (4.10)$$

Eqn. (4.8) is the Dirichlet inlet boundary condition derived from the Danckwerts boundary condition with high axial Peclet number (~ 300). Eqns. (4.9) and (4.10) describe the flux

balance at fluid-washcoat and washcoat-monolith wall interface, respectively. For the dual-layer ASC, mass balance is equated in the top and base washcoat layers by

$$\varepsilon_{wc,scr} \frac{\partial x_{wc,scr,j}}{\partial t} = D_{e,scr,j} \frac{\partial^2 x_{wc,scr,j}}{\partial y^2} + \frac{1}{c_{Tm}} (\sum_{r=1}^{n_r} \vartheta_{jr} R_{r,scr}(T, \theta, x_{wc,scr,j})) \quad (4.11)$$

and $\varepsilon_{wc,pgm} \frac{\partial x_{wc,pgm,j}}{\partial t} = D_{e,pgm,j} \frac{\partial^2 x_{wc,pgm,j}}{\partial y^2} + \frac{1}{c_{Tm}} (\sum_{r=1}^{n_r} \vartheta_{jr} R_{r,pgm}(T, \theta, x_{wc,pgm,j})). \quad (4.12)$

The subscripts “scr” and “pgm” distinguish the common parameters and variables. Boundary conditions for the single-layer SCR (eqns. (4.8) – (4.9)) are applicable to the top SCR layer. Additional boundary conditions include continuity of concentration and diffusive flux at the interface of the two layers; the diffusion flux continuity is as follows:

$$-D_{e,scr,j} \left. \frac{\partial x_{wc,scr,j}}{\partial y} \right|_{x_{wc,scr,j}=x_{s,j}} = -D_{e,pgm,j} \left. \frac{\partial x_{wc,pgm,j}}{\partial y} \right|_{x_{wc,pgm,j}=x_{s,j}} \quad \text{at } y = R_{\Omega,scr}. \quad (4.13)$$

Finally, the no-flux condition applies to the bottom PGM layer; eqn. (4.10) translates to eqn. (4.14) for the dual-layer ASC:

$$\frac{\partial x_{wc,pgm,j}}{\partial y} = 0 \quad \text{at } y = R_{\Omega 2}. \quad (4.14)$$

It should be noted that $R_{\Omega 1}$ and $R_{\Omega 2}$ values are different for the single-layer SCR and dual-layer ASC samples. The parameter values are reported in Tables 4.1 and 4.2.

Adsorbed species balances for each site type completes the model which is given by following surface species balance equations:

$$\frac{\partial \theta_k}{\partial t} = \frac{1}{c_{s1}} (\sum_{r=1}^{n_r} \vartheta_{kr} R_{r,scr}(T, \theta, x_{wc,scr,j})) \quad , \quad (4.15)$$

$$\frac{\partial \theta_k}{\partial t} = \frac{1}{c_{s2}} (\sum_{r=1}^{n_r} \vartheta_{kr} R_{r,scr}(T, \theta, x_{wc,scr,j})) \quad , \quad (4.16)$$

and $\frac{\partial \theta_k}{\partial t} = \frac{1}{c_{pt}} (\sum_{r=1}^{n_r} \vartheta_{kr} R_{r,pgm}(T, \theta, x_{wc,pgm,j})). \quad (4.17)$

Table 4.1. Modeling parameter for single layer SCR sample Cu(2.1)

Parameter	Value
R_{O1}	0.250e-3m
R_{O2}	50e-6m
R_{SCR}	35e-6m
R_{PGM}	15e-6m
$\epsilon_{wc,SCR}$	0.3
$\epsilon_{wc,PGM}$	0.4
λ_{PGM}	27.5
L	0.4e-2m
C_{pt}	1.6 mol exposed Pt/(m ³ of washcoat)

Table 4.2. Modeling parameter for ASC sample Pt(1.46)Cu(2.90)

Parameter	Value
a	1.1e -3m
R_{O1}	0.262e-3m
R_{O2}	25e-6m
$\langle u \rangle$	$0.49 \left(\frac{T}{273.15} \right) \left(\frac{a}{a-2R_{O2}} \right) \text{ (m/s)}$
ϵ_{wc}	0.3
λ_{SCR}	65
L	2e-2m
C_{Tm}	$(12187.3/T) \text{ mol/m}^3$
C_{S1}	600 moles/(m ³ of washcoat)
C_{S2}	290 moles/(m ³ of washcoat)
Sh_e	48/11

The program code for reactor model was written in MATLAB. A second order finite difference method was used to spatial discretize the species balances. These together with the surface species balances were integrated in time using a stiff solver “ode15s”.

4.3.2 Kinetic and mass transport parameter estimation

Two kinetic models are needed, one each for the ASC and the SCR. For ASC, the Pt-catalyzed NH₃ oxidation multi-step micro-kinetic reaction scheme reported by Shrestha

et al. [33] is used here without modification. Table 4.3 lists the reaction steps and the parameter values used.

A key first task at hand is to develop a predictive kinetic model for Cu-SSZ-13 catalyzed standard SCR that satisfactorily predicts the data reported in chapter 3 and is consistent with other literature. As highlighted above, several researchers have reported kinetic models for SCR on various metal-exchanged zeolites, including Cu-SSZ-13. An Eley Rideal type mechanism involving reaction between adsorbed NH_3 reacting with gas phase NO_x and O_2 has been shown to satisfactorily predict SCR data (Joshi et al. [64,83], Olsson et al. [62] & Metkar et al. [19]). The SCR reaction scheme provided in Table 4 consists of NH_3 adsorption-desorption, NH_3 oxidation and standard SCR elementary steps. Kinetic parameters are estimated through a fit of experimental data for transient NH_3 uptake and TPD, steady state NH_3 oxidation and standard SCR. It is instructive to explain how we converged on the set of reactions.

A limited number of NO oxidation experiments were carried out and very low NO conversion was observed even in the absence of water. This finding is in line with previous results [85]. Metkar et al. [86] showed that NO oxidation on Cu-SSZ-13 is inhibited by the formed product NO_2 with the reaction rate negative order with respect to NO_2 [86,87]. To this end, a scheme that includes steps for NO oxidation and fast SCR cannot be ruled out. However, with our intent to minimize the number of reaction steps, these steps were not included. Also, the experimental results show negligible N_2O formation (< 10 ppm), hence N_2O formation steps are not included in the reaction scheme.

Table 4.3. Reaction scheme for NH₃ oxidation over Pt

No.	Reaction Step	Parameter Values		Rate Expression (R_i)
P1	$\text{NH}_3 + \text{b} \rightarrow \text{NH}_3 - \text{b}$	A'_1 E'_1	5.9e1 0	$k_1 C_{pt} X_{\text{NH}_3} \theta_b C_{Tm} T$
P2	$\text{NH}_3 - \text{b} \rightarrow \text{NH}_3 + \text{b}$	A'_2 E'_2	6.4e4 105.1	$k_2 C_{pt} \theta_{\text{NH}_3}$
P3	$\text{O}_2 + 2\text{a} \rightarrow 2\text{O} - \text{a}$	A'_3 E'_3	1.6e2 0	$k_3 C_{pt}^2 X_{\text{O}_2} \theta_a^2 C_{Tm} T$
P4	$2\text{O} - \text{a} \rightarrow \text{O}_2 + 2\text{a}$	A'_4 E'_4	7.4e11 123.7	$k_4 C_{pt}^2 \theta_{\text{O}}^2$
P5	$\text{NH}_3 - \text{b} + 1.5\text{O} - \text{a}$ $\rightarrow \text{N} - \text{a}$ $+ 1.5\text{H}_2\text{O}$ $+ 0.5\text{a} + \text{b}$	A'_5 E'_5	6.1e15 139.3	$k_5 C_{pt}^2 \theta_{\text{NH}_3} \theta_{\text{O}}$
P6	$\text{NO} - \text{a} \rightarrow \text{NO} + \text{a}$	A'_6 E'_6	6.1e17 116.3	$k_6 C_{pt} \theta_{\text{NO}}$
P7	$\text{NO} + \text{a} \rightarrow \text{NO} - \text{a}$	A'_7 E'_7	2.8e2 0	$k_7 C_{pt} X_{\text{NO}} \theta_a C_{Tm} T$
P8	$2\text{N} - \text{a} \rightarrow \text{N}_2 + 2\text{a}$	A'_8 E'_8	1.1e19 172.3	$k_8 C_{pt}^2 \theta_{\text{N}}^2$
P9	$\text{N} - \text{a} + \text{O} - \text{a} \rightarrow \text{NO} - \text{a} + \text{a}$	A'_9 E'_9	1.1e14 129	$k_9 C_{pt}^2 \theta_{\text{N}} \theta_{\text{O}}$
P10	$\text{NO} - \text{a} + \text{N} - \text{a} \rightarrow \text{N}_2\text{O} + 2\text{a}$	A'_{10} E'_{10}	4.6e19 131.2	$k_{10} C_{pt}^2 \theta_{\text{NO}} \theta_{\text{N}}$
P11	$\text{NO} - \text{a} + \text{O} - \text{a}$ $\rightarrow \text{NO}_2 - \text{a} + \text{a}$	A'_{11} E'_{11}	2.5e14 102.4	$k_{11} C_{pt}^2 \theta_{\text{NO}} \theta_{\text{O}}$
P12	$\text{NO}_2 - \text{a} + \text{a} \rightarrow \text{NO} - \text{a} + \text{O} - \text{a}$	A'_{12} E'_{12}	5.6e9 76.3	$k_{12} C_{pt}^2 \theta_{\text{NO}_2} \theta_a$
P13	$\text{NO}_2 - \text{a} \rightarrow \text{NO}_2 + \text{a}$	A'_{13} E'_{13}	1.3e14 118.8	$k_{13} C_{pt} \theta_{\text{NO}_2}$
P14	$\text{NO}_2 + \text{a} \rightarrow \text{NO}_2 - \text{a}$	A'_{14} E'_{14}	4.8e4 0	$k_{14} C_{pt} X_{\text{NO}_2} \theta_a C_{Tm} T$

E_r is reported in kJ mol⁻¹

Experiment results including NH₃ TPD and SCR over a range of temperatures show evidence of at least two types of active sites for the Cu-SSZ-13 catalyst. Previous works have reported several active sites in Cu-SSZ-13, including Cu²⁺, [Cu(OH)]⁺, CuO and Brønsted acid sites, denoted by H⁺. We define the S1 site to represent the cupric cation in

the form of Cu^{2+} and $\text{Cu}(\text{OH})^+$ species while the S2 site represents H^+ . Cu may also exist in the form of CuO clusters which are known to be active for NO oxidation but have negligible activity for SCR [85]. High temperature hydrothermal aging eliminates a significant fraction of the S2 sites; this is discussed in more detail in the next section. The final set of estimated parameters for SCR is provided in Table 4.5.

Table 4.4. Reaction scheme for SCR over Cu-SSZ-13

Rxn. No.	Reaction Stoichiometry	Parameter	Rate Expression (R_i)
R1	$\text{NH}_3 + \text{S1} \leftrightarrow \text{NH}_3 - \text{S1}$	A_1, E_1	$k_{1f}C_{\text{cu},1}\theta_{v1}X_{\text{NH}_3} - k_{1b}C_{\text{cu},1}\theta_{\text{NH}_3-\text{S1}}$
R2	$\text{NH}_3 + \text{S2} \leftrightarrow \text{NH}_3 - \text{S2}$	A_2, E_2	$k_{2f}C_{\text{cu},2}\theta_{v2}X_{\text{NH}_3} - k_{2b}C_{\text{cu},2}\theta_{\text{NH}_3-\text{S2}}$
R3	$2\text{NH}_3 - \text{S1} + 1.5\text{O}_2 \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 2\text{S1}$	A_3, E_3	$k_3X_{\text{O}_2}C_{\text{cu},1}\theta_{\text{NH}_3-\text{S1}}$
R4	$2\text{NH}_3 - \text{S2} + 1.5\text{O}_2 \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 2\text{S2}$	A_4, E_4	$k_4X_{\text{O}_2}C_{\text{cu},2}\theta_{\text{NH}_3-\text{S2}}$
R5	$4\text{NH}_3 - \text{S1} + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} + 4\text{S1}$	A_5, E_5	$k_6X_{\text{NO}}C_{\text{cu},1}\theta_{\text{NH}_3-\text{S1}}$
R6	$4\text{NH}_3 - \text{S2} + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} + 4\text{S2}$	A_6, E_6	$k_7X_{\text{NO}}C_{\text{cu},2}\theta_{\text{NH}_3-\text{S2}}$

Table 4.5. Kinetic parameter values for Cu-SSZ-13

Parameter	Pre-aging value	Post-aging value	Parameter	Pre-/post- aging value
A1f	2.70E+01	3.70E+01	E1f	0
A1b	6.66E+07	5.70E+07	E1b	$120(1-0.25*\theta_{\text{NH}_3-\text{S1}})$
A2f	4.14E+02	1.33E+03	E2f	0
A2b	1.40E+03	8.88E+08	E2b	$142(1-0.09*\theta_{\text{NH}_3-\text{S2}})$
A3	4.66E+03	1.71E+03	E3	60
A4	2.07E+08	2.00E+08	E4	130
A5	2.16E+06	3.29E+06	E6	54
A6	1.72E+11	1.77E+10	E7	120

4.3.3 SCR kinetic experiments

Kinetic experiments were conducted using the standard SCR feed (500 ppm NO and NH_3 , 5% O_2 , balance Ar) to provide intrinsic differential rate data to augment integral

reactor data. In the temperatures range between ~150 to 175 °C the conversion varied between 7.7 to 14.6%. The measured activation energy was estimated to be 54 kJ/mol (Fig. 4.2a). With the assumption that site S1 is responsible for this low temperature activity, reaction step R5 activation energy was fixed at this value. Variation in the NH₃ concentration gave a NO reaction order of 0.83 for the NH₃ concentration fixed at 500 ppm and temperature fixed at 165 °C (Fig. 4.2b). Variation in the NH₃ concentration gave an apparent NH₃ order of -0.16 at a temperature of 168 °C (Fig. 4.2c) and fixed NO concentration of 500 ppm. The kinetic values found are consistent with previous literature reporting [19,62,88-91].

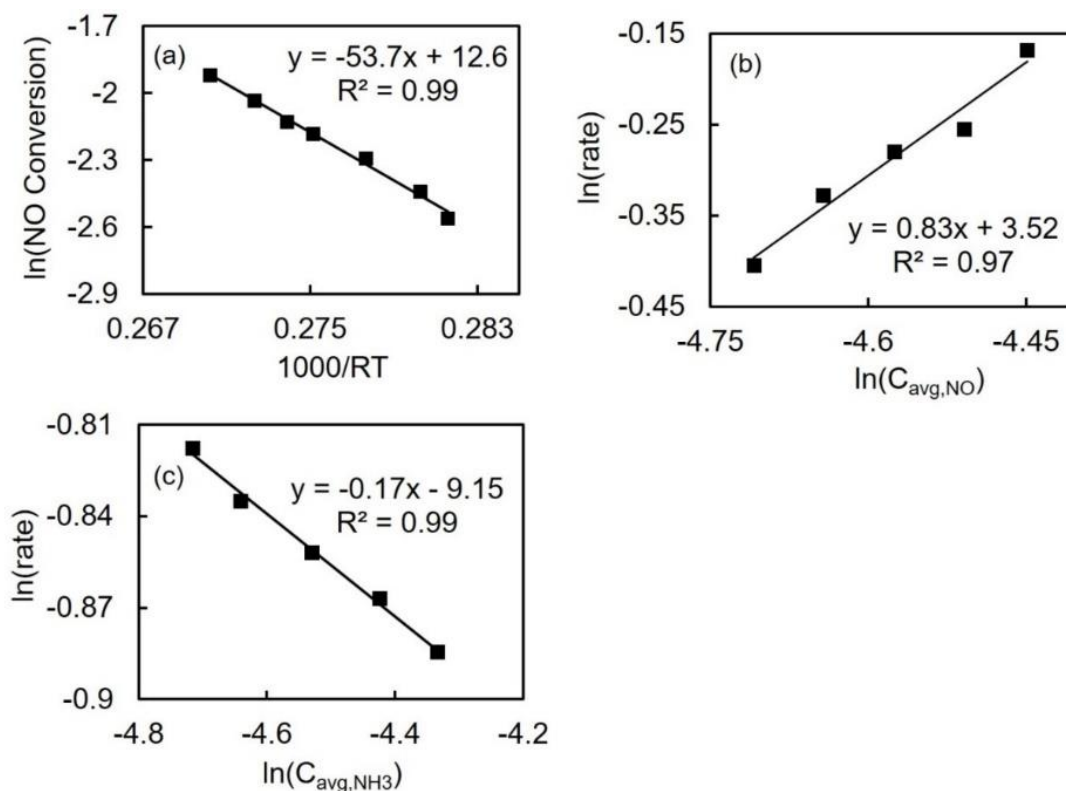


Figure 4.2 Activation energy plot (a), reaction order plot for NO (b) and NH₃ (c). Feed consists of NO, NH₃, O₂ and balance Ar at 66k h⁻¹; catalyst is Cu(2.1).

4.4 Results and Discussion

4.4.1 *NH₃ temperature programmed desorption*

The experimental protocol involved NH₃ exposure (220 ppm in Ar) for a prescribed time period (120 min) followed by a temperature ramp at 10 °C/min to 550 °C (see chapter 3 for more experiment details). The NH₃ uptake data reported in Figs. 4.3(a), (b) and (c) show typical breakthrough followed by an increase towards the feed concentration of ~220 ppm for the unmodified samples [4.3a: Cu(2.1); 4.3b: Cu(3.2)] and modified sample [4.3c: Cu(2.1)y]. Upon turning off the NH₃ feed, a sharp drop followed by a gradual elution of NH₃ occurred until the temperature ramp was initiated. At that point a sharp evolution of desorbing NH₃ in a first peak approximately 9,000 s into the ramp (~250 °C). A second, less pronounced peak occurred at ~400 °C. Eventually the NH₃ concentration approached 0 by 550 °C.

The data for Cu(2.1) were used to estimate kinetic parameters for steps R1 and R2 (Table 4.4). The NH₃ adsorption on both sites (E_{f1} and E_{f2}) was assumed to be inactivated, consistent with previous studies (Joshi et al. [64,78], Metkar et al. [19], Olsson et al. [62,92]). The desorption activation energies determined from a fit of the data revealed a coverage dependence for each site were as follows:

$$E_{b1} = 120(1 - 0.25\theta_{\text{NH}_3\text{-S1}}) \quad E_{b2} = 142(1 - 0.09\theta_{\text{NH}_3\text{-S2}}).$$

This coverage dependent Tempkin isotherm phenomenon has been reported by several researchers (Tronconi et al. [93], Chatterjee et al. [94], Joshi et al. [64,78], Olsson et al. [62,92], Busco et al. [95], Felix et al. [96] and Wilken et al. [97,98]). It is noted that the binding on site S1 involves isolated Cu cations and is a stronger function of NH₃ coverage than site S2, which comprises Brønsted sites.

The solid line in Fig. 4.3(a) is the model fit of the unmodified Cu(2.1) sample. The model satisfactorily predicts the uptake and release. Even subtle features such as the small overshoot during the uptake and the second peak appearing as a shoulder on the main desorption peak. Validation of the NH_3 uptake parameters was done for sample Cu(3.2) which had the same washcoat morphology and Cu wt.% in the washcoat but a higher washcoat loading (3.2 g/in^3). With the thickness of washcoat proportional to the Cu-SSZ-13 loading, $R_{\Omega 2}$ ($R_{\Omega 1}$) was accordingly increased (decreased) to 40 (250) μm . The absolute value of the washcoat thickness is based on SEM images. The kinetic parameters and λ_{SCR} value of 65 value was kept the same for Cu(3.2). The good agreement between the measured and predicted NH_3 concentration in Fig. 4.3(b) indicates that the model is adequately validated.

The modified sample Cu(2.1)y required estimation of λ_{SCR} as a result of porosity created by the yeast addition and calcination. Complicating this estimate is a possible effect of the yeast combustion on the Cu contained in the layer. That is, the combustion generates localized heat which might result in sintering and/or redistribution of the Cu cations. Moreover, post-combustion product of unknown composition is unavoidably left in the washcoat.

For these reasons, the λ_{SCR} value used for the modified sample was estimated from the model tuning of ammonia conversion data for the dual-layer modified ASC sample, Pt(1.46)Cu(2.90)y. As we show below, the λ_{SCR} value for the SCR layer is an important parameter impacting the conversion beyond the kinetic regime. Further, the estimated λ_{SCR} value should be less affected by possible changes in the Cu distribution and particle size. With this approach, the λ_{SCR} value for the modified washcoat was estimated to be ~ 32 .

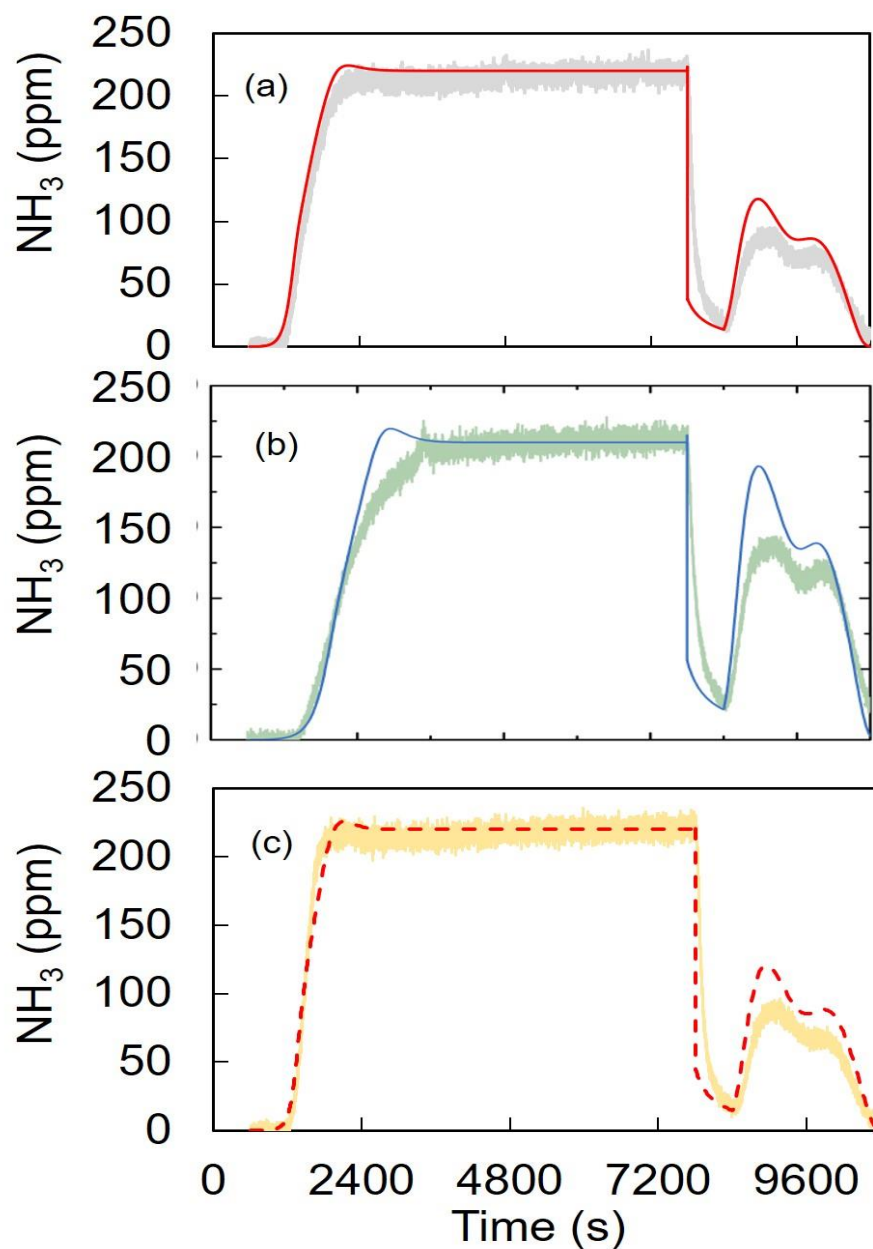


Figure 4.3 Transient NH₃ adsorption and temperature programmed desorption as a function of time in seconds. Experimental data (markers) and model predictions (lines) for Cu(2.1) sample (a), Cu(3.2) (b) and Cu(2.1)y (c).

The NH₃ transient plot for modified sample was calculated using $\lambda_{scr} \sim 32$ (Fig. 4.3c). The model predicts a somewhat more gradual NH₃ uptake than the measured value. This may be attributed to the aforementioned potential catalyst activity changes during the yeast

combustion. To investigate this further, it is found that slightly higher value of the pre-exponential factor A_{1f} of 31 give better fit compared to the original value of 27. In the next sections, we observe that model under-predicts NH_3 oxidation and standard SCR activity for the modified single layer sample. This may be explained by the aforementioned impact of the sacrificial component oxidation.

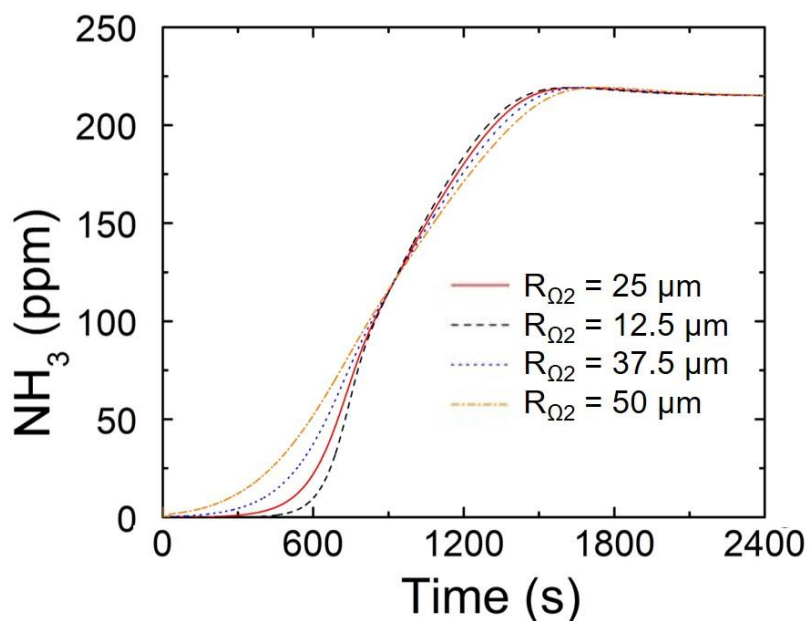


Figure 4.4 Simulation results showing effect of $R_{\Omega 2}$ (washcoat thickness) variation on transient NH_3 uptake utilizing fitted model for Cu(2.1).

Additional simulations for varied washcoat thickness were conducted, the results of which are shown in Fig. 4.4. λ_{SCR} was fixed at 65 while $R_{\Omega 2}$ was varied, and accordingly $R_{\Omega 1}$. Fig. 4.4 represents four different cases in which the thickness was increased from 12.5 to 50 μm and the corresponding length was adjusted from 1 to 4 cm, keeping the catalyst loading constant. It is seen that the washcoat with the thicker film and shorter length exhibits a more gradual NH_3 uptake compared to the longer samples with thinner washcoats. This further indicates that the washcoat diffusion limitations in Cu-SSZ-13 may

be lessened by enhancing the transport through washcoat using sacrificial agents [67].

4.4.2 NH_3 oxidation over Cu-SSZ-13

Steady-state NH_3 oxidation experiments using a feed of 500 ppm NH_3 and 5% O_2 were conducted to further assess the impact of transport. Three different SCR samples were compared; unmodified (Cu(2.1) & Cu(3.2)) and modified Cu(2.1)y. More details of the samples are provided in chapter 2. Fig. 4.5(a) represents experiment (symbols) and predicted (lines) values for the unmodified sample Cu(2.1). The Cu catalyst is not very active for NH_3 oxidation and require high temperature ($\sim 400^\circ\text{C}$) to initiate the reaction. Experimental data of Cu(2.1) was used to estimate kinetic parameters for steps R3 and R4. The nature of the experimental NH_3 conversion curves indicated the need to add NH_3 oxidation over both sites (S1 and S2). The contribution of each site may be examined by setting the respective adsorption constant equal to zero. Shown in Fig. 4.5(b) for simulated sample Cu(2.1), it is seen that S1 is active from 200-350 $^\circ\text{C}$ while site S2 is active at higher temperatures. Activation energies for R3 and R4 were estimated to be 60 and 130 kJ/mol. These values are comparable to previously reported values [62,64]. Recalling that site S2 represents Brønsted acid sites, the results indicate a higher activity for NH_3 oxidation on S2 compared to site S1. These findings are supported by experimental evidence that Brønsted sites favor NH_3 oxidation versus isolated Cu site [72,98].

Following the previous section, the kinetics were validated satisfactorily by simulating the higher loading unmodified Cu(3.2) sample (Fig. 4.6(a)). Further, the modified sample Cu(2.1)y was simulated by decreasing λ_{scr} to its estimated value of 32. Fig. 4.6(a) shows that the model slightly under-predicts NH_3 conversion attributed to kinetic changes with modification that has been discussed in previous section.

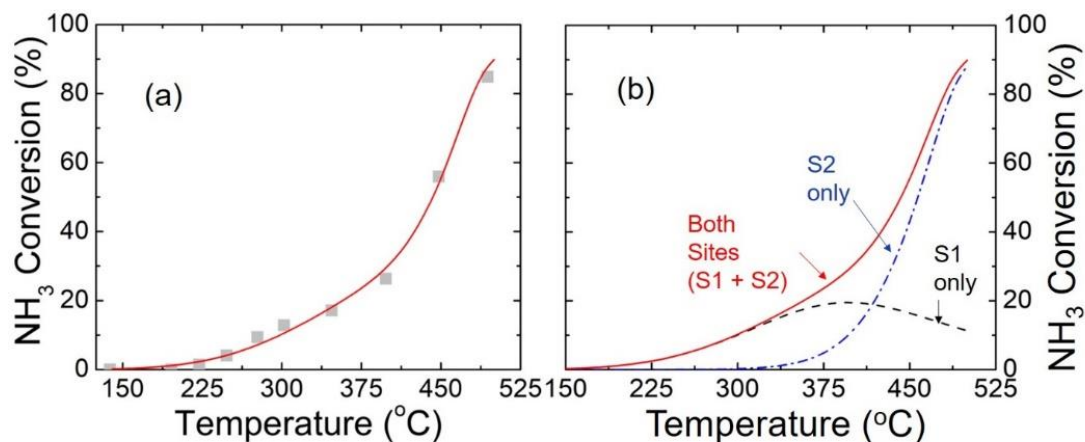


Figure 4.5 (a) Steady state NH₃ conversion function of temperature over Cu(2.1) with feed 500 ppm NH₃, 5% O₂ and balance Ar at 66k h⁻¹, (b) Active sites (S1 and S2) are deconvoluted and compared.

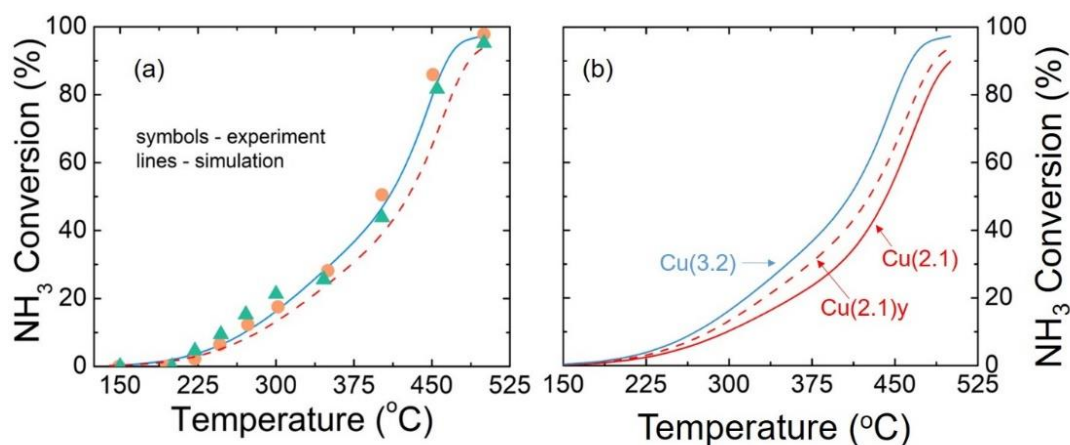


Figure 4.6 (a) Steady state NH₃ conversion as a function of temperature with feed consisting of 500 ppm NH₃, 5% O₂ and balance Ar at 66k h⁻¹ for Cu(3.2) (triangles and solid line) and Cu(2.1)y (circle and dashed line), (b) model comparison.

The NH₃ conversion improvements with washcoat modification that has been clearly seen in experiments are now confirmed with the model predictions. The effect of enhanced transport through washcoat is clearly evident (Fig. 4.6(b)); the enhancement is the largest at intermediate temperatures, bounded by the kinetic (low temperature) and external mass transfer (high temperature) regimes.

4.4.3 Selective catalytic reduction ($\text{NO}_x + \text{NH}_3 + \text{O}_2$)

Steady state SCR experiments were conducted for a feed containing 500 ppm NH_3 and NO, 5% O_2 and balance Ar at a space velocity of 66 k h^{-1} . The standard SCR reaction steps R5 and R6 were added to the mechanistic sequence. Earlier parameters associated with NH_3 uptake and TPD and NH_3 oxidation were fixed at their tuned values. An activation energy of 54 kJ/mol for step R5 was determined in kinetics measurements, as discussed earlier. The “sea-gull” shape of the NO conversion curve seen in Fig. 4.7a suggests that SCR occurs on two different active sites (S1 and S2). An attempt was made to simulate the SCR data by considering that SCR occurred on a single site (S1). Clearly, as seen in Fig. 4.7b, a single site model is unable to satisfactorily predict NO reduction at higher temperature. For this reason, step R6 involving site S2 was added to improve the model prediction. The activation energy for R6 was found using the aforementioned model tuning approach, giving an estimate of 120 kJ/mol. A much improved result is gotten by including R6. However, as seen in Fig. 4.7a, while the two-site model is able to predict an inflection point at an intermediate temperature, the model cannot predict the more prominent cusp of the sea-gull shape in the 250-300 °C temperature range. We expand on this point next.

Gao et al. [77] observed the sea-gull NO conversion versus temperature trend and attributed it to two different reaction paths at low and high temperatures. However, this interesting data feature has not been reported by many other researchers. This appears to be a result of the operating regime and catalyst properties, specifically the space velocity and Cu loading. More specifically, the sea gull feature was only observed at rather high space velocity and relatively low Cu loading. Too low a space velocity and/or too high a

Cu loading results in the NO conversion approaching 100%. This prevents the appearance of the sea gull feature.

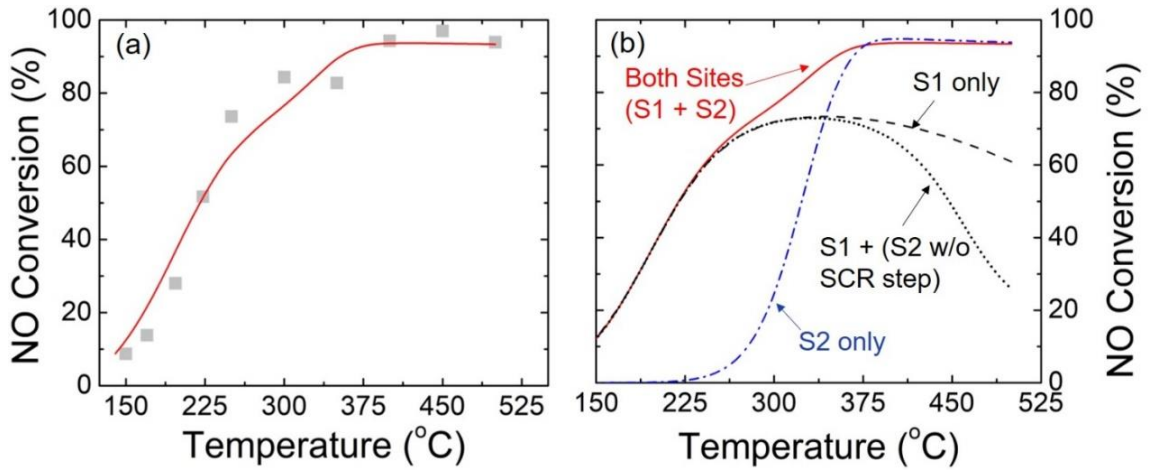


Figure 4.7 (a) Steady state NO conversion function of temperature over Cu(2.1) with feed 500 ppm NO, 500 ppm NH₃, 5% O₂ and balance Ar at 66k h⁻¹, (b) Active sites (S1 and S2) are deconvoluted and compared.

It is instructive to decipher the conditions in terms of key characteristic times of the relevant kinetic and transport processes. The characteristic times for convection, washcoat diffusion, standard SCR, and NH₃ desorption are given by the following:

τ_c : convection time

τ_d : washcoat diffusion time

τ_{R5} : Standard SCR (step R5) time

τ_{R1-} : NH₃ desorption time (Step R1 reverse)

Fig. 4.8 shows the variation of the characteristic times as a function of temperature. The convection time is the highest of the four times over the entire temperature range. Further, above 225 °C, the washcoat diffusion time exceeds the standard SCR time. This shows that at low temperature the conversion is kinetically limited but at intermediate temperatures

the conversion is washcoat diffusion limited. This explains why the NO conversion with enhanced washcoat diffusion in intermediate regime.

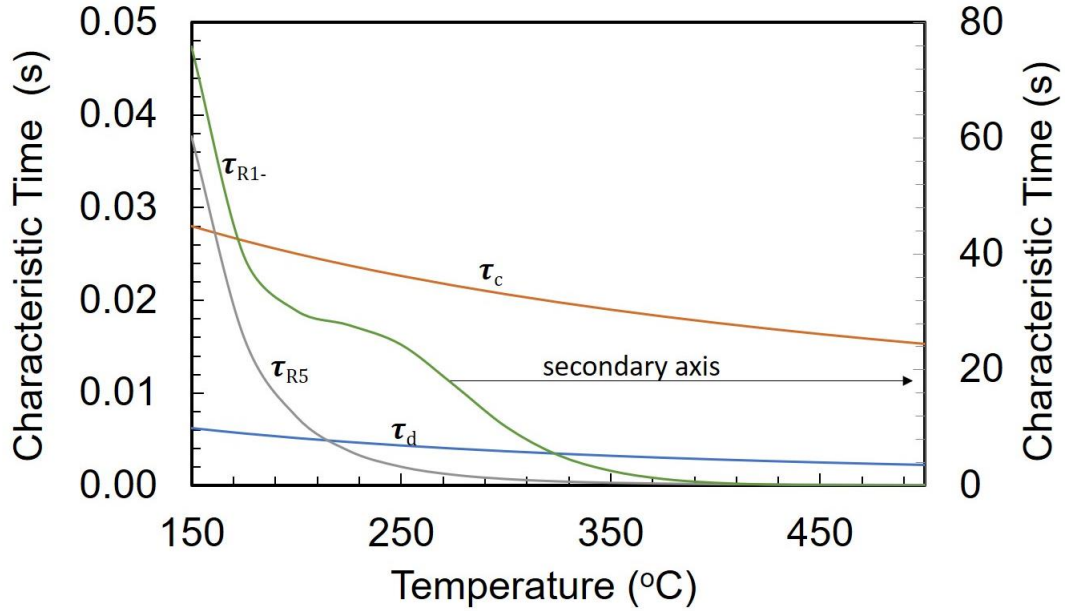


Figure 4.8 Characteristic time scales (s) for convection (τ_c), washcoat diffusion (τ_d), reverse reaction (τ_{R1-}) and reaction R5 (τ_{R5}) as a function of temperature (°C).

Fig. (4.7b) compares the NO conversion for four different cases; (i) R1-R5, (ii) R1-R6, (iii) reaction on S1 site only, and (iv) reaction on S2 site only. It can be seen in (i) that NO conversion significantly drops at high temperature. This is attributed to the cumulative effect of both NH_3 desorption from S1 and NH_3 oxidation over S2 at high temperature. Previously the explanation for this type of behavior had been obfuscated with NH_3 oxidation. Recently, Joshi et al. [78] reported an apparent negative activation energy for SCR reaction at high temperature attributed to NH_3 desorption. Following this argument, we eliminated all reactions on S2 that results in the Fig. (7b) scenario (iii); still some decline in NO conversion is noticed. This analysis again shows the necessity of including reaction step R6 i.e. SCR on S2 to satisfactorily predict the experimental findings.

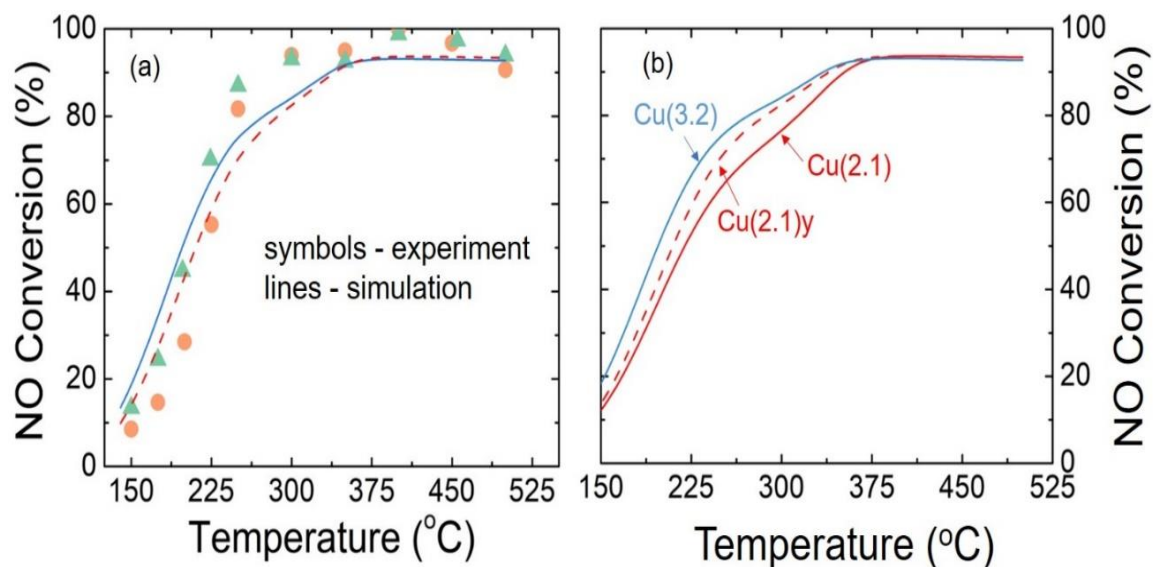


Figure 4.9 (a) Steady state NO conversion as a function of temperature with feed of 500 ppm NO and NH₃ each, 5% O₂ and balance Ar at 66k h⁻¹ for Cu(3.2) (triangles and solid line) and Cu(2.1)y (circle and dashed line), (b) Model comparison.

Kinetic parameters for steps R5 and R6 were validated through simulation of the higher loading, unmodified sample Cu(3.2), shown in Fig. 4.9a. Similar to Cu(2.1), the model shows some discrepancy for ~250-300 °C. Otherwise, the model predictions are satisfactory. The NO conversion increases with catalyst loading in the differential kinetic regime; this feature is captured well by the model. At temperatures above 375 °C, the NO conversion is controlled by external mass transfer since both samples exhibit the same high temperature limit. In the external mass transfer controlled regime, the transverse Peclet number ($Pe_t = \frac{R_{01}^2 \langle u \rangle}{LD_f}$) $\ll 1$ for the given reported conditions would suggest that the limiting conversion be 100%, which is not observed here. However, the faster NH₃ oxidation at high temperature prevents 100% NO conversion through SCR. This point is confirmed in Fig S3 in the Supplementary Material which shows the NO conversion when the ammonia oxidation steps (R3 and R4) are turned off. In that case the NO conversion

approaches 100% at high temperatures.

The modified sample Cu(2.1)y was modeled using the estimated kinetic parameters, $\lambda_{SCR} \sim 32$ and $R_{\Omega} = 28 \mu\text{m}$. A comparison of the modeling (dashed line) and experimental (symbols-circles) results show good agreement (Fig. 4.9a). The model predictions for each of the three samples are compared in Fig. 4.9b. The lower value of λ_{SCR} commensurate with the porosity increase leads to higher conversion in the intermediate temperature regime (250 – 400 °C) for the samples with the same washcoat loading. The results are consistent with experimental trends where washcoat modification show improvements in the intermediate temperature window.

It is of interest to determine if the incremental conversion gain achieved through the porosity creation is sustained for an aged catalyst. The unmodified and modified Cu-SSZ-13 samples were hydrothermally aged at 800 °C in 5% H₂O and balance Ar. Fig. 4.10(a) shows that the second TPD peak at higher temperature associated with site S2 almost disappears with the aging treatment. Nevertheless, amount of NH₃ storage remains nearly the same as the pre-aged samples as a result of an enlargement of the S1 desorption peak. This phenomenon has been studied in detail by Luo et al. [72] and Gao et al. [100]. Gao et al. [100] explained that two NH₃ molecule adsorb on isolated Cu²⁺ while Cu(OH)⁺ and Brønsted (H⁺) sites bind one NH₃ molecule each. Hydrothermal aging treatment transforms Cu(OH)⁺ to Cu²⁺ by reacting with its neighboring Brønsted site (H⁺), forming water. The fraction of site transformation depend upon temperature and aging time. It is shown that isolated Cu²⁺ sites are more active for low temperature activity while Cu(OH)⁺ facilitate high temperature SCR reaction.

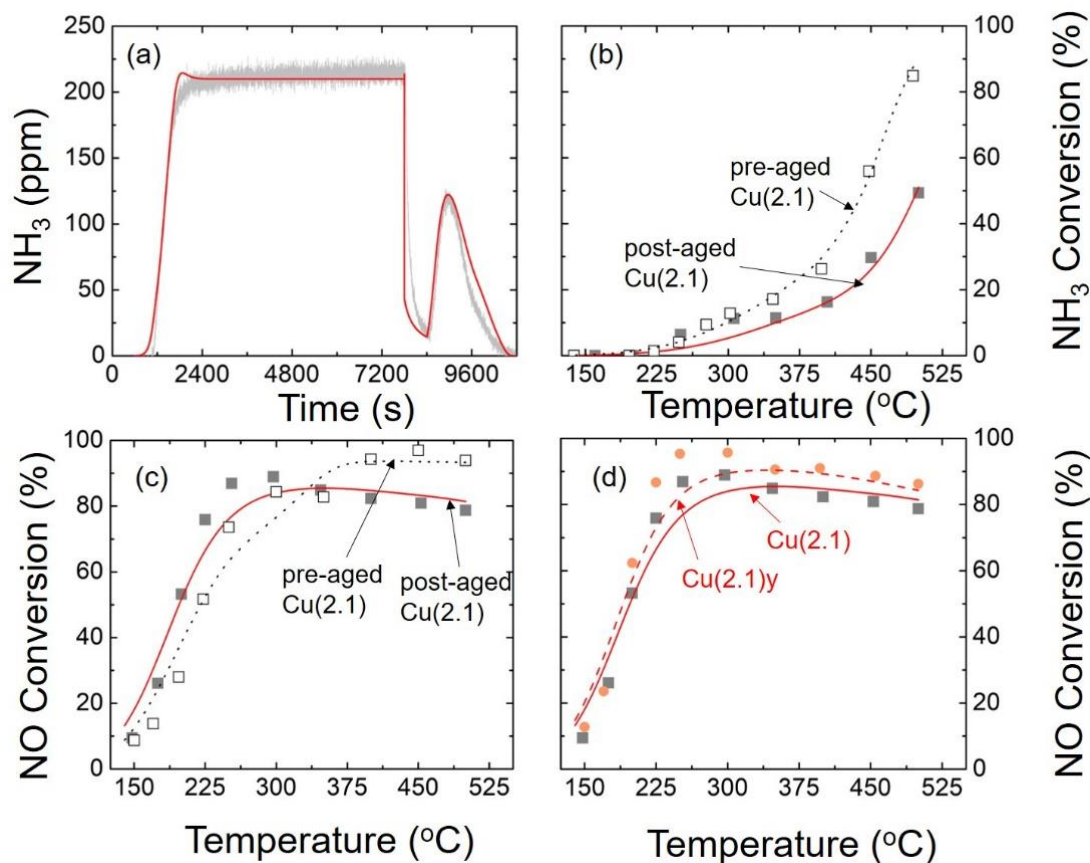


Figure 4.10 (a) Transient NH_3 adsorption and temperature programmed desorption, pre-aged and post-aged comparison using NH_3 oxidation (b) and SCR reaction (c). (d) Comparison performed for aged Cu(2.1) and Cu(2.1)y using SCR feed.

Now, as developed, site S1 represents isolated Cu^{2+} while S2 represents Brønsted (H^+) and $\text{Cu}(\text{OH})^+$ species. The S2 site density, C_{S2} was reduced from 290 moles/(m^3 washcoat) to ~ 90 moles/(m^3 of washcoat) to achieve a satisfactory fit for the NH_3 TPD data while increasing C_{S1} from 600 to 700 moles/(m^3 washcoat). Similarly, the kinetics for NH_3 oxidation and standard SCR were slightly modified to get a better fit. It is seen in Fig. 4.10(b) that NH_3 oxidation activity declines since the active site S2 is destroyed during the hydrothermal treatment. Post aging, the NH_3 oxidation rates (R3 and R4) reduce approximately to one-third of the pre-aged values. On the other hand, the NO conversion

during standard SCR actually increases. The SCR rate R_5 on the low temperature site S1 increases to ~ 1.75 times of the pre-aged R_5 while R_6 reduces to 0.03 times that of the pre-aged sample. The aged catalyst kinetic parameters are reported in Table 4.6. The low temperature NO conversion increases for both modified and unmodified samples. Finally, as before, the modified sample results were modeled using λ_{SCR} as 32 and modified $R_{\Omega 2}$. Unlike pre-aged samples, it is seen in Fig. 10d that effect of λ_{SCR} persists even at high temperature showing that the reaction remains in the mixed reaction + washcoat diffusion controlled regime.

4.4.4 Effect of space velocity

Space velocity is an important parameter that mainly determines the size of the SCR converter for a given feed flow rate. Experiments and simulations were conducted to study the washcoat diffusion impact as a function of space velocity. Fig. 4.11 shows the difference in the steady state NO conversion at 275 °C for the modified (Cu(2.1)y) and unmodified (Cu(2.1)) samples, with the lines and markers representing the simulated and experimental results, respectively. The data show a maximum in the % conversion enhancement at an intermediate space velocity. To the left of the maximum the decrease in the conversion enhancement with decreasing space velocity is attributed to the emergence of kinetics as the rate controlling process. At low space velocities the reactor residence time is sufficiently long to lessen the significance of external or internal mass transport. The maximum in the conversion enhancement for space velocity in the range of 100k – 150k h^{-1} conveys the importance of washcoat diffusion in that regime. Further increases in the space velocity leads to a decrease in the enhancement. At high space velocities the

reaction tends to occur at fluid-washcoat interface and external mass transfer tends to control the process. The model predictions capture the experimental trends. For both the pre- and post-aged samples the nonmonotonic trend is preserved. However, the post-aging washcoat modification effect at higher space velocity predominate the pre-aged.

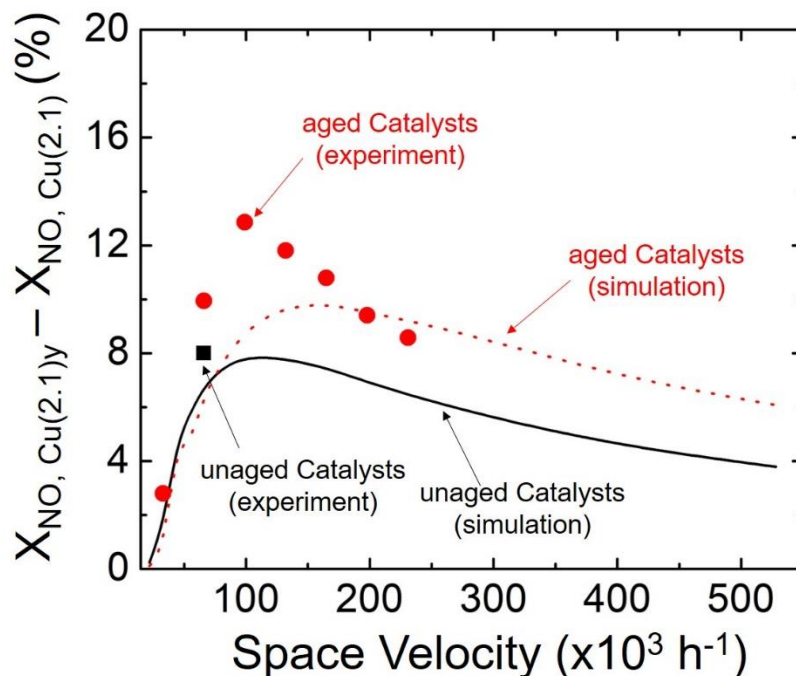


Figure 4.11 Steady state difference in NO conversions (%) for modified Cu(2.1)y and unmodified Cu(2.1) samples as a function of gas hourly space velocity (GHSV) using 500 ppm NH₃ and NO, 5% O₂ and balance Ar at 275 °C.

4.4.5 ASC NH₃ conversion and product distributions

The impact of porosity creation is anticipated to be particularly important for the dual-layer ASC, which by design operates in a washcoat diffusion controlled regime. Here we use an ASC reactor model to simulate earlier experimental results in which porosity creation was shown to be beneficial. The above-described SCR model is combined with a model for Pt/Al₂O₃ catalyzed NH₃ oxidation. The latter comprises the microkinetic scheme

originally developed by Scheuer et al. [26] which was successfully applied earlier by Shrestha et al. [33] and chapter 2. The kinetic parameters for the current study are reported in Table 4.5.

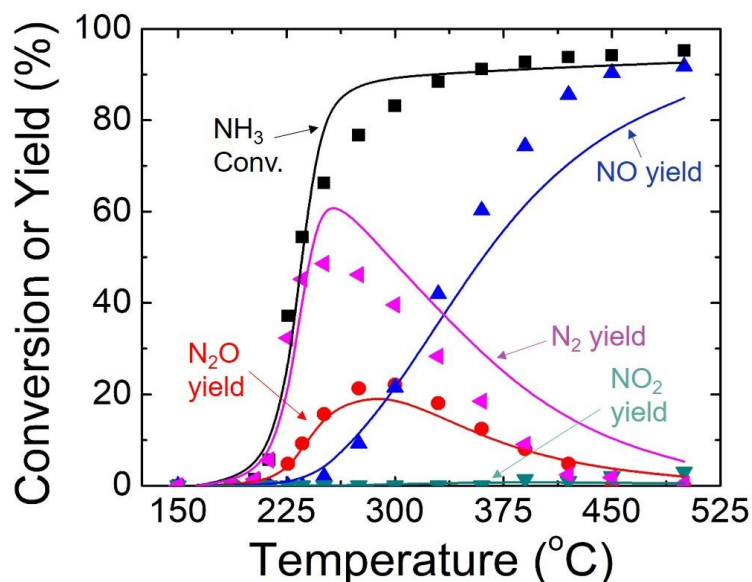


Figure 4.12 Steady state NH_3 conversion and product (NO , N_2O , N_2 , NO_2) yields as a function of temperature over sample Pt(1.45). Feed: 500 ppm NH_3 , 5% O_2 and balance Ar at 332 k h^{-1} . Symbols: Experiment, Lines: simulations.

Fig. 4.12 compares experimental (points) and predicted (lines) results for the single layer Pt/ Al_2O_3 ASC sample for a feed consisting 500 ppm NH_3 , 5% O_2 and balance Ar at 332 k h^{-1} . It is seen that NH_3 oxidation is highly active over Pt but poorly selective to N_2 . The light-off temperature is $\sim 225^\circ\text{C}$ for the 500 ppm NH_3 feed with the conversion rising steeply to $\sim 80\%$ by $\sim 300^\circ\text{C}$, and approaching 100% by $\sim 450^\circ\text{C}$. At temperatures below 300°C N_2 is the major product. The N_2 yield reaches a maximum at $\sim 240^\circ\text{C}$ and tends to 0 at 500°C . NO appears at $\sim 275^\circ\text{C}$ and increases towards 100% at temperatures exceeding 450°C . N_2O is another undesired product forms at low to moderate temperature.

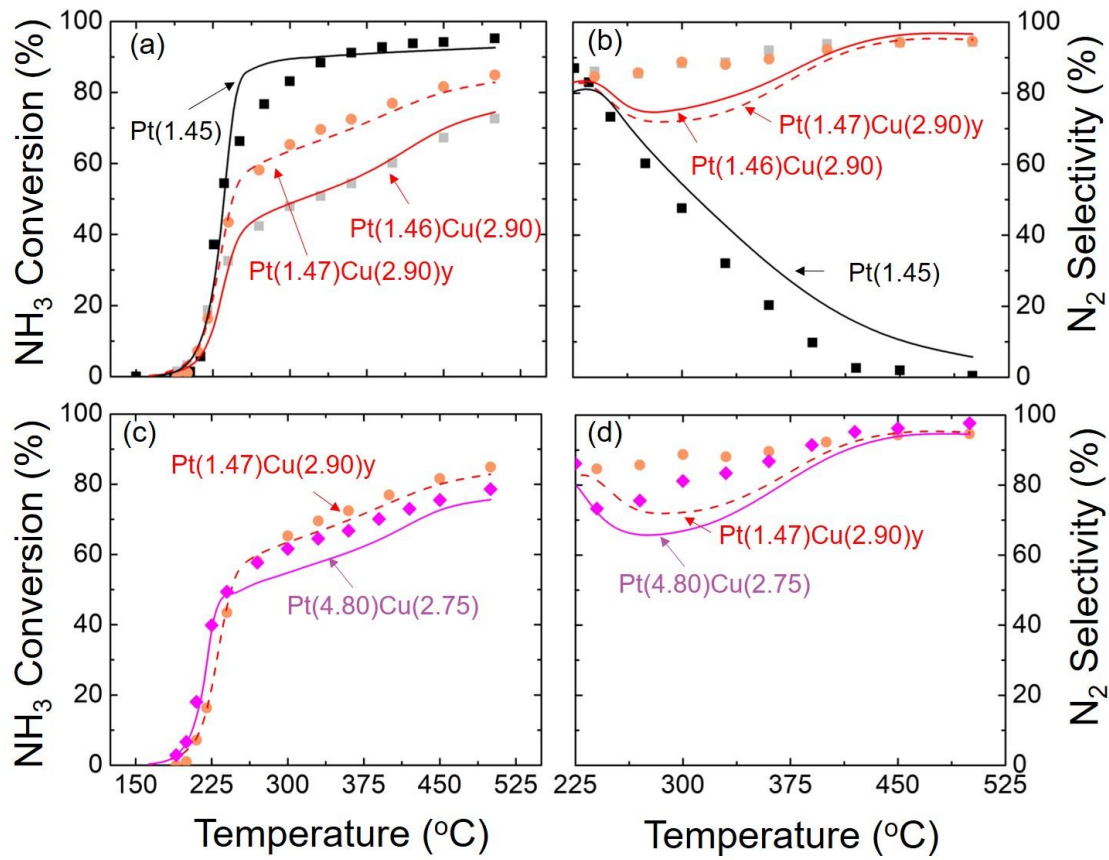


Figure 4.13 Steady state NH₃ conversion (a, c) and N₂ selectivity (b, d) as a function of temperature (°C) for differed samples. Feed: 500 ppm NH₃, 5% O₂ and balance Ar at 332k h⁻¹.

The model was validated in simulations of ASC's with different loading and with/without porosity modification, shown in Fig. 4.13. Without any adjustment in kinetic parameters for Pt or Cu, the unmodified Pt(1.46)Cu(2.90) sample results are simulated using λ_{SCR} as 65. A very good fit is evident in Fig. 4.13(a). This further validates the kinetic models for Cu-SSZ-13 and Pt/Al₂O₃. Figure 4.13(a) shows a significant decrease in NH₃ conversion with application of the top SCR layer. On the other hand, a decrease in NH₃ conversion is comparatively lower for the modified Pt(1.46)Cu(2.90)y sample (λ_{SCR} ~32 and R_{SCR} = 40 μ m). The NH₃ conversion increases by 10-15% above 225 °C with washcoat

modification and further substantiates the presence of diffusion limitations in the top SCR layer. For the unmodified sample, a sharpened increase in NH_3 conversion above 375 °C could be a result of direct NH_3 oxidation over site S2 of Cu-SSZ-1. The model predicts a slight decline in N_2 selectivity with modification (Fig. 4.13(b)), while experiment show negligible change.

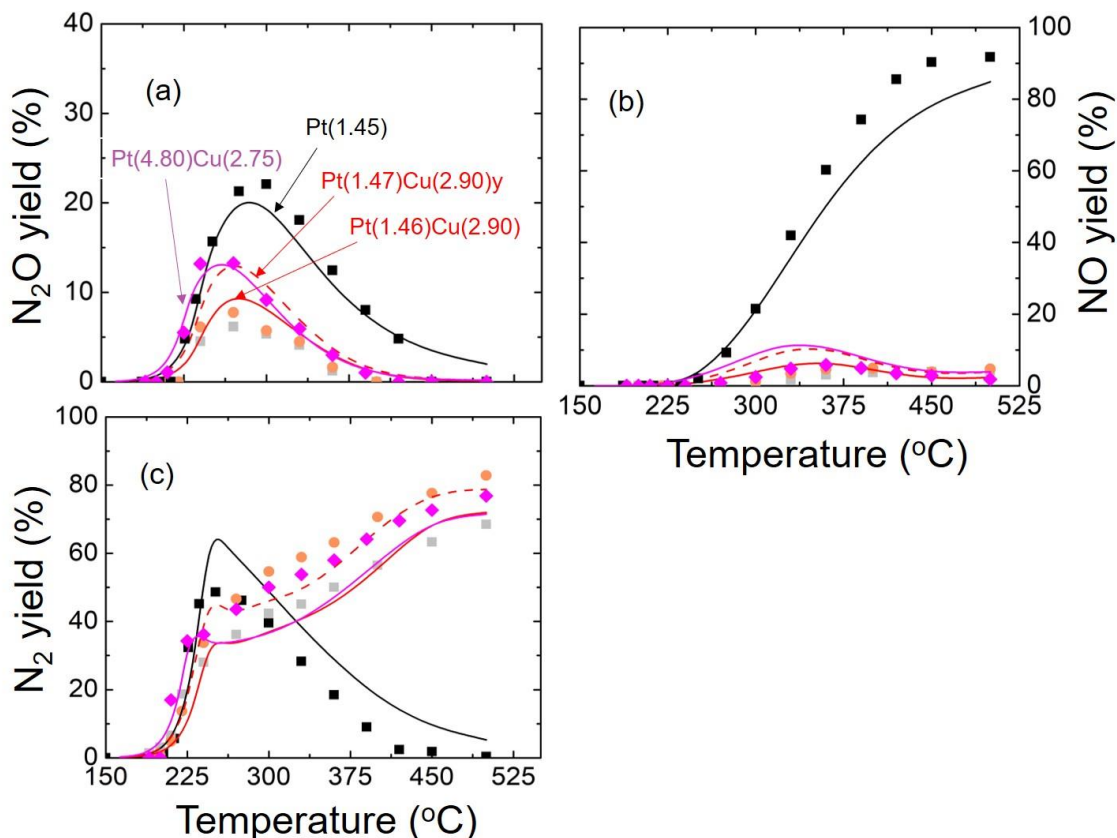


Figure 4.14 Steady state N_2O (a), NO (b) and N_2 (c) yield (%) as a function of temperature (°C) for different samples. Feed: 500 ppm NH_3 , 5% O_2 and balance Ar at 332k h^{-1} .

In another comparison, a dual layer, unmodified Pt(4.80)Cu(2.75) sample with very high bottom layer Pt loading of 4.8 g/ft^3 is compared to the low Pt loading modified sample Pt(1.46)Cu(2.90)y (Fig. 4.13c & 4.13d). The parameter C_{Pt} was increased from 1.6 moles/(m^3 of washcoat) to 4.5 moles/(m^3 of washcoat) to model the Pt high loading sample.

It is noted that at higher temperatures ($>300\text{ }^{\circ}\text{C}$), the low Pt loaded modified sample outperforms the higher Pt loaded unmodified sample. Further, the precious metal content can be reduced by $\sim 66\%$ with optimized architecture of top SCR layer while maintaining the same NH_3 conversion. Similar study [9] reporting better utilization of metallic sites with optimized washcoat has been performed for diesel oxidation catalyst. Fig. 4.14 provides the N_2O , NO and N_2 yields. It is noted that product yields do change accordingly with increase in conversion but the selectivities are only slightly impacted.

4.5 Conclusions

This modeling study is the continuation of our experimental study of enhanced transport through the Cu-SSZ-13 washcoat. The beneficial effects of modified (more-porous) washcoated Cu-SSZ-13 are further investigated through a kinetic model developed for Cu-SSZ-13. The kinetic parameters were estimated following a systematic approach of sequentially fitting transient NH_3 TPD, steady-state NH_3 oxidation and finally steady-state SCR. The impact of transport the variable λ_{SCR} (fluid diffusivity to effective diffusivity ratio) was estimated through a fit of the modified washcoat samples. A good fit of these data with a decrease in λ_{SCR} by 50% corroborated the earlier conclusion that the porosity increased enhanced the catalyst performance in the washcoat diffusion controlled regime. In addition, the study confirms that washcoat diffusion is a critical process for SCR on Cu/SSZ-13 over a wide range of operating conditions.

The estimated Cu-SSZ-13 kinetics were used to model dual-layer ASC comprising base Pt/ Al_2O_3 and top Cu-SSZ-13 layer. In case of dual-layer ASC, the λ_{SCR} value of the top SCR layer is found to be a very sensitive parameter with high degree of rate control.

The model verified the experimental results that more porous top SCR layer significantly improves NH_3 conversion while negligibly impacting product selectivities.

Chapter 5. ASC washcoat architecture optimization

5.1 Introduction

The ammonia slip catalyst (ASC) is the last of several catalytic reactors in the diesel engine aftertreatment system and serves the role of selectively oxidizing NH_3 to N_2 . Urea dosing to the upstream SCR is designed to provide a $\sim 1.1:1$ $\text{NH}_3:\text{NO}_x$ ratio to account for NH_3 oxidation losses. Unfortunately, the slip of NH_3 from the SCR is unavoidable and must be minimized [26-30]. A large number of catalysts have been studied for NH_3 oxidation, out of which Pt exhibits the highest activity [101-104]. However, Pt is poorly selective to N_2 , particularly at high temperatures ($> 300^\circ\text{C}$) where NO is the major product. [Remark: This obviously is a benefit for the classic Ostwald process for nitric acid production.] An additional undesired byproduct obtained at intermediate temperatures is the potent greenhouse gas N_2O .

For these reasons, a catalyst consisting of a mixture of Pt (oxidation activity) and $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ (reduction activity) is used to achieve a combination of high NH_3 conversion and high N_2 selectivity. The dual layer ASC is the commercial technology of choice which comprises a Pt/ Al_2O_3 base (bottom) layer and a Cu-exchanged zeolitic top layer. The latter is typically Cu-exchanged SSZ-13, which has emerged as the SCR catalyst of choice. The dual-layer architecture enhances N_2 selectivity in such a way that NO and NO_2 generated in the base Pt layer react with a fraction of counterflowing NH_3 in the top Cu/SSZ-13 layer to produce N_2 . The top layer increases N_2 selectivity at the cost of NH_3 conversion. The reason is straightforward: The diffusional resistance offered by the mesoporous top layer provides Cu and Bronsted acid sites for NH_3 uptake and reaction with NO/ NO_2 but also

lowers the NH_3 flux to the underlying $\text{Pt}/\text{Al}_2\text{O}_3$ layer. In chapter 3, we reported enhancement in the diffusional flux through a modified top $\text{Cu}/\text{SSZ-13}$ layer by a pore forming method that can increase NH_3 conversion by up to 15% without negatively impacting N_2 selectivity. Another way to reduce the detrimental diffusion resistance while retaining the coupling between the two functions is to combine the $\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{Cu}/\text{SSZ-13}$ as a single mixed washcoat. However, this approach has the drawback of NH_3 oxidation over Pt sites that are located at the fluid-washcoat interface which leads to an undesired increase in the NO selectivity [33].

In this study, a hybrid layer design combines a base layer of $\text{Pt}/\text{Al}_2\text{O}_3$ + $\text{Cu}/\text{SSZ-13}$ and a top $\text{Cu}/\text{SSZ-13}$ is examined. Shrestha et al. [27] has earlier introduced the hybrid sample morphology in 2016. More recently, Johnson Matthey researcher have introduced similar concepts in a series of patents [105-107]. To this end, we conduct a systematic study in which the hybrid design is compared to single and dual layer ASC catalysts for fixed overall loading of Pt and Cu/zeolite. The intent is to converge to an optimal catalyst that achieves the desired balance between NH_3 conversion and N_2 selectivity. A 1+1 dimensional monolith reactor model used to simulate the experiments which assists in interpreting trends and guiding experiments. The developed model is followed from Chapter 4.

5.2 Experimental Methods

5.2.1 Catalyst synthesis

Four different types of washcoated monoliths were prepared: (I) single $\text{Pt}/\text{Al}_2\text{O}_3$ layer; (II) dual layer with base $\text{Pt}/\text{Al}_2\text{O}_3$ layer and top $\text{Cu}/\text{SSZ-13}$ layer; (III) single layer

with a mixture of Pt/Al₂O₃ and Cu/SSZ-13; and (IV) hybrid layer with bottom mixed (Pt/Al₂O₃ + Cu/SSZ-13) layer and top Cu/SSZ-13 layer. Fig. 1 is a schematic that depicts the dual, mixed and hybrid layer sample types. The detailed specifications for each of the samples are provided in Table 5.1. All the synthesized samples had a 0.5 cm in length with a cross-section that numbered 28 channels cut from a 400 cpsi monolith core.

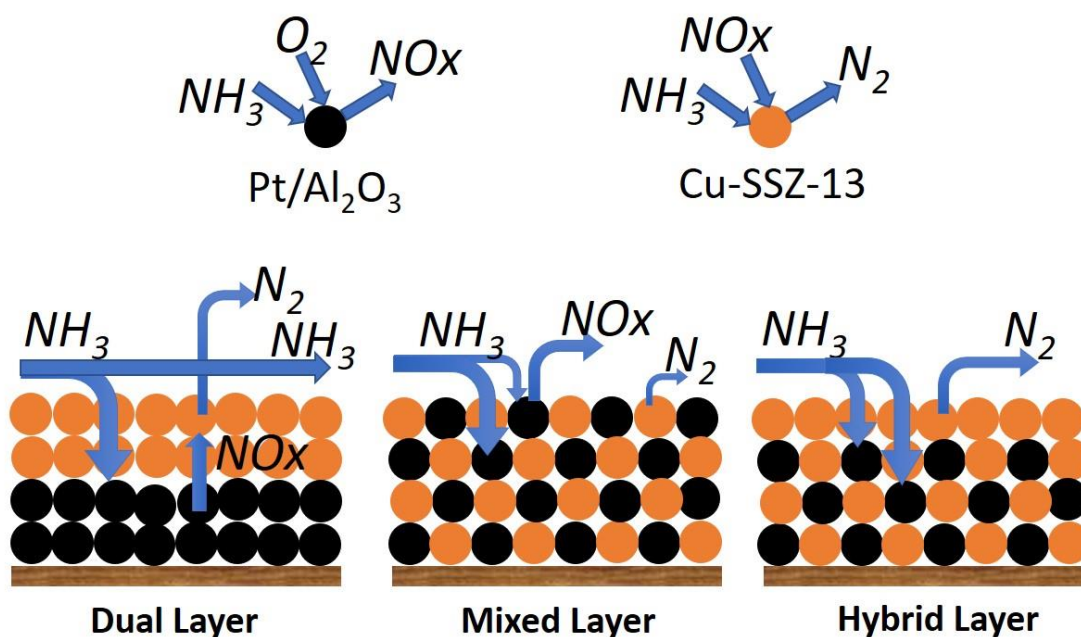


Figure 5.1 Schematic diagram representing bi-functional ammonia slip catalyst in three different washcoat structured morphology.

For Type I samples, Pt was impregnated into the γ -Al₂O₃ using the wetness impregnation of precursor chloroplatinic acid. A catalyst slurry was then prepared by mixing powdered Pt/Al₂O₃ with boehmite (20% AlOOH) and water in a ratio of 4:5:8. The pH of the slurry was maintained in the range of 3.5 to 4 to achieve the desired viscosity, using acetic acid or ammonia hydroxide. The slurry was ball milled for 20 h to reduce Al₂O₃ particles size to the 1-3 μ m range. For washcoating, the blank monolith was dipped

in the slurry for 30 s, followed by air blown through the channels for 10 s. The wet washcoated monolith was dried at 120 °C for 2 h. The dipping procedure was repeated to achieve the prescribed catalyst loading. Finally, the dried monolith sample was calcined at 500 °C for 5 h using a ramp up/down of 1 °C/min. The freshly prepared monolith was contacted with 2% H₂ at 500 °C to remove any residual Cl from the precursor.

Table 5.1 Samples description

Sample	base layer Pt loading g/ft ³ (Pt/Al ₂ O ₃ g/in ³)	base layer Cu-SSZ-13 g/in ³	top layer Cu-SSZ-13 g/in ³
S1	1 (1)	0	0
S2	1 (1)	3.1	0
S3	1 (1)	2.25	0.9
S4	1 (1)	1.5	1.6
S5	0.9 (0.9)	0.7	2.2
S6	1 (1)	0	3.1
S7	9 (0.9)	0	0
S8	10 (1)	3	0
S9	10 (1)	2.1	1.2
S10	10 (1)	1.5	1.8
S11	10 (1)	0	3.1
S12	1 (1)	2.5	0.35
S13	1 (1)	2.4	0.55

For Type II samples, the base Pt/Al₂O₃ layer was first applied over the blank monolith. A second slurry containing the zeolite was prepared by mixing Cu/SSZ-13 powder (provided by Johnson Matthey), boehmite, and water in the ratio of 4:5:8. Again, the pH was maintained to 3.5-4, and then ball milled for 20 h. The dipping-drying-calcination procedure was followed as described above to coat Cu/SSZ-13 over the Pt/Al₂O₃ coated monolith.

For Type III samples, the Cu/SSZ-13 and Pt/Al₂O₃ powder catalysts were physically mixed to achieve the desired loading ratios. The catalyst powder was then used

to prepare slurry by mixing it with boehmite and water in ratio 4:5:8. The same washcoating and drying steps were followed.

For Type IV hybrid samples, the mixed layer slurry was used to coat blank monoliths, followed by drying and calcination steps. The Cu/SSZ-13 was then coated over the mixed base layer. In order to achieve target loadings, several mixed layer slurries were prepared by mixing prescribed ratios of Pt/Al₂O₃ and Cu/SSZ-13 catalyst powders.

5.2.2 Reaction testing

The prepared monolith samples were tested in a bench scale reactor setup using a FTIR spectrometer to measure effluent concentrations. The monolith samples were wrapped in ceramic fibrefax and fitted in quartz tubes (I.D. 0.87 cm and O.D. 1.1 cm). The quartz tube was then installed in a furnace with thermocouple positioned at the center of the monolith (radially and axially). The feed conditions used to test all the samples were 500 ppm NH₃, 5% O₂ and balance Ar. The total gas flow was 1000 sccm which corresponds to a GHSV of 265k h⁻¹ (@ STP). The space velocity was intentionally kept high to more separate the performance of each of the samples. A lower space velocity would have a tendency to compress the conversions beyond the light-off point. All samples were pretreated for 90 minutes in 5% O₂ and balance Ar at 500 °C every time prior to reaction testing.

5.3 Model Description

5.3.1 Reactor model

The mathematical model used is followed from the modeling study explained in chapter 4 that investigated the performance of ASC washcoat morphology modification for the ASC. The 1+1 dimensional mathematical model consists of a fluid phase that is

discretized in the axial direction and a solid phase discretized in the radial direction. A single monolith channel is modeled assuming that each is identical. The following set of equations comprise the model:

$$\frac{\partial x_{f,j}}{\partial t} = -\langle u \rangle \frac{\partial x_{f,j}}{\partial z} - \frac{k_{me,j}(Z)}{R_{\Omega 1}} (x_{f,j} - x_{s,j}) \quad , \quad (5.1)$$

$$\varepsilon_{wc} \frac{\partial x_{wc,j}}{\partial t} = D_{e,j} \frac{\partial^2 x_{wc,j}}{\partial y^2} + \frac{1}{c_{Tm}} (\sum_{r=1}^{n_r} \vartheta_{jr} R_r(T, \theta, x_{wc,j})) \quad , \quad (5.2)$$

and
$$\frac{\partial \theta_k}{\partial t} = \frac{1}{c_{sites}} (\sum_{r=1}^{n_r} \vartheta_{kr} R_r(T, \theta, x_{wc,j})) \quad (5.3)$$

Equation 5.1 describes the transport in fluid phase with terms that account for axial convection and transverse diffusion, the latter using a mass transfer coefficient, $k_{me,j}(z)$. Axial dispersion is ignored due to the high axial Peclet number, $Pe \sim 75$. For the given flow rate the flow is laminar ($Re \sim 60$). Equation 5.2 describes diffusion and reaction in the transverse direction within the washcoat. An effective diffusion coefficient is used for each of the reacting species with the ratio of the fluid phase to solid phase diffusivity being given by the washcoat tortuosity to porosity ratio ($\frac{D_{f,j}}{D_{e,j}} = \tau/\varepsilon_{wc}$). Equation 5.3 describes the surface species balances involving surface coverages. The boundary conditions and inlet condition, are as follows:

$$x_{f,j}(t) = x_{f,j}^{in}(t) \quad \text{at } z = 0 \quad , \quad (5.4)$$

$$k_{me,j}(z)(x_{f,j} - x_{s,j}) = -D_{e,j} \frac{\partial x_{wc,j}}{\partial y} \Big|_{x_{wc,j}=x_{s,j}} \quad \text{at } y = 0 \quad , \quad (5.5)$$

and
$$\frac{\partial x_{wc,j}}{\partial y} = 0 \quad \text{at } y = R_{\Omega 2}. \quad (5.6)$$

The parameter values are provided in Table (5.2).

Table 5.2 Parameters used in reactor model

Parameter	Value
$R_{\Omega 1}$	0.250e-3m
$R_{\Omega 2}$	45e-6m
R_{SCR}	35e-6m
R_{PGM}	10e-6m
$\varepsilon_{wc,SCR}$	0.3
$\varepsilon_{wc,PGM}$	0.4
λ_{PGM}	27.5
L	0.5e-2m
C_{pt}	0.8 mol exposed Pt/(m ³ of washcoat)
a	1.1e -3m
$\langle u \rangle$	$0.49 \left(\frac{T}{273.15} \right) \left(\frac{a}{a-2R_{\Omega 2}} \right) \text{ (m/s)}$
λ_{SCR}	65
C_{Tm}	(12187.3/T) mol/m ³
C_{S1}	600 moles/(m ³ of washcoat)
C_{S2}	290 moles/(m ³ of washcoat)
Sh_e	3.608

5.3.2 Reaction kinetics

The reaction scheme over Pt reported Table 4.3 is based on a collection of elementary and quasi elementary steps involving various surface and gas phase species. The reaction scheme was developed from a first-principles DFT study for ammonia oxidation on Pt [111] based on two types of Pt(111) sites; top (a) and hollow (b) sites [108]. The top site facilitates NH₃ adsorption and desorption while hollow site involves the rest of the steps. The kinetic parameters reported in Table 4.3 were slightly adjusted to predict the experiment results for the Pt/Al₂O₃ layer sample (S1). Further refinement of the Pt ammonia oxidation kinetic model is underway and will be published elsewhere. The Cu/SSZ-13 reaction model also follows from modeling study explained in Chapter 4. The reaction scheme includes NH₃ adsorption-desorption, standard SCR and NH₃ oxidation

reactions. It adopts the Eley-Rideal mechanism in which reaction occurs between adsorbed ammonia and gas phase NO. The reaction steps are reported in Table 4.4.

5.4 Results

5.4.1 *NH₃ oxidation over single Pt/Al₂O₃ layer*

Fig. 5.2 represents experimental (symbols) and simulation (lines) results for NH₃ oxidation over Pt/Al₂O₃ (sample S1) with a Pt volumetric loading of 1 g/ft³ monolith. The light-off for the NH₃ oxidation occurs at ~275 °C (T₂₀ value – temperature giving 20% conversion) and increases sharply to 80% conversion by 300 °C. This is consistent with the study of Chapter 2 in which light-off in which the light-off occurred at ~225 °C for a Pt loading of 3 g/ft³ at the same flow rate and feed composition. A tuned monolith reactor model was used to simulate the data (Fig. 5.2). The model satisfactorily predicts the data with some discrepancy at lower temperatures. The model under prediction of the NH₃ conversion and N₂ yield is linked to the use of the dual site. An ongoing ammonia oxidation kinetics study is underway in which some refinement improves the low temperature predictability. Besides that point, the model predictions are within 5%.

The main product of the reaction is N₂ at low temperatures with a N₂ yield achieving a maximum at an intermediate temperature (~330 °C) before decreasing to 0 by 500 °C (Fig. 5.2). The model predicts that N adatoms are the main surface species at low temperature as the NH₃ sequentially loses H. The N adatoms combine, producing N₂ which quickly desorbs. The N₂O yield follows a similar trend, with its maximum encountered at ~340 °C. In order to form N₂O, a fraction of the N adatoms combine with O adatoms. Reaction between adsorbed NO and N produces N₂O. In addition, some researchers [40,41] have reported that adsorbed NO dissociates into N and O in the presence of a low

coverage of oxygen, particularly at low temperatures. Competition ensues between N_2O and NO production. That the N_2O yield goes through a maximum suggests that its rate of formation is eventually exceeded by the NO desorption rate. The NO/ N_2O ratio is a critical one since while NO may be catalytically reduced by NH_3 while N_2O is not. The NO desorption increases monotonically with temperature. At temperature exceeding $\sim 350^\circ\text{C}$, the Pt surface is predominantly occupied by O adatoms which facilitates NO and NO_2 formation [40]. NO oxidation to NO_2 occurs readily on Pt although the reaction is thermodynamically limited at high temperatures [109]. In the current experiments, the NO_2 formed was below the detection limit, likely due to a very low Pt loading. Previous works [109] have shown that the NO oxidation activity (turnover number) increases with Pt particle size. This is attributed to the oxidation of smaller Pt crystallites to Pt oxide which is less active than metallic Pt.

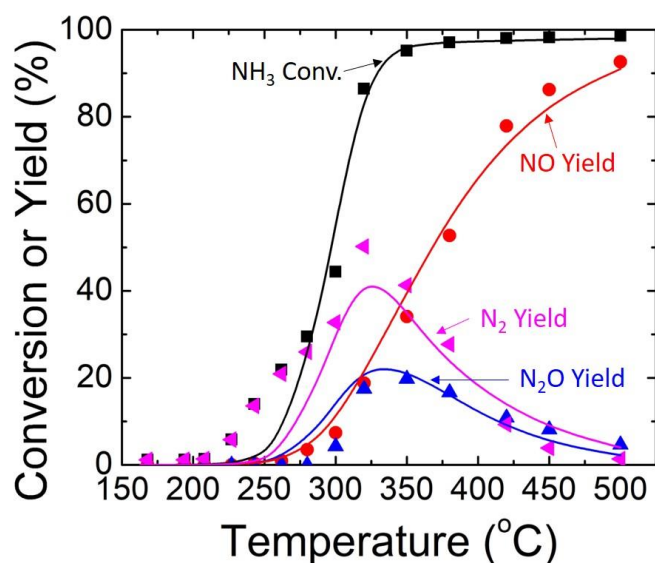


Figure 5.2 Steady state NH_3 conversion and product yields as a function of temperature over $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. Feed: 500 ppm NH_3 , 5% O_2 , Balance Ar and 265 k h^{-1} GHSV. (symbols: experiments, lines: simulations)

5.4.2 NH_3 oxidation over conventional dual-layer and uniform mixed layer

Fig. 5.3(a) compares experimental and simulation results for the dual-layer ASC sample (sample S6). The dual layer ASC is a bifunctional catalyst comprising a base Pt/ Al_2O_3 layer and top Cu/SSZ-13 layer. Application of the top Cu/SSZ-13 layer reduces the undesired products NO and N_2O to less than 10% with N_2 becoming the major product with a selectivity of $\sim 80\%$. The top Cu/SSZ-13 layer serves the dual role of catalyst and diffusion barrier, respectively causing reaction between the counter-diffusing NO and NH_3 and lowering the flux of NH_3 to the underlying Pt/ Al_2O_3 layer. The data show that by $\sim 500^\circ\text{C}$ the N_2 yield approaches $\sim 70\%$ for the dual layer catalyst but is $< 5\%$ for the Pt-only catalyst (Fig. 5.2). On the other hand, the data also show that at $\sim 500^\circ\text{C}$ the NH_3 conversion approaches $\sim 75\%$ with the dual-layer compared to $> 95\%$ for the Pt only layer (Fig. 5.2). This notable decrease in the NH_3 conversion is attributed to the transport limitation imposed by the top Cu/SSZ-13 layer [27].

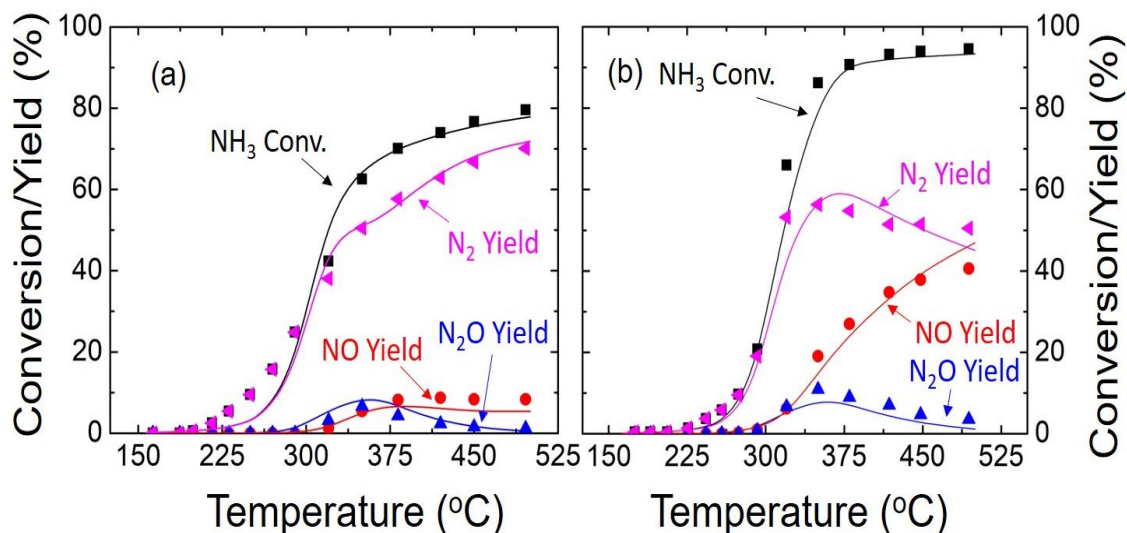


Figure 5.3 Steady state NH_3 conversion and product yields as a function of temperature over dual-layer (a) and mixed layer (b) ASC catalysts. Feed: 500 ppm NH_3 , 5% O_2 , Balance Ar and 265 k h^{-1} GHSV.

Figure 5.3(b) shows the experimental and predicted results for a uniform mixed layer ASC sample (S2). This bifunctional single layer catalyst contains a mixture of Pt/Al₂O₃ and Cu/SSZ-13. The NH₃ conversion approaches ~90% at high temperature, nearly as high as the Pt-only sample (Fig. 5.2) but the N₂ selectivity drops to ~50% compared to ~80% for the dual-layer sample. In addition, the NO yield for the mixed layer sample is ~40% (Fig. 5.3(b)) which is quite high compared to ~10% for dual-layer sample (Fig. 5.3(a)). The mixed layer washcoat architecture exposes some fraction of Pt directly to the flowing gas phase. As a result, fraction of the NO that is produced during the oxidation of NH₃ desorbs and enters the gas phase without encountering NH₃ and the Cu/SSZ-13 catalyst. As a result, the increase in NH₃ conversion comes at the expense of a decrease in the N₂ selectivity. The N₂O selectivity remains nearly the same for the dual layer and layer catalyst since N₂O is formed over Pt sites and remains unaffected by washcoat structure (Fig. 5.3).

The results shown in Fig. 5.3 suggests that either the dual layer or the mixed washcoat architecture do not provide an optimum solution. While the dual-layer is an improvement over the Pt-only catalyst and has outstanding performance at lower space velocity, further improvement is needed at higher space velocity in particular.

5.4.3 NH₃ oxidation over Hybrid ASC samples

With the dual-layer ASC sample exhibiting a high N₂ selectivity and moderate NH₃ conversion and the mixed layer ASC exhibiting high NH₃ conversion and mediocre N₂ selectivity, a compromise design is needed. The so-called “hybrid” ASC balances the higher conversion achieved with the mixed layer and the higher selectivity achieved with the dual layer. Hybrid samples comprise a base mixed layer of Pt/Al₂O₃ + Cu/SSZ-13 and

a thin top layer Cu/SSZ-13 layer. The details concern the targeted Pt and Cu loadings. To this end, two sets of hybrid ASC samples were synthesized; a low Pt loading set (1 g/ft³) and a high Pt loading set (10 g/ft³). For each set the Cu loading was distributed between the bottom mixed layer and the top zeolite layer. More specifically, five of the samples (S2-S6) have a fixed overall Pt loading (1 or 10 g/ft³) and Cu/SSZ-13 loading (3 g/in³); sample S1 is the single Pt/Al₂O₃ layer and is included for reference only. Samples S2 and S6 are mixed and dual layer sample, respectively, and were presented in the previous section. Samples S3, S4 and S5 are hybrid ASC samples with a base mixed layer and top SCR layer with loadings specified in Table 5.1. For example, sample S5 had a Cu/SSZ-13 loading of 2.2 g/in³ in the top layer with the balance of 0.7 g/in³ mixed with the Pt/Al₂O₃ in the bottom layer. This compares to sample S3 which has a Cu/SSZ-13 loading of 0.9 g/in³ in the top layer with the balance of 2.25 g/in³ mixed with the Pt/Al₂O₃ in the bottom layer. Samples S7 – S11 correspond to the higher Pt loading set (10 g Pt/ft³).

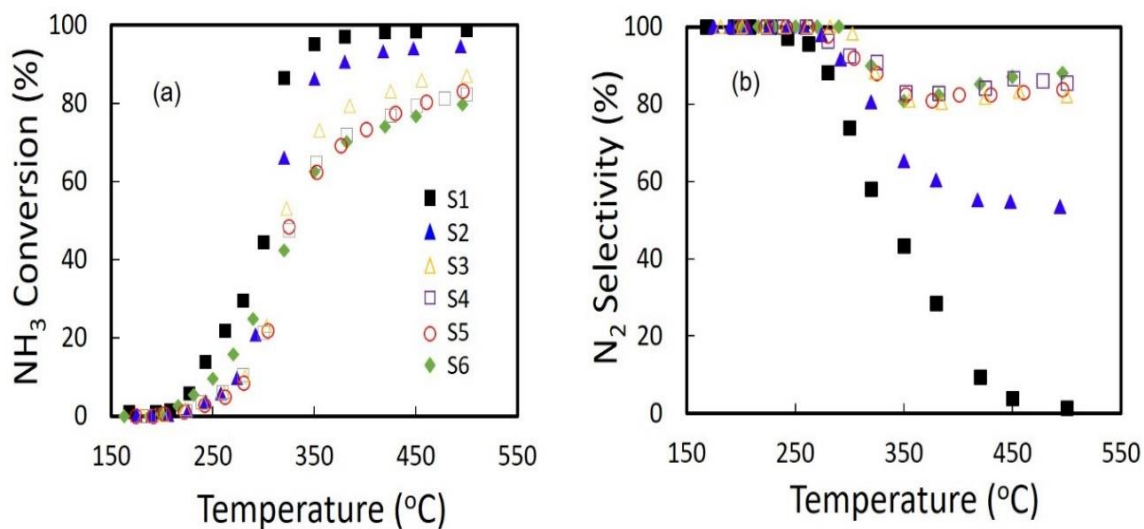


Figure 5.4 Experimental steady state NH₃ conversion (a) and N₂ selectivity (b) as a function of temperature for various ASC samples (details for samples are given in Table 1). Feed: 500 ppm NH₃, 5% O₂, balance Ar and 265k h⁻¹ GHSV.

Fig. 5.4 shows the steady state NH_3 conversion (4a) and N_2 selectivity (4b) for the six ASC samples (S1-S6) of the lower Pt loading (1g/ft^3). The same NH_3 oxidation operating conditions as in earlier experiments were used for the comparison. Sample S5 is essentially equivalent to the conventional dual layer sample (S6). Fig. 5.4 also shows that in the lower temperature regime ($< 300\text{ }^\circ\text{C}$), the single mixed layer (S2) or hybrid samples (S3 – S5) have a slightly lower NH_3 conversion than the dual-layer sample (S6). Since the physical mixture of $\text{Pt/Al}_2\text{O}_3$ and Cu/SSZ-13 were ball milled, a fraction of small $\text{Pt/Al}_2\text{O}_3$ (Nano) particles may have migrated within the cages of SSZ-13 zeolite, making it difficult to be accessed by the reacting species. At higher temperatures the NH_3 conversion for the mixed single layer sample (S2) exceeds that for all of the other samples except for the Pt only sample (S1). Further, the N_2 selectivity for the sample S2 is below that for all of the other samples (Fig. 5.4b). These results reflect the earlier findings in Fig. 5.3 comparing the mixed ASC with the dual layer ASC. The general trend is that as Cu/SSZ-13 is moved from the mixed layer to the top layer ($\text{S2} \rightarrow \text{S3} \rightarrow \text{S4} \rightarrow \text{S5}$) the high temperature NH_3 conversion decreases to the lower limit of the dual layer sample (S6). The decrease in conversion is clearly seen in Fig. 5.4. The enhanced conversion is a result of increased access to Pt sites while sufficient top layer Cu sites are available to maintain a high N_2 selectivity.

It is interesting to note that samples S4, S5, and S6 have nearly identical performance despite their composition differences. For example, for sample S4 the top SCR layer loading is 1.6 g/in^3 while the balance is mixed with the base $\text{Pt/Al}_2\text{O}_3$; this keeps the total Cu/SSZ-13 loading fixed at $\sim 3\text{ g/in}^3$. However, when compared to hybrid sample S5 or dual layer sample S6, the NH_3 conversion and N_2 selectivity show no noticeable

difference. The Hybrid samples facilitate a shorter diffusion distance (top layer thickness) for NH_3 from the bulk to the bottom layer but the dilution of the bottom layer $\text{Pt}/\text{Al}_2\text{O}_3$ layer with $\text{Cu}/\text{SSZ-13}$ makes the effective diffusion distance longer. Essentially, the effective number of Pt sites reached by NH_3 in samples S4 – S6 are the same. If enough $\text{Cu}/\text{SSZ-13}$ is moved from the top layer to the bottom mixed layer a shift is noted in the NH_3 conversion and N_2 selectivity. For example, sample S3 shows a 10% increase in NH_3 conversion compared to the dual layer sample S6.

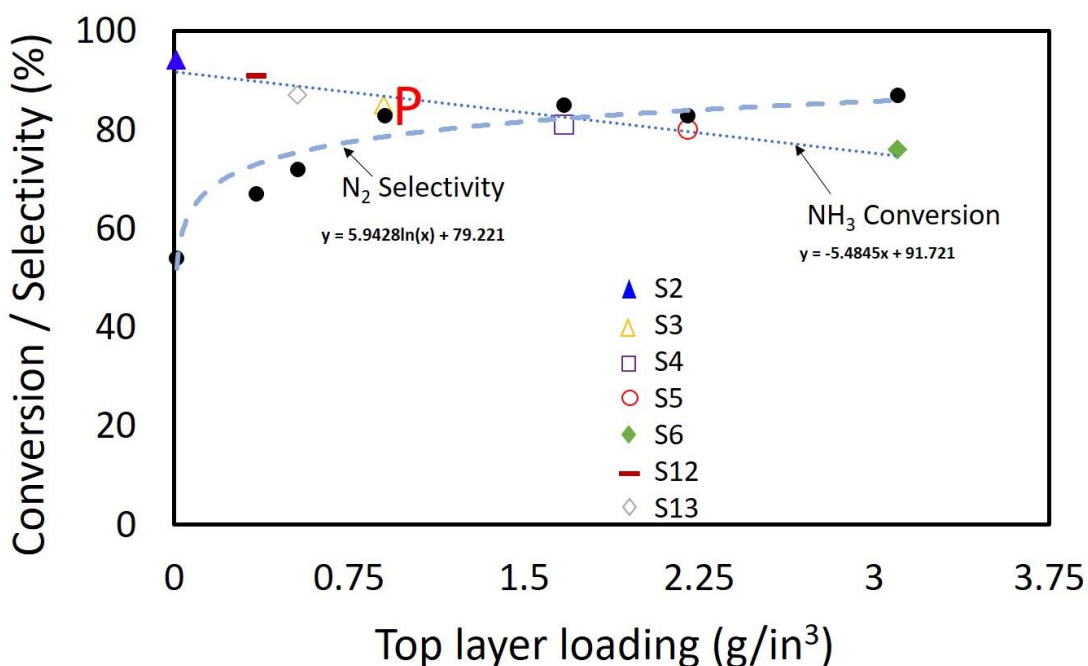


Figure 5.5 NH_3 conversion and N_2 selectivity analysis for various ASC samples at 450 °C. The conversion and selectivity are plotted as a function of top $\text{Cu}/\text{SSZ-13}$ layer loading. (symbols: experiments, lines: curve fit)

A plot of the NH_3 conversion and N_2 selectivity as a function of the top layer $\text{Cu}/\text{SSZ-13}$ loading (g/in³) is shown in Fig. 5.5. The reported data are for a temperature 450 °C. This plot provides a way of determining the optimal balance between the opposing

conversion and selectivity trends. The uniform mixed layer sample S1 corresponds to the none top layer Cu/SSZ-13 while the dual layer sample S6 corresponds to the right-most point at 3.1 g/in³. The points between these two extremes are hybrid the samples S2 – S5. Two additional hybrid samples S12 and S13 were synthesized having 0.35 and 0.55 g/in³ top layer loading, respectively. The trends in Fig. 5.5 show that NH₃ conversion decreases linearly with the top layer Cu loading while the N₂ selectivity increases logarithmically.

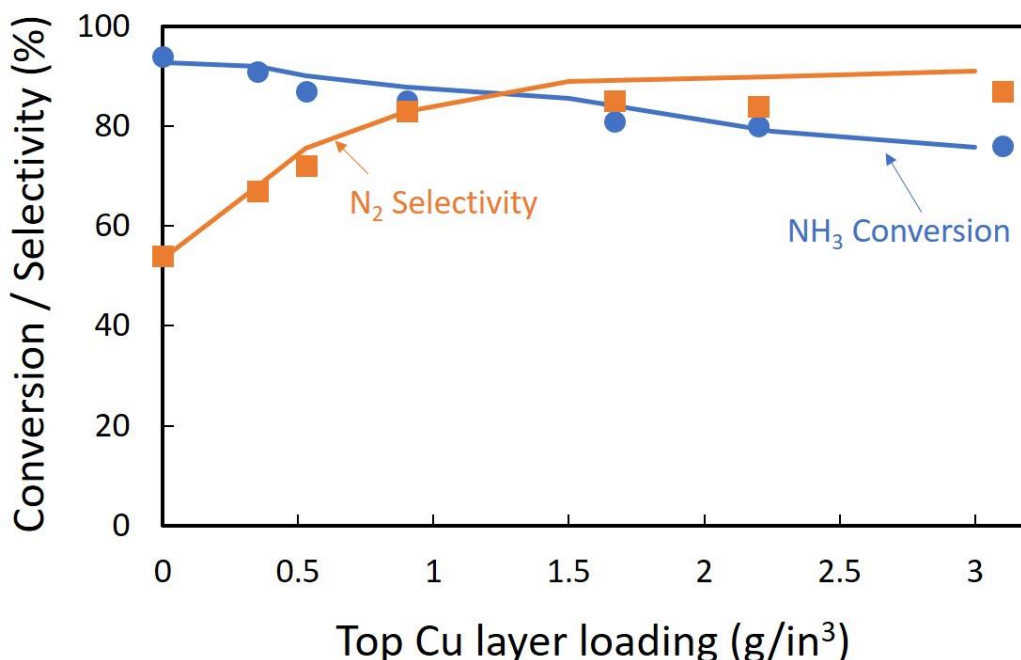


Figure 5.6 NH₃ conversion and N₂ selectivity of various ASC samples at 450 °C. The conversion and selectivity are plotted as a function of top Cu-SSZ-13 layer loading. (symbols: experiments, lines: Simulations)

The differences in the dependence in each creates a logical optimal point where the two functions intersect at point P. That is, a further increase in the loading beyond P leads to a disproportionate decrease in NH₃ conversion and negligible increase in N₂ selectivity. Thus, the optimal dual layer catalyst corresponds to sample S3 with a top SCR layer loading of 0.9 g/in³. These experimental trends of the NH₃ conversion and the N₂ selectivity

were further validated using the model prediction as shown in Fig. 6. The model predicts the nearly linear drop in NH_3 conversion and a logarithmic increase in the N_2 selectivity. The conversion and selectivity curves intersect at $\sim 1.2 \text{ g/in}^3$ top layer Cu loading which is close to the experimental finding of sample S3 (0.9 g/in^3) having the optimal loading.

The second set of ASC samples having a higher Pt loading (10 g/ft^3) were compared for the same NH_3 oxidation conditions. Fig. 5.7 shows the NH_3 conversion and N_2 selectivity for samples S7 to S11. Sample S7 is the single Pt layer, S8 is the uniform mixed layer, S11 is conventional dual layer, while S9 and S10 are hybrid samples in which different amounts of Cu have been distributed between the top and bottom layers. The NH_3 conversion increased as the Cu/SSZ-13 loading was decreased from the top layer to the bottom layer ($\text{S11} \rightarrow \text{S10} \rightarrow \text{S9} \rightarrow \text{S8} \rightarrow \text{S7}$). Concurrent with the NH_3 conversion increase was a N_2 selectivity decline (Fig. 5.7b). On the other hand, the dependence of the NH_3 conversion and N_2 selectivity as a function of the top layer Cu/SSZ-13 loading had the same features as the lower Pt loading samples. Further, Fig. 5.8 show a linear decrease in the conversion and logarithmic selectivity increase when shifting from the mixed to dual-layer sample. For this higher Pt loading of samples the optimal point corresponds to be sample S9 with a top layer loading of 1.2 g/in^3 .

The approach to identifying the optimal hybrid sample shows that for both sets of samples the function forms of the NH_3 conversion and N_2 selectivity have close resemblance (compare Figs. 5.5 and 5.8). That is, the conversion decline has a slope of -5.48 and -6.59 for the low and high Pt loading ASC samples. These values are very close and further substantiates that the decline is mainly due to washcoat structure changes and not influenced by increasing or decreasing of Pt loading. In effect, the washcoat diffusion

is the dominant process. Similarly, the multiplication factor to the log term in N_2 selectivity curve is 5.94 and 5.50 for low and high Pt loaded samples respectively. The similar magnitude of the two numbers show the fundamental sensitivity of washcoat morphology to product selectivity irrespective of Pt loading.

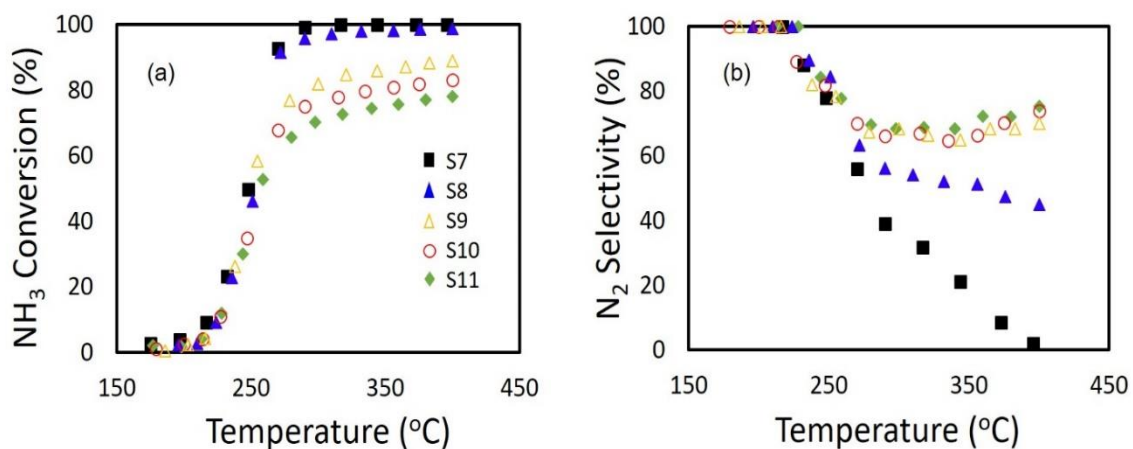


Figure 5.7 Steady state NH_3 conversion (a) and N_2 selectivity (b) as a function of temperature for various ASC samples (details for samples are given in Table (1). Feed: 500 ppm NH_3 , 5% O_2 , balance Ar and $265k\ h^{-1}$ GHSV.

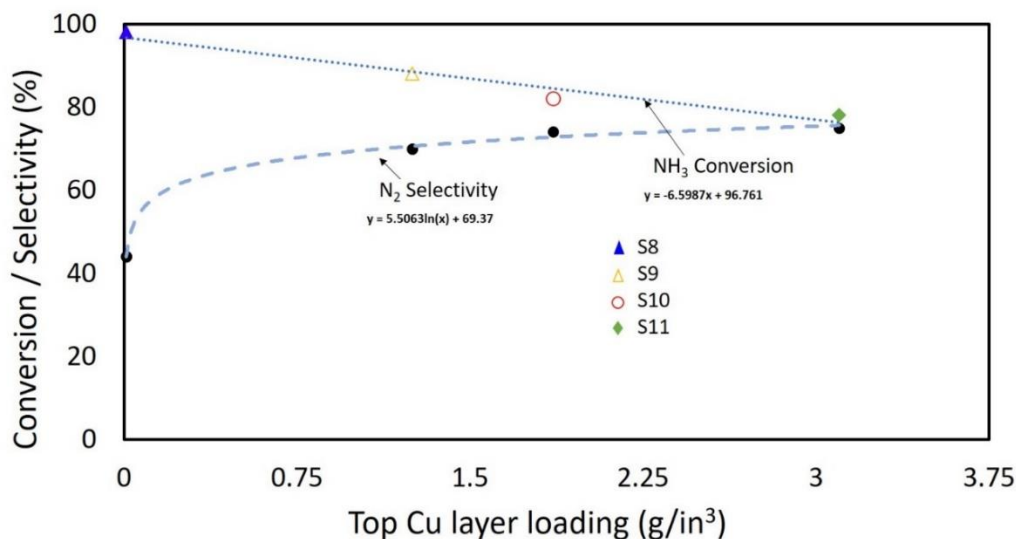


Figure 5.8 NH_3 conversion and N_2 selectivity analysis for various ASC samples at constant temperature of $450\ ^\circ C$. The conversion and selectivity are plotted as a function of top Cu-SSZ-13 layer loading. (symbols: experiments; lines: curve fit)

5.4.4 Model prediction for dual, mixed and hybrid samples

The above described mathematical model was used to simulate results for the dual, mixed and hybrid layer samples (Fig. 5.3, 5.6 and 5.9). Fig. 5.3(a) shows the model predictions for the dual-layer ASC sample (S6). With satisfactory validation of Pt model demonstrated (Fig. 2), the Cu/SSZ-13 kinetics were added to simulate the dual-layer sample. The model predictions are in good agreement with the experimental data such as decline in NH_3 conversion and changing product distributions. The model prediction of NH_3 conversion drop compared to single Pt layer anticipate the transport limitation behavior of top Cu layer. The low temperature discrepancy is a result of the aforementioned dual site feature of the Pt kinetic model (Fig. 5.2).

Fig. 5.3(b) compares experiment and modeling results for the mixed layer sample. The Pt and Cu model accurately predicted mixed layer sample results without any kinetic parameter tuning. Also, in the case of the hybrid samples, the Pt and Cu kinetics were used as such. On the other hand, the washcoat structure parameter λ_{mixed} (tortuosity/porosity) was adjusted to attain good fit and found out to be 50. The $\lambda_{\text{scr}} = 65$ and $\lambda_{\text{pgm}} = 27$ for pure SCR and PGM layer respectively is adopted from modeling study [33], hence the fitted value of $\lambda_{\text{mixed}} = 50$ seem very reasonable and were used for the bottom mixed layer in hybrid samples.

The combination of the dual and mixed layer model simulated hybrid layer. Fig. 5.9 represent experimental (symbols) and simulation (lines) results for the three hybrid layer samples (S12, S13 and S3). The top layer thickness varied linearly with top layer loading. It can be seen that the simulated conversion and product distribution show close proximity to experiment data (Fig. 5.9). The model also corroborates the non-linear increase in N_2

selectivity and linear decrease in NH_3 conversion when switching from mixed to dual layer morphology (Fig. 5.6).

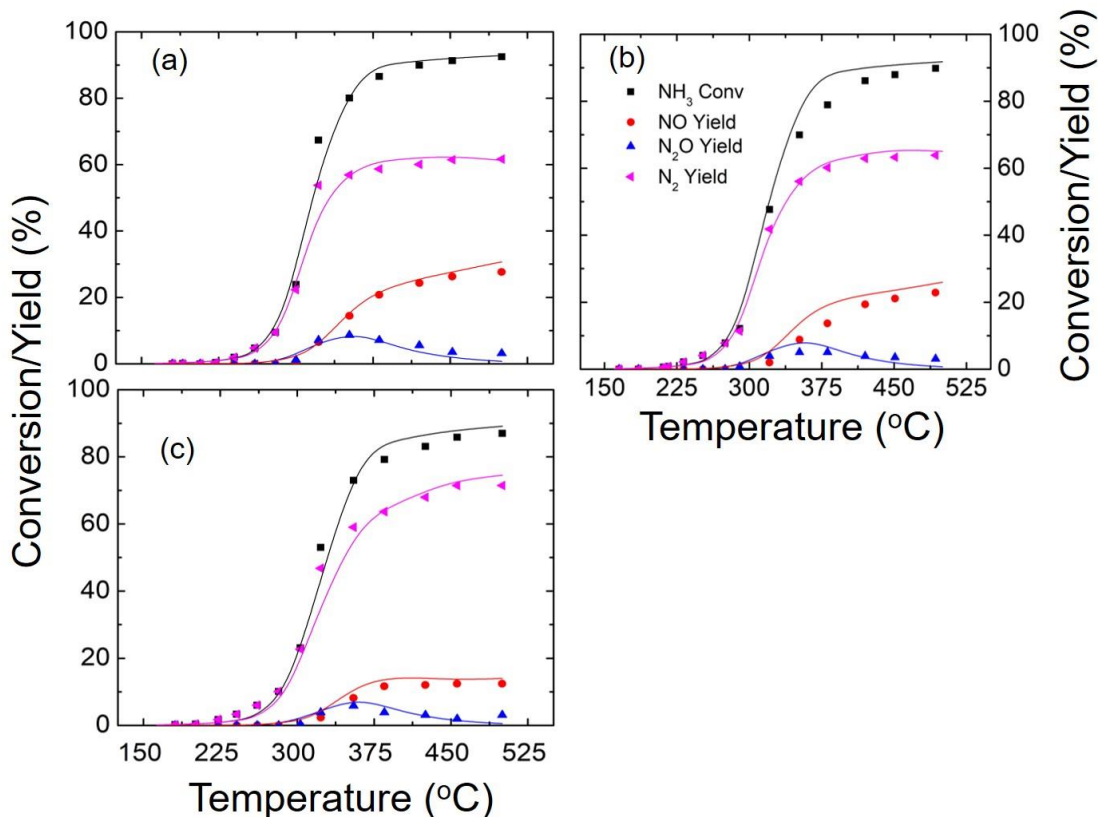


Figure 5.9 Steady state NH_3 conversion and product yields as a function of temperature over hybrid ASC samples S12 (a), S13 (b), and S3 (c). Feed: 500 ppm NH_3 , 5% O_2 , Balance Ar and 265 k h^{-1} GHSV.

5.4.5 Model predicted Hybrid sample Cu and Pt loading impact

The model may be used to identify the best combination of Cu loading distribution and Pt loading. Fig. 5.10 shows the model predicted NH_3 conversion, N_2 selectivity, and N_2 yield as a function of the Pt loading (C_{pt}) for a sample having a Cu loading distribution equivalent to that of Hybrid sample S3 with α value of 0.28 (Cu loading distribution: 2.25 g/in^3 in base and 0.9 g/in^3 in top layer). The calculations are for a temperature of $450\text{ }^\circ\text{C}$

and space velocity of 245 k h^{-1} . The model predicts that an increase in Pt loading leads to an increase in NH_3 conversion and decrease in N_2 selectivity, reflecting the trade-off of these two key performance metrics. The NH_3 conversion and N_2 selectivity curves intersect at $\sim 0.75\text{ g/ft}^3$ Pt loading; after this point the conversion remains nearly constant with increasing Pt loading while the N_2 selectivity decreases significantly. These results show that for the hybrid architecture an intermediate Pt loading gives a maximum N_2 yield, again illustrating the trade-off between conversion and selectivity. For this particular value of α ($= 0.28$) a maximum N_2 yield of 80% occurs at a Pt loading of $\sim 0.4\text{ g/ft}^3$. The N_2 yield maximum shifts to higher Pt loading for samples with larger values of α (Fig. 5.10). Too large or small of a top layer Cu loading at a given Pt loading leads to a sharp fall-off in the maximum yield. It is interesting to note that the model predicts the highest N_2 yield values are obtained at rather low values of the Cu top layer loading and Pt loading (Fig. 5.10).

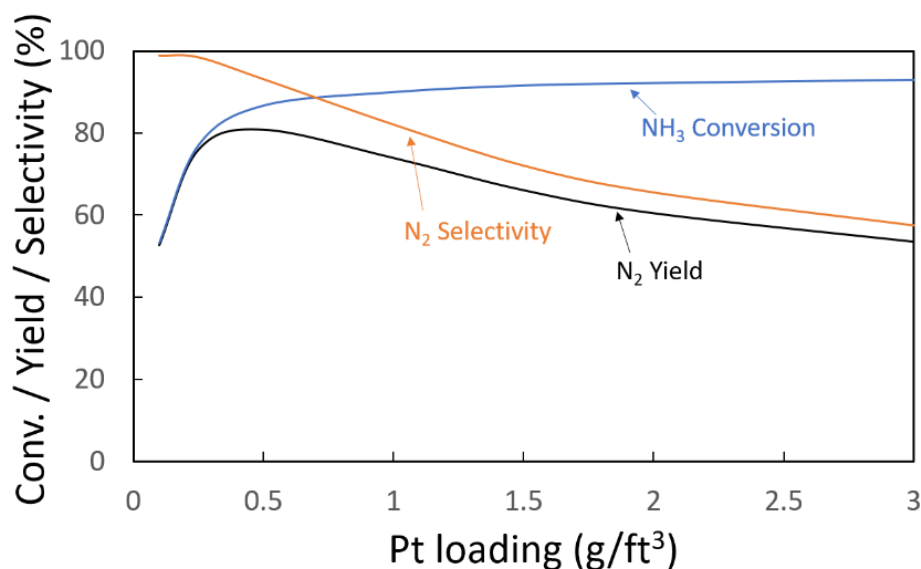


Figure 5.10 Model predicted steady state NH_3 conversion, N_2 selectivity and N_2 yield at fixed temperature of $450\text{ }^\circ\text{C}$ as a function of overall Pt loading (g/ft^3) for the Hybrid sample (S3).

These predictions can be extended to a range of Cu loading distribution values. Fig. 5.11 shows extensive model predictions in which both the Pt loading and Cu loading distribution are varied. The Cu distribution is defined by the parameter α which is the ratio of the Cu loading in the top layer to the overall Cu loading, which is fixed at 3 g/in³. Also shown in the figure are the corresponding experimental values measured for the seven samples (S2-S6, S12, S13) having an overall Cu loading in the range of 2.9 to 3.15 g/in³ (see Table 5.1). The model predictions show that an intermediate Cu loading is needed in the top layer to maximize the N₂ yield for varied Pt loading. The reader is referred to Figure S1 of the Supplementary Material for the corresponding NH₃ conversion and N₂ selectivity predictions. The top layer Cu loading giving the maximum N₂ value tends to increase with increasing Pt loading.

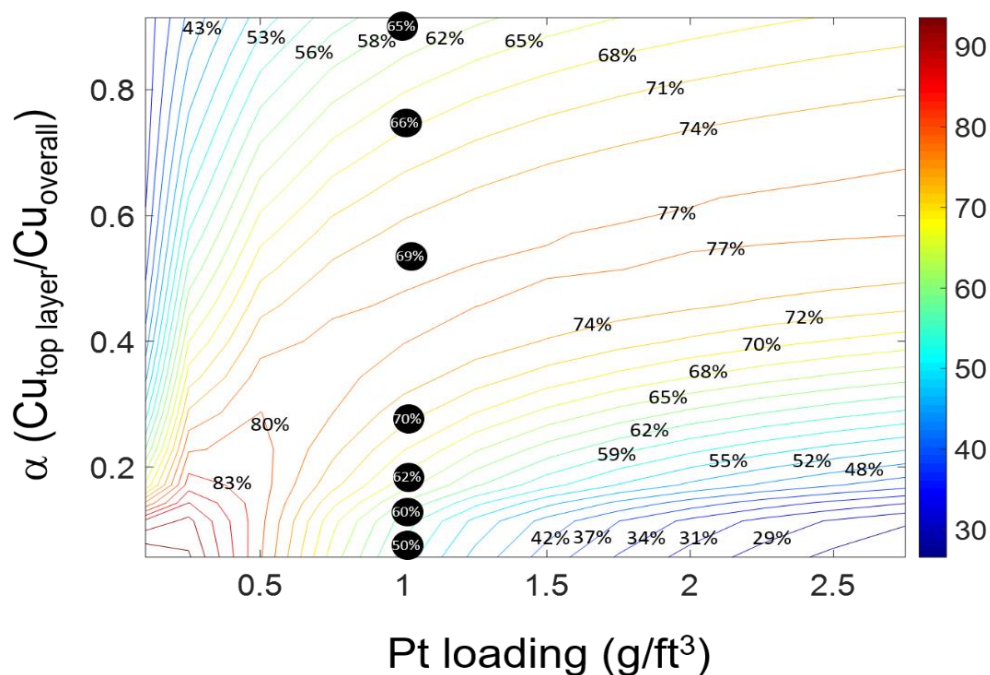


Figure 5.11 Experimental (black circles) and modeling (lines) N₂ yield (%) as a function of Pt loading and Cu distribution. Feed conditions: 500 ppm NH₃, 5% O₂ and balance Ar at 265k h⁻¹ GHSV.

5.5 Conclusions

NH₃ oxidation was carried out over a group of catalysts spanning single layer Pt/Al₂O₃, dual-layer comprising base Pt/Al₂O₃ and top Cu/SSZ-13 layer, uniform mixed layer of Cu/SSZ-13 and Pt/Al₂O₃, and hybrid samples having a bottom mixed layer and top Cu/SSZ-13 layer. The study shows that NH₃ conversion and N₂ product selectivity are sensitive functions of the arrangement of Pt and Cu sites in the overall washcoat. In the high temperature limit the Pt/Al₂O₃ layer provides almost complete conversion and practically zero N₂ selectivity. On the other hand, the dual-layer exhibits a significant increase in the N₂ selectivity but the NH₃ conversion is limited by the diffusion barrier imposed by the Cu/SSZ-13 top layer. The mixed layer facilitates high conversion with compromised N₂ selectivity. Thus, a hybrid sample were synthesized to find the trade-off between the dual and the mixed layer. The hybrid design comprising a bottom layer mixed washcoat and top SCR layer. It is found that while moving from mixed to hybrid to dual layer, the N₂ selectivity increase logarithmically while the NH₃ conversion drop linearly. An optimal combination achieves the balance of a high NH₃ conversion and high N₂ selectivity. Overall the study shows that the washcoat structure is as important as catalyst activity and finding the best combination of catalytic sites in multi-functional catalysts could attain desired conversion and product selectivities.

Chapter 6. Conclusion and suggestions for future work

6.1 Conclusion

This dissertation study investigated various aspects of ammonia slip catalyst ranging from its catalytic activity, internal washcoat diffusion, washcoat architecture and deactivation characteristics. The state-of-the-art ASC for selective oxidation of NH_3 is the dual-layered washcoated catalyst with bottom $\text{Pt}/\text{Al}_2\text{O}_3$ and top Cu-SSZ-13 . The bottom Pt layer oxidize NH_3 to NO/NO_2 at high temperature while top Cu layer selectively reduce NO/NO_2 to N_2 by reacting with counter flowing NH_3 .

In first part of the study, an accelerated hydrothermal aging over bottom $\text{Pt}/\text{Al}_2\text{O}_3$, top $\text{Cu}/\text{SSZ-13}$ and combined dual-layer is discussed. Reaction experiments of NH_3 oxidation were carried out at different aged levels followed by catalyst characterization and model development. The catalyst aging was performed in the flow reactor itself at moderately high temperature of 550°C and controlled atmosphere consisting of O_2 , CO_2 and H_2O . Results showed monotonic decline in NH_3 conversion over Pt layer at high temperatures with negligible change in low temperature activity. The catalyst characterization including BET, chemisorption, and mathematical model describe the mass transport as the underlying cause for the activity drop of $\text{Pt}/\text{Al}_2\text{O}_3$. It was found that $\gamma\text{-Al}_2\text{O}_3$ transform into $\text{Al}(\text{OH})_3$ with moderate temperature aging in presence of water for prolonged period of time. C_3H_6 oxidation was also used as a test reaction to further validate the $\text{Pt}/\text{Al}_2\text{O}_3$ activity decline. After investigating $\text{Pt}/\text{Al}_2\text{O}_3$ layer, the hydrothermal aging was carried out on top layer Cu-SSZ-13 and dual-layer ASC. NH_3 oxidation and Standard SCR feed ($\text{NO} + \text{NH}_3 + \text{O}_2$) experiments were performed over Cu-SSZ-13 layer at different aged levels. The results show no significant drop in activity at 550°C aging

temperature. On the other hand, the dual-layer was aged at higher temperature of 650 °C with shortened aging time and negligible change in NH₃ conversion was noticed post-aging.

The dual-layer ASC design exhibit high N₂ selectivity but at the cost of NH₃ conversion attributed to the washcoat diffusion limitations offered by top Cu-SSZ-13 layer. The next part of this dissertation study explained the enhanced mass transport through top Cu-SSZ-13 layer to increase NH₃ conversion. The macroporosity of the Cu-SSZ-13 layer was increased using a pore-forming technique, incorporating very economical templates such as yeast and poly-tert-butyl-acrylate. This significantly increased NH₃ conversion for dual-layer ASC without impacting N₂ selectivity. Steady state SCR experiments and transient NH₃ adsorption experiments were also performed over more-porous single layered Cu-SSZ-13 which show enhanced catalyst productivity and further validated the phenomenon of increased mass transport through washcoat.

A mathematical model was developed to predict experimental results of enhanced mass transport study. A kinetic model for Cu-SSZ-13 was developed based on kinetic experiments, earlier literature reporting and statistical data fitting. The SCR kinetic model combines multi-step Eley-Rideal kinetics with a dual-site description and the model parameters are systematically tuned to data sets for NH₃ uptake and TPD, steady state NH₃ + O₂ oxidation, and standard SCR (NH₃ + NO + O₂), the latter including differential kinetics. The SCR model is validated for a range of operating conditions and catalyst compositions. Modeling and analysis of washcoated single- and dual-layer monolith catalysts is presented for selective catalytic reduction (SCR) on Cu-SSZ-13 and ammonia oxidation on Cu-SSZ-13 + Pt/Al₂O₃ ammonia slip catalyst (ASC). The model is used to

simulate the performance of the modified porosity Cu-SSZ-13 washcoat for SCR on the single-layer catalyst and for SCR + ammonia oxidation on the dual-layer ASC. The model predicts that a ~50% increase in the effective diffusivity serves to enhance the conversion in the intermediate temperature regime in which washcoat diffusion is controlling.

Next, we describe a systematic study to identify the ASC architecture and composition that optimize the trade-off. The in-house synthesized ASC samples span the single layer Pt/Al₂O₃, conventional dual-layer Pt/Al₂O₃ + Cu/SSZ-13, uniform single layer of mixed Pt/Al₂O₃ + Cu/SSZ-13, and a hybrid design comprising a bottom layer of mixed Pt/Al₂O₃ + Cu/SSZ-13 and a thin top layer of Cu/SSZ-13. The overall Pt and Cu loadings are fixed across the series of samples with the Cu split between the two layers. The best results are obtained with the combination of a base mixed layer that provides for effective coupling between Pt and Cu active sites and a top Cu/SSZ-13 layer of an intermediate thickness and nominally half of the total Cu loading. This design has sufficient oxidation activity to convert the NH₃ and reduction activity to limit NO_x slippage. The hybrid design exhibits a linearly decreasing dependence of the NH₃ conversion and logarithmically increasing dependence of the N₂ selectivity on the top layer Cu loading. The intersection of the two functions is shown to provide a good balance between the two opposing performance variables.

During the last part of the study, the effect of sulfur poisoning was being studied over dual-layer ASC. The reactor set up was modified for sulfur aging and testing. The initial testing of sulfur poisoned ASC show significant catalyst deactivation due to sulfur poisoning. This is an ongoing study and is discussed in future work section.

6.2 Suggestions for future Work

This study explains a lot about ammonia slip catalyst but few questions remains that are still to be answered and the research is always a continual challenge. Some of the recommendations for future work include minimizing Pt loading, investigation and minimization of N_2O formations, low-dimensional modeling for ASC, catalyst deactivation and regeneration properties with sulfur poisoning.

The optimization study performed during the last part of this work show the Hybrid design ASC provide better trade-off for NH_3 conversion N_2 selectivity. Also, a comprehensive simulation plot is reported showing constant N_2 yield for varied Pt loading and Cu distributions at constant temperature of 450 °C. The simulations found that lower Pt loading ($\sim 0.5 \text{ g/ft}^3$ or even less) with $\sim 0.5 \text{ g/in}^3$ Cu in top layer while overall Cu is fixed at 3 g/in^3 can offer more than 80% N_2 yield. This still need to be validated with experimental data, so working with lower Pt loadings will provide new insights. Also, the overall Cu is fixed at 3 g/in^3 in this simulation that can also be varied to attain optimum NH_3 conversion and N_2 selectivity.

N_2O is a potent greenhouse gas and its emission should be minimized. N_2O formed on Pt site do not reduce back to N_2 on SCR catalyst. Therefore, it is important to study N_2O formation over Pt and how to minimize it. TAP reactor facility available at University of Houston can be helpful in studying N_2O formation over Pt at intermediate temperature. Another hypothesis is that N_2O selectivity depend upon Pt particle size, larger the particle more the N_2O selectivity. It would be good to study N_2O selectivity vs Pt dispersion in Pt/ Al_2O_3 .

The modeling of ASC include kinetic model of Pt and Cu. Pt kinetic model consist of 14 elementary steps while Cu kinetic has six reaction steps. These many reaction steps with 1+1 dimensional model is computationally intensive. Parameter estimation take several hours to converge. A low dimensional model can significantly reduce computational effort and speed the simulations. Mozaffari et al. [82] and Ratnakar et al. [110] has reported low dimensional reactor models for multi-layer washcoated monoliths.

It is found in this study that hydrothermal aging has negligible impact on ASC. On the other hand, few experiments performed on commercial dual-layer ASC showed that low temperature sulfur poisoning significantly deactivate catalytic sites which is partial reversible. It is recommended to study sulfur poisoning on separated Pt and Cu layer followed by combined dual-layer. Much research has been reported in literature for sulfation effect on Pt/Al₂O₃ and Cu-SSZ-13 catalyst in relevance to DOC and SCR reactions respectively. However, it would be interesting to study the transformation of NH₃ oxidation reaction mechanism with sulfur poisoning over ASC.

LIST OF NOTATION

$D_{f,j}$	<i>Diffusivity in fluid phase of species 'j'</i>
$D_{e,scr,j} / D_{e,pgm,j}$	<i>Effective diffusivity of species 'j' in SCR/PGM washcoat</i>
$D_{e,c}$	<i>Diffusivity inside zeolite crystal</i>
$\lambda_{scr/pgm}$	$D_{f,j}/D_{e,scr/pgm,j}$
$t_c / t_e / t_w / t_r / t_{d,c}$	<i>Convective / External mass transfer / Washcoat diffusion / Reaction / Crystallite time scale</i>
L	<i>length of monolith channel</i>
$\langle u \rangle$	<i>cross-section average velocity in fluid phase</i>
$R_{\Omega 1} / R_{\Omega 2}$	<i>Hydraulic radius / Effective washcoat thickness</i>
$R_{\Omega,scr}$	<i>SCR washcoat thickness in dual-layer ASC</i>
$R_e / R_w / R_{rxn} / R_t$	<i>External / Internal / Reaction / Total resistance</i>
$Sh_e(z) / Sh_i(z)$	<i>Position dependent External / Internal Sherwood number</i>
$k_{me,j}(z)$	<i>External mass transfer coefficient for species 'j'</i>
R	<i>Universal gas constant</i>
$x_{f,j}$	<i>cup-mixing concentration of species 'j' in fluid phase</i>
$x_{s,j}$	<i>concentration of species 'j' at fluid-washcoat or washcoat-washcoat interface</i>
$x_{wc,scr,j} / x_{wc,pgm,j}$	<i>concentration of species 'j' in SCR / PGM washcoat</i>
$\epsilon_{wc,scr} / \epsilon_{wc,pgm}$	<i>SCR / PGM washcoat porosity</i>
$R_{r,scr} / R_{r,pgm}$	<i>Reaction rate in SCR / PGM washcoat</i>
ϕ	<i>Thiele modulus</i>
C_{S1} / C_{S2}	<i>Cu active site S1 / S2 density</i>
C_{pt}	<i>Pt active site density</i>
C_{tm}	<i>Total molar concentration</i>
ϑ_{jr}	<i>Stoichiometric coefficient</i>
ϑ_k	<i>Surface species 'k' concentration</i>
a	<i>Dimension of monolith channel cross-section</i>
Re	<i>Reynolds number</i>
Pe/Pe_t	<i>Axial/Transverse Peclet number</i>

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