ENHANCED SELECTIVE OXIDATION OF NH₃ IN A Pt/Al₂O₃@CU-ZSM-5 CORE-SHELL CATALYST

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ABSTRACT

The ammonia slip catalyst (ASC) is an essential final step in the emission control system and involves the selective oxidation of NH₃ to N₂. The state-of-the-art ASC has a dual-layer architecture comprised of a Pt/Al₂O₃ (PGM) bottom layer and a metal (Fe, Cu)-exchanged zeolite (M-Z) top layer. The first part of the project deals with the challenges of reducing the PGM loading and ASC volume while enhancing low temperature activity. This is done by scaling down the dual-layer concept to the level of a single core-shell catalyst particle, Pt/Al₂O₃@Cu/ZSM-5, comprised of a PGM core and M-Z shell. The coreshell catalyst had an equivalent activity to that of a conventional Pt/Al₂O₃ catalyst containing 3-times higher Pt loading. The core-shell catalyst showed exceptional NH₃ oxidation activity and N₂ selectivity.

The second part of the research is to investigate the NH₃ oxidation kinetics over Pt/Al₂O₃ catalysts under atmospheric conditions for a wide range of NH₃ concentration. We were able to show the non-monotonic reaction rate as a function of NH₃ concentration for Pt/Al₂O₃ catalysts in presence of excess oxygen. We also showed the variation in reaction order from positive to negative order with zero order reaction at maximum reaction rate. Milling of Pt/Al₂O₃ resulted in enhanced NH₃ oxidation activity. A microkinetic model with site-competition was developed which could predict the variation in reaction rate and order of the reaction.

The final part of the research deals with the development of a working model for the core-shell catalyst with the microkinetics derived from the kinetic study over Pt/Al_2O_3

and along with multi-step SCR kinetic formulations to simulate the ASC performance of the $Pt/Al_2O_3@Cu/ZSM-5$ core-shell catalyst. Using the model we showed an optimized core-shell structure by investigating the ASC performance based on Pt loading and shell thickness. Finally, we discuss the scope of the future work based on our results and observations.

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Chapter 1: Introduction

1.1. Emissions overview

The rapid development in different parts of the world has led to an exponential growth of industrial and vehicular emissions adding to the concerns of the already fragile ecosystem of the earth. Specifically, the transportation sector has become one of the largest greenhouse gas (GHGs) emitters accounting to 28 % of the all the GHGs emitted in the US in the year of 2018 [1]. Cars, trucks and buses powered by fossil fuels are a major contributors to the air pollution and accounts for more than half of the NOx emitted in the US. Other than NOx, the transportation sector is also responsible around 10 % each of the volatile organic compounds (VOCs) and particulate matter (PM_{2.5} and PM₁₀) emissions in the US [2]. These pollutants have been linked to adversely affect the human health and ultimately deteriorate the standard of living in the highly populated areas. The transportation sector, especially the buses and trucks play a major role by hauling goods and provide connectivity to most remote parts of the world. Heavy duty vehicles although they comprise a small fraction of the total number of vehicles plying on our roads, they generate more than 25 % of global warming emissions in form of NOx, CO, CO₂. In this dissertation we focus on the eliminating the harmful exhausts emitted from the diesel combustion engines via chemical synthesis, extensive reaction testing and modeling routes to further enhance the current after-treatment capabilities.

Diesel engines are lean burn engines and operated with an excess of air. Unlike spark-ignited combustion in gasoline engines, the combustion in diesel engine takes place by compression of the diesel + air mixture under high temperature and pressure. Diesel engines are generally categorized as lean burn engines with very high air to fuel ratio in the combustion chamber. But combustion results in a lot of unburnt hydrocarbons, lube oil emissions. The combustion reaction of fuel and air mainly produce CO_2 and H_2O , however there are other side reactions that place as well. The oxidation of nitrogen in the air forms NOx and this reaction is catalyzed with the increase in operating temperature that generally happens during high engine load. At low engine load, when the temperature inside the combustion engine is cooler, soot formation increase but there is decrease in NOx emission[3,4]. The presence of impurities such as sulphur within the fuel is also a cause for major concern, as it results in the formation of SO_X . The following are the major pollutants from diesel vehicles:

 Particulate matter (PM): These are particles found in the exhaust of the combustion engines. Its composition often includes hundreds of chemical elements, including sulfates, ammonium, nitrates, elemental carbon, condensed organic compounds and even carcinogenic compounds [5]. These essentially include carbon (soot), HCs adhering to soot, sulphates, corrosion products from engines and combustion products from engine oil [6]. The particle size ranges from coarse particles (10 microns) to fin particles (<2.5 microns) to ultra-fine particulates (<0.1 microns). These ultra-fine particulates are small enough to penetrate the cells of the lungs makes up to 80-95 % of the diesel soot pollution. The particulate matter irritates eyes, nose, throat and lungs contributing to respiratory and cardiovascular illnesses. Generally a diesel particulate filter (DPF) is added to capture these particles, however the challenge still lies in capturing the ultra-fine soot particles.

- 2. Carbon monoxide (CO): The partial oxidation of HCs often leads to the formation of carbon monoxide. CO is a potent greenhouse gas which leads to global warming which has become an important issue. It is also a deadly poison which is highly reactive with Hemoglobin(HbA) which a protein used to deliver oxygen to different cells in our body. HbA has more affinity towards CO which leads to poisoning by starving the vital organs of oxygen [7]. CO is a colorless odorless gas and impossible to detect my human eye and nose making it far more deadly. In order to mitigate with CO, a diesel oxidation catalyst (DOC) is added to convert CO to CO₂.
- 3. Oxides of Nitrogen (NOx): The emission of NOx is a major issue in the diesel engines [8,9]. The inherent N₂ concentration of 78 % within the air along high A/F ratio, high operating temperature and pressure leads to formation of different oxides of Nitrogen upon combusting the diesel fuel. These oxides include NO, NO₂, N₂O. NO being the major component, while NO₂ is formed upon further oxidation of NO. Diesel emissions of nitrogen oxides contribute to the formation of ground level ozone, which irritates the respiratory system, causing coughing, choking, and reduced lung capacity. Ground level ozone pollution, formed when nitrogen oxides and hydrocarbon emissions combine in the presence of sunlight, presents a hazard for both healthy adults and individuals suffering from respiratory problems. In order to mitigate with this issue, selective catalytic reduction (SCR) catalyst is added. This is generally a Cu-chabazite washcoated onto monolith reduces NOx to

 N_2 by using NH₃ as a reducing agent using SCR chemistry [10,11]. SCR unit is an essential part of the diesel after-treatment system. NH₃ is injected in slight excess to deal with varying engine loads by onboard thermal decomposition of Urea or Diesel exhaust fluid (DEF). The advent of SCR catalyst has solved the issue of NOx emission to a large extent however the injection of excess NH₃ leads to its own issues. Unreacted NH₃ from SCR unit cannot be let out into the exhaust stream. This is also known as NH₃ slippage, hence an additional Ammonia slip catalyst (ASC) is added to convert NH₃ to N₂.

4. Other gases: Other pollutants such as SOx from oxidation of sulphur within the diesel fuel can be dealt by usage of ultra-low sulphur diesel. These sulphur oxides however do pose a major threat to the catalytic units present in the diesel aftertreatment system. Further work still needs to be done to tend to this issue.

1.2 Emission standards

The public health problems along with rise in air pollution from the diesel emissions have led to development of various emission standards. The emission standards provide a guideline for the maximum permissible emissions that can be let out in the exhaust for various gases but mostly concerns with CO, NOx, VOCs, SOx and particulate matter. These standards depends on various factors such as type of engines diesel or gasoline, lightduty or heavy duty and also on the specific country. The increase in the number of vehicles every year leads to further stringent conditions set up in the emission standards. US federal emission standards for engines and vehicles are established by the US environmental protection agency (EPA) and California standards established by the California Air resources board (ARB) are the two sets of emission standards followed within the US. Generally the emission standards set by ARB are more stringent compared to the EPA standards. Based on current emission regulations release, every country is expected to cut CO₂ by 3-4% per year [12]. 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 NOx 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 [13,14]. 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 NOx, 215 mg/km THC+NOx and 4.5 mg/km PM [15].

In order to deal with the growing emissions, we strictly need to follow the emission standards. The introduction of diesel exhaust after-treatment unit has definitely helped in meeting the current standards however still further research needs to be done in this area to meet the future emission standards.

1.3 Diesel engine exhaust after-treatment system

Diesel engine after-treatment system is a series of catalytic components designed to eliminate and treat all harmful engine exhaust before releasing into the atmosphere. The diesel exhaust is generally a mixture of CO/CO₂, H₂O, N₂, NOx, N₂O, SOx and unburnt HCs which upon treating through an after-treatment system should ideally oxidize any unburnt HCs/CO to CO₂, various oxides of Nitrogen(NOx) to N₂. The multiple reaction chemistry required for the treatment of the individual exhaust gases leads to a complex series of catalytic components aligned in a systematic architecture working in tandem. A typical diesel exhaust after-treatment system consists of a diesel oxidation catalyst (DOC), diesel particulate filter (DPF), selective catalytic reduction (SCR) catalyst and ammonia slip catalyst (ASC) arranged in a series (Fig. 1). In other words, an after-treatment system is no less than a chemical plant on wheels. Each of the catalytic components are washcoated monolith, where the active catalyst is coated over monolith core. The washcoated monolithic catalysts are commonly used in exhaust after-treatment systems for both diesel and gasoline engine vehicles. The monoliths are in form of a honeycomb like structure consisting of straight parallel channels having defined geometry, highly tunable crosssectional shapes. The washcoated monoliths are preferred as they offer very low pressure drop compared to conventional packed bed reactors.



Figure 1. Schematic of diesel after-treatment unit.

Diesel oxidation catalyst (DOC), first in the series of catalytic components of the exhaust after-treatment system functions to oxidize unburnt hydrocarbons and CO into CO₂. The DOC comprises of PGM (Pt/Pd) supported over Al₂O₃. Even though Pt is a

highly active oxidation catalyst it gets poisoned by CO, so Pd and Pt and are used in combination to achieve high performance [16]. The DOC also promotes the oxidation of NO to NO₂ which benefits the down-stream SCR catalyst as presence of NO₂ in the exhaust feed initiating fast SCR reaction. The various challenges associated with DOC are to reduce the loading of the precious group metals (Pt/Pd), prevent the sintering of Pt/Pd from due to high temperature of exhaust directly from the engine. Several recent studies include investigating the effect of Pt-Pd composition, washcoat structure (layer or zone), single atom catalysis and development of new catalysts (formation of Pt-Pd alloys) to further enhance the performance and improve the thermal stability of the DOC catalyst.

Diesel particulate filter (DPF) is the second in series right after the DOC. This functions as a unit to capture any large carbonaceous particles such as coke, soot and particulate matter [17]. The commercial DPFs are generally incorporated with active sites that oxidizes carbon to CO_2 and facilitate self-regeneration.

Selective catalytic reduction (SCR) catalyst is used to convert NOx to N₂ with the help of NH₃ as a reducing agent [18]. The NOx emissions is a big challenge associated with diesel vehicles if let out unchecked results in smog, ground level ozone formation and breath disorders. Hence in order to mitigate the adverse impact of NOx emission a lot of work has been done in SCR catalysts. In the late 1970s, metal oxide mixtures of V, Ti, and/or W were found to be promising deNOx NH₃ SCR catalysts [11]. These vanadia based catalysts offered a number of advantages, low catalyst cost, high sulphur tolerance however the NOx reduction efficiency drastically falls at higher temperature (>425°C) which is

insufficient for applications in diesel exhaust. These catalysts have been found to have reduced stability at higher temperatures and the toxicity also raised health concerns. The state-of-art SCR catalysts these days consists of a Cu/Fe metal exchanged zeolites which proved to have good thermal stability with high N_2 selectivity for the entire operating temperature range. Notably, Cu-exchanged SSZ-13 (a small-pore zeolite) is the most active, selective, and durable SCR catalyst for diesel vehicles [19]. It is well documented that SCR proceeds through the standard $(NH_3 + NO + O_2)$, fast $(NH_3 + NO + NO_2)$, and slow $(NH_3 + NO_2)$ conversion of NH_3 to N_2 and H_2O [20–26]. The Cu resides within the small pores of the SSZ-13 zeolite which restricts HC entry and prevent Cu poisoning. The Cu-SSZ-13 catalysts also has excellent resistance to thermal degradation. A dedicated onboard urea dosing system is required for generating NH_3 feed to SCR. The requisite NH₃/NOx ratio is slightly over unity as a result of the undesired oxidation of NH₃, which is most prominent at higher temperature on Cu-exchanged zeolites. The reaction of NH₃ and NO₂ can lead to the generation of greenhouse gas N_2O , while the N_2O precursor NH₄NO₃ may accumulate in the pores, leading to lower activity.

In commercial SCR emission control, urea-based systems are effective in meeting stringent NOx emission targets [12], yet there are existing challenges that include low temperature activity, urea deposits, sulfur tolerance, hydrothermal stability, and dynamic performance under "real world" operation [27,28]. Moreover, NOx emission targets during transient operation with a temperature-dependent catalyst activity and NH₃ sorption cannot be satisfactorily achieved due to the undesired slip of NH₃. Despite sophisticated urea dosing strategies, the combination of NH₃ adsorption at lower temperature and rapid

exhaust temperature increases unavoidably result in the release of unreacted NH_3 from the SCR unit. This release of noxious NH_3 has led to the development and application of an ammonia slip catalyst (ASC), which is responsible for converting NH_3 to N_2 , as the final unit in a modern diesel vehicle emission control system. The main research objective is to improve the existing ammonia slip catalyst.

1.4 Ammonia slip catalyst

The state-of-the-art ASC has a dual-layer architecture comprised of a base Pt/Al₂O₃ (PGM) layer and a top Cu-zeolite (SCR) layer to selectively oxidize NH₃ to N₂. The oxidation of NH_3 over the base PGM layer, is especially sensitive to both temperature and NH₃ concentration, and leads to four major N-containing products (N₂, NO, NO₂, N₂O). The formation of molecular nitrogen (N₂) dominates at $T < 250^{\circ}$ C, while the main product shifts to NO at temperatures exceeding 350°C. N₂O and NO₂ appear at intermediate temperatures. The complex product distribution is of utmost importance in the aforementioned HNO₃ and emission control applications. For the former, the desired products are NO and NO₂ during the selective oxidation of NH₃ over Pt/Rh catalysts at temperatures over 600°C [29]. For the latter, the desired product is N_2 . For both, N_2O is a highly undesired byproduct given its potency as a greenhouse gas. In order to improve the N₂ selectivity over the entire range of temperature there is a need of an additional SCR layer over the PGM layer. The high N₂ selectivity obtained with the dual layer ASC catalyst over a wide range of temperatures demonstrates the desired selective reduction of NOx (NO and NO₂) by NH₃ in the Cu-SSZ-13 SCR layer. This occurs by design of the duallayer ASC [21,23,24]. The Pt/Al₂O₃ base PGM layer catalyzes the oxidation of NH₃ to a

mixture in the order N_2 , N_2O , NO, and NO_2 with increasing temperature. The overall reactions occurring in the Pt-Al₂O₃ core are as follows:

$$4 NH_3 + 3 O_2 \rightarrow 2 N_2 + 6 H_2 O, \tag{1-1}$$

$$2 NH_3 + 2 O_2 \rightarrow 1 N_2 O + 3 H_2 O,$$
 (1-2)

$$4 NH_3 + 5 O_2 \rightarrow 4 NO + 6 H_2O \tag{1-3}$$

and
$$4 NH_3 + 7 O_2 \rightarrow 4 NO_2 + 6 H_2O$$
 (1-4)

The undesired oxidation products NO and NO₂ react with counter-diffusing NH_3 in the Cu-SSZ-13 SCR layer, through selective SCR chemistry forming N₂ [22,30]. The selective catalytic reduction reactions occurring in the Cu-SSZ-13 layer are as follows:

$$4 NH_3 + 4 NO + O_2 \rightarrow 4 N_2 + 6 H_2O, \tag{1-5}$$

$$2 NH_3 + NO + NO_2 \rightarrow 2 N_2 + 3 H_2O,$$
 (1-6)

$$4 NH_3 + 3 NO_2 \rightarrow 3.5 N_2 + 6 H_2 O \tag{1-7}$$

and
$$4 NH_3 + 3 O_2 \rightarrow 2 N_2 + 6 H_2 O_2$$
. (1-8)

Even though, the dual-layer architecture has been shown to be reasonably efficient at converting NH_3 to N_2 [22] it is still not considered as a best solution. It has several drawbacks that are discussed throughout this study.

1.5 Research outline

The overall objective of this study is focused on enhancing the performance of the ammonia slip catalyst (ASC). The state-of-the-art ASC consisting of a dual layer morphology presents a unique optimization challenge between the PGM and SCR layer. The addition of top SCR layer does improve the N₂ selectivity for the entire temperature range, however the SCR layer also provides the diffusional barrier restricting NH₃ to reach the bottom PGM layer and decrease NH₃ conversion as shown in Fig. 2. Another challenge being reducing the Pt loading in the base PGM layer without adversely affecting the NH₃ conversion. There are different approaches that can be taken to improve the NH_3 conversion. Some of these approaches have been studied extensively by former graduate students in our lab. First approach was the creation of pores in top SCR layer reduced the diffusion barrier and improved the NH_3 conversion without adversely affecting the N_2 selectivity. The second approach used was to optimize the dual layer architecture, having a mixed (PGM + SCR) bottom layer and a thin top SCR layer which resulted in increasing NH₃ conversion along with the added advantage of lowering Pt/Cu loading without any big detrimental impact on N_2 selectivity. For this work, we have taken the approach of developing a new catalyst which emulates the dual layer architecture down to the particle level. The chapter 2 describes the development of a Pt/Al₂O₃@Cu-ZSM-5 core-shell catalyst as an ammonia slip catalyst. The dual-layer concept is scaled down to the level of a single core-shell catalyst particle, Pt/Al₂O₃@Cu/ZSM-5, comprised of a PGM core and M-Z shell, with the intent to meet the aforementioned challenges. The core-shell catalyst was realized by rational design of key synthesis steps, the most critical being the initial

growth of an intermediate silicalite-1 layer to prevent Al leaching during the secondary growth of the ZSM-5 shell. Characterization of the core-shell spherical catalyst reveals a mesoporous PGM core (ca. 40 µm diameter) that is active and a nearly dense zeolitic shell (ca. 1 µm thick). Evaluation of the core-shell catalyst in a fixed-bed reactor shows excellent NH₃ oxidation activity and N₂ selectivity. In addition, we obtained an unanticipated enhancement of the Pt/Al₂O₃ performance within the core-shell configuration that gives an exceptional light-off of the NH₃ oxidation. Our findings reveal that the core-shell catalyst has an equivalent activity to that of a conventional Pt/Al₂O₃ catalyst containing 3-times higher Pt loading. Further, a dual layer ASC comprised of a bottom layer containing the seeded core Pt/Al₂O₃ and a Cu-SSZ-13 top layer achieves the same performance as a dual layer ASC having 3-fold higher Pt loading but with unmodified Pt/Al₂O₃.



Figure 2. Comparison of NH₃ conversion and N₂ yield for (a) Single layer PGM catalyst (b) Dual layer ASC

The enhanced activity of the Pt/Al₂O₃ catalyst is attributed to a modification of the reducibility of oxides of Pt crystallites owing to the overgrowth of silicalite-1 and ZSM-5 layers in the core-shell configuration. Finally, the separate impacts of H₂O in the feed and of hydrothermal aging (HTA) on catalyst performance is reported. H₂O in the feed is shown to have a negligible impact on conversion and product distribution. The Silicalite-modified Pt/Al₂O₃ catalyst is more resilient to HTA treatment than conventional Pt/Al₂O₃.

The Pt/Al₂O₃@Cu/ZSM-5, comprised of a PGM core and M-Z shell was found to be a very good ammonia slip catalyst, with enhanced NH₃ oxidation activity and high N₂ selectivity. The high N₂ selectivity of Pt/Al₂O₃@Cu/ZSM-5 was due to the close interactions between the PGM and SCR catalyst resulting from the core-shell geometry. The silicalite-1 modified Pt/Al_2O_3 core showed enhanced NH_3 activity which resulted in exceptional NH₃ oxidation light-off. While we did investigate the reasoning behind this enhancement in activity, we were curious about learning more about the NH₃ oxidation kinetics taking place within the seeded core which would help us in modeling study of the core-shell catalyst. But another reason behind investigating the NH₃ oxidation kinetics over Pt/Al_2O_3 was to bridge the gap between experimental rate-measurements done on single Pt crystallites at low pressure contrary to the real world applications where reactions take place on Pt-supported catalysts with various defects and different crystallites at atmospheric pressure. So before moving ahead with the core-shell catalyst modeling, we decided to perform a detailed NH₃ oxidation kinetic study over Pt/Al₂O₃ catalysts. The chapter 3 combined experimental kinetics and modeling study for NH₃ oxidation on Pt- Al_2O_3 and development of a predictive microkinetic model valid over a range of conditions.

The NH_3 oxidation rate (TOF) dependence is reported for a wide range of NH_3 concentrations (10 – 25,000 ppm) and temperatures below 250°C for Pt-Al₂O₃ powder and washcoated monoliths. The data reveal a shift from positive- to negative-order dependence on NH₃ with the rate maximum dependent on the processing of Pt-Al₂O₃; unmilled Pt-Al₂O₃ powder exhibits a rate maximum at 500 ppm NH₃, while ball-milled Pt-Al₂O₃ has a maximum at ~10,000 ppm. This unexpected enhancement of Pt-Al₂O₃ activity from milling results in a lowering of the light-off temperature (T50) by up to 100° C. Further examination rules out the extent of pore diffusion limitations as the root cause, but rather an increase in the fraction of stepped crystalline planes and destabilization of Pt oxides shown using XRD and H₂-TPR characterization. The dependence of a shift in the rate maximum to higher NH3 concentrations with milling extent is shown to require single- and dual-site reaction pathways. The kinetic scheme also captures a subtle shift in the apparent NH_3 reaction order for both unmilled and milled Pt-Al₂O₃. The microkinetic scheme is incorporated into fixed-bed and monolith reactor models which show excellent agreement with the NH₃ conversion and product distribution data.

The NH₃ oxidation kinetic study over Pt-Al₂O₃ showed the non-monotonic rate trend with respect to NH₃ which could be modeled using a two site microkinetic scheme reaction scheme for both powder and monolith based Pt catalysts. Now that we have a better understanding of the NH3 oxidation over Pt, we decided to move ahead with the modeling study of the Pt/Al₂O₃@Cu/ZSM-5 core-shell catalyst. The chapter 4 deals with the simulation and optimization of the synthesized micro-sized core-shell catalyst particle, Pt/Al₂O₃@Cu/ZSM-5 for the selective oxidation of NH₃ to N₂ in a fixed bed reactor. The state-of-the-art ammonia slip catalyst (ASC) converts NH₃ to N₂ using a dual layer structure of base PGM layer and top metal exchanged zeolite layer. This work is an extension of our previous work we were able to scale down the dual-layer concept down to the level of a single core-shell catalyst particle, Pt/Al₂O₃@Cu/ZSM-5, comprised of a PGM core and M-Z shell and showed its efficacy as an ASC. The core-shell catalyst had enhanced activity and good N₂ selectivity. The enhanced activity was attributed to the zeolite growth around the core which involved seeding, and the high N_2 selectivity was attributed to the close proximity of PGM core and Cu/ZSM-5 SCR shell in core-shell configuration. A 1D heterogeneous fixed bed model reactor was developed that coupled the contributions of NH_3 oxidation taking place in the seeded Pt/Al_2O_3 core and the SCR reactions taking place in Cu-ZSM-5 shell to simulate the enhanced performance. The NH₃ oxidation kinetics were measured for the Silicalite-1 seeded core of Pt/Al₂O₃ which revealed a non-monotonic rate dependence with respect to NH₃. The kinetic model was developed with parameters estimated from the kinetic study. We also measured the intracrystalline diffusivity of gases in the zeolite shell by fitting diffusivities of gases to the steady state NH₃ oxidation over an active core (PGM) and inert shell (Na-ZSM-5). The estimated diffusivities of NH₃, N₂, NO, NO₂ and N₂O were found to be in the range of configurational diffusivity were used in the modeling of SCR kinetics in Cu-ZSM-5. The modeling of SCR reactions in Cu-ZSM-5 shell was done by systematic parameter tuning of NH₃ uptake/desorption, NH₃ oxidation, NO oxidation, standard SCR, fast SCR and NO₂ SCR. The combined model of PGM core and Cu-ZSM-5 shell for simulating the steady state NH3 oxidation over Pt/Al2O3@Cu-ZSM-5 was validated over two synthesized coreshell catalysts of 1.2 and 0.5 micron thick shell. The model predicts the enhanced activity and N₂ selectivity in addition to the shell thickness related variation in performance. This model is also effective on converging on an optimal loading of Pt and shell thickness. The model predicted optimized core-shell catalyst has 50 % less Pt loading with a thinner Cu-ZSM-5 shell resulted in further 30 % enhancement in NH₃ oxidation activity while maintaining high N₂ selectivity for the entire operating conditions.

The chapter 5 conclude the research study along with the recommendations for future work.

Chapter 2: Enhanced Selective Oxidation of Ammonia in a Pt/Al₂O₃@Cu/ZSM-5 Core Shell Catalyst

2.1. Introduction

Developing new technologies and materials to handle NOx (NO + NO₂) emissions is necessary for limiting ozone formation. The emergence of selective catalytic reduction (SCR) of NOx with NH₃ has been critical in mitigating NOx emissions from diesel vehicles; however, the combination of transient operation and NH₃ dosing, as well as SCR catalyst deactivation, leads to the undesirable slip of unreacted NH₃ from the SCR unit. Catalysts typically employed in stationary source applications are mixed metal oxides containing V, Ti, and/or W [29], whereas the catalysts developed for vehicles tend to be metal-exchanged zeolites. Notably, Cu-exchanged SSZ-13 (a small-pore zeolite) is the most active, selective, and durable SCR catalyst for diesel vehicles [2]. It is well documented that SCR proceeds through the standard $(NH_3 + NO + O_2)$, fast $(NH_3 + NO + O_2)$ NO₂), and slow (NH₃ + NO₂) conversion of NH₃ to N₂ and H₂O [19,21,31]. The requisite NH_3/NOx ratio is slightly over unity as a result of the undesired oxidation of NH_3 , which is most prominent at higher temperature on Cu-exchanged zeolites. The reaction of NH₃ and NO₂ can lead to the generation of greenhouse gas N_2O , while the N_2O precursor NH₄NO₃ may accumulate in the pores, leading to lower activity.

In commercial SCR emission control, urea-based systems are effective in meeting stringent NOx emission targets [10], yet there are existing challenges that include low temperature activity, urea deposits, sulfur tolerance, hydrothermal stability, and dynamic performance under "real world" operation [27,28]. Moreover, NOx emission targets during transient operation with a temperature-dependent catalyst activity and NH₃ sorption cannot be satisfactorily achieved due to the undesired slip of NH₃. Despite sophisticated urea dosing strategies, the combination of NH₃ adsorption at lower temperature and rapid exhaust temperature increases unavoidably result in the release of unreacted NH₃ from the SCR unit. This release of noxious NH₃ has led to the development and application of an ammonia slip catalyst (ASC), which is responsible for converting NH₃ to N₂, as the final unit in a modern diesel vehicle emission control system.

The state-of-the-art ASC has a dual-layer architecture comprised of a base Pt/Al_2O_3 (PGM) layer and a top Cu-zeolite (SCR) layer to selectively oxidize NH_3 to N_2 . The base PGM layer oxidizes the NH_3 to a mixture of N_2 , N_2O , NO, and NO_2 , in that order, with increasing temperature (Figure 3(a), reactions in PGM layer). In the dual-layer system, the undesired products NO and NO_2 react with counter-diffusing NH_3 in the top Cu-zeolite layer, through selective NO/NO_2 reduction chemistry (Figure 3(a), reactions in SCR layer) to form N_2 [22,30]. The dual-layer architecture has been shown to be reasonably efficient at converting NH_3 to N_2 [22]. The top SCR layer improves N_2 selectivity but does so at the expense of NH_3 conversion given that the SCR layer adds a diffusion barrier. Shrestha et al., [22] showed a monotonic decrease in NH_3 conversion with increasing thickness of the top SCR layer. In addition, Dhillon et al., [32] demonstrated that modifying the diffusional resistance in the top layer by a pore-forming method can be accomplished without compromising the N_2 selectivity. Despite these developments, challenges remain in achieving NH_3 conversion and N_2 selectivity targets while minimizing the ASC volume

and Pt loading via methods that do not compromise the mechanical integrity of the monolith catalyst.



Figure 3. (a) Commercial dual layer ammonia slip catalyst performing bifunctional catalysis: SCR (gold layer) and PGM (grey layer). (b) Multiple synthesis steps involved in the preparation of core-shell catalysts with a Cu-ZSM-5 shell (SCR catalyst) and Pt/Al₂O₃ core (PGM catalyst).

To further advance ASC technology, new strategies are needed to increase the NH₃ oxidation activity and N₂ selectivity at minimal Pt loading and reactor size. In this study we apply the dual-layer ASC concept at a single particle level with the goal of reducing the light-off temperature and N₂O selectivity in a more compact and less costly reactor. Our approach is to synthesize core-shell particles that emulate the dual-layer monolith. Coreshell catalysts have been known to be versatile, tunable, stable, and durable in selected applications [33–36]. Furthermore, the core-shell architecture has been used to improve the

activity and selectivity of the reactions such as Fisher-Tropsch synthesis (FTS) and dimethyl ether (DME) synthesis, among others [37,38]. In this study, the core-shell catalyst Pt/Al₂O₃@Cu/ZSM-5 is designed with an oxidation catalyst as its core (Pt/Al₂O₃) and a NOx reduction catalyst (Cu/ZSM-5) as its shell. We adopt zeolite synthesis methods to grow the shell through *in situ* seeding and secondary growth steps [38]. To our knowledge, application of the core-shell architecture for a selective oxidation reaction for NH₃ has not been reported. Here, we evaluate the activity of the Pt/Al₂O₃@Cu/ZSM-5 catalyst in a fixed bed reactor with attention placed on the light-off temperature and product distribution. The core-shell catalyst is active at low temperature and displays excellent selectivity towards N₂ with a relatively low Pt loading. Direct comparisons are made between physical mixtures of each catalyst (Pt/Al₂O₃ and Cu-ZSM-5) and a dual-layer washcoated catalyst with the core-shell ASC catalyst to assess the relative performance of each system.

2.2. Experimental Section

2.2.1 Catalyst Synthesis

The nomenclature and composition of all catalyst samples tested in this study are listed in Table 1. The preparation of the core-shell Pt/Al₂O₃@Cu/ZSM-5 catalyst involves four steps, as depicted in Figure 3(b). The first step is the addition of Pt to commercial grade γ -Al₂O₃ (Puralox SCFa 140/L3, Sasol) using incipient wetness impregnation. In the second step, *in situ* seeding of the Pt/Al₂O₃ particle with silicalite-1 (MFI type zeolite) nanocrystals is conducted. This is followed by the third step involving secondary growth of a ZSM-5 shell onto the seeded core. Finally, the fourth step focuses on metal
incorporation by Cu ion exchange with the protonated ZSM-5 shell. Details of each step are described next.

Addition of Pt to the γ -Al₂O₃ particle (step 1): The Pt/Al₂O₃ catalyst powder, denoted as P(x)-A (where *x* is the weight percent of Pt and *A* is alumina), was synthesized by incipient wetness impregnation using tetraamine platinum nitrate (Pt(NH₃)₄(NO₃)₂, 99.995%, Sigma Aldrich) as the precursor. The γ -Al₂O₃ powder was dispersed over a quartz glass boat and an aqueous solution of the Pt complex was added dropwise uniformly over the particles. The volume of the aqueous solution was calculated based on the pore volume of alumina powder (0.5 cm³/g). 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.

Abbreviation	Туре	Cu-ZSM5 [wt%] in total catalyst ^(a)	Pt[wt%] in Al ₂ O ₃
CS	Core-shell, Pt/Al ₂ O ₃ @Cu/ZSM-5	10	0.05
P(0.05)-A	Pt/Al ₂ O ₃	0	0.05
+ 10 wt% CuZ	Physical mixture of P(0.05)-A and Cu-ZSM-5	10	0.05
+ 20 wt% CuZ	Physical mixture of P(0.05)-A and Cu-ZSM-5	20	0.05
P(0.05)-AS	Seeded core	0	0.05
P(0.05)-AS-S1	Sample after first stage of secondary growth	0	0.05
P(0.15)-A	Pt/Al ₂ O ₃	0	0.15

Table 1. Composition and nomenclature of catalyst samples.

(a) Cu loading in ZSM-5 is ca. 2.93 wt%

In situ seeding (step 2): A silicalite-1 growth solution was prepared according to a previously reported protocol [38] to achieve a molar composition of 1 SiO₂: 0.16 TPA₂O: 29 H₂O: 4 EtOH. Tetrapropylammonium hydroxide (TPAOH, 40%, Alfa Aesar) was used

as an organic structure-directing agent (OSDA) for the synthesis. TPAOH was diluted with deionized (DI) water, followed by the dropwise addition of the silica source, tetraethylorthosilicate (TEOS, 98%, Sigma-Aldrich), under continuous stirring. The solution was stirred overnight at room temperature to yield a clear solution, which was combined with Pt/Al₂O₃ particles (1 wt% of solution) in a Teflon-lined stainless-steel autoclave (Parr Instruments). The autoclave was heated in a ThermoFischer Precision 3050 series gravity oven at 100°C under constant rotation (30 rpm) to prevent sedimentation of core particles. After 24 h the autoclave was removed from the oven and quenched to room temperature. The seeded core, or P(0.05)-AS particles, were isolated from the mother liquor by filtration (Filter Paper, Qualitative, 415, VWR) and washing with DI water.

Secondary growth (step 3): The secondary growth of a ZSM-5 shell over P(0.05)-AS seeds was accomplished using a solution with the following molar composition: 10 TPAOH: 31.5 TEOS: 1 NaAlO₂: 1483 H₂O [39]. The ZSM-5 growth solution was prepared by adding an appropriate amount of TEOS (dropwise) to a solution containing TPAOH, NaAlO₂ (Alfa Aesar) and DI water. The solution was stirred at room temperature overnight. The formation of a ZSM-5 shell was carried out by adding the seeded core (1 wt% P(0.05)-AS) to the growth solution. The resulting mixture was then placed in a Teflon-lined stainless-steel autoclave that was heated at 180°C under rotation for 48 h. To obtain a complete coverage of ZSM-5 shell around the core, we employed a secondary growth step involving the resuspension of solids recovered from the first batch in a fresh growth solution and repeating the same synthesis procedure for a second time at the same synthesis conditions (180°C, 48 h). The resulting core-shell particles were recovered by vacuum

filtration and washing with DI water. The sample was allowed to dry followed by calcination at 550°C for 6 h with a temperature ramp rate of 5°C/h to remove the OSDA. The resulting Na-form zeolite was triple exchanged with a 0.5 M solution of NH_4NO_3 (Sigma Aldrich) at 80°C for 1 h per cycle with sequential filtration and washing. The recovered solids were dried at 60°C and then calcined at 550°C for 6 h with a ramp rate of 5°C/h to generate the active protonated shell (H-ZSM-5).

Copper ion exchange (step 4). Copper was added to the H-ZSM-5 shell by ion exchange using copper acetate (Cu(CH₃-COO)₂.H₂O > 99.995%, Sigma Aldrich) as the precursor. The core-shell catalyst was ion-exchanged three times in 1 L of 0.01 M copper acetate at room temperature for 6 h. The resulting Cu-exchanged core-shell catalyst was then dried at 130°C and calcined in air at 500°C for 4 h using a temperature ramp of 0.5° C/min.

2.2.2 Bench scale reactor setup

Catalytic activity and performance measurements were carried out in both fixed bed and monolith reactors in an overall set-up that is described elsewhere [40]. A quartz tube (OD 12.75 mm and ID 10.5 mm) containing the catalyst sample was placed in an electric furnace equipped with a programmable temperature controller. The catalyst was packed at the center of the quartz tube with quartz wool on either end of the bed. The thermocouple end point was positioned in the middle of the catalyst bed both radially and axially. The feed gas flows were metered by MKS mass flow controllers, and the gases used in our work were purchased from Matheson Inc. The concentrations of outlet gases from the reactor were analyzed by a FTIR (Thermo-Nicolet Nexus 470; Nicolet Analytical Instruments) with OMNIC software. The pressure inside the flow lines was maintained at 760 Torr by using a globe valve positioned downstream of the FTIR. The steady state N_2 yield reported in this paper is calculated by difference using an overall nitrogen balance.

2.2.3 Steady state reaction experiments

All flow lines were heated to 150° C by electrical heating tape to prevent condensation and/or adsorption of the water vapor and NH₃ onto the tube surfaces. All lines were flushed with Ar for 1 h before collecting background spectra. After taking the background spectra, 500 ppm NH₃ in 5 vol% O₂ and balance Ar were directed through a reactor bypass line to measure the feed concentration of NH₃ for reference. The flow was then switched to the reactor side, and reaction performance was tested at steady state in the temperature range from 150 to 400°C. Once the gas concentrations remained constant for ca. 30 min, the steady state data was collected. Selected experiments were conducted with H₂O (5%) and CO₂ (8%) in the feed.

2.2.4 Aging

The fixed bed containing the following catalyst samples P(0.05)-A, P(0.05)-AS and CS each with mass of 0.18 g were aged at 550°C in a flowing gas of 5% O₂, 5% H₂O, 8% CO₂ and balance Ar at 1000 sccm. The catalyst samples were aged for a period of 10 h followed by reaction testing under steady state conditions.

2.2.5 H₂-temperature programmed reduction

The catalysts tested were pretreated at 500°C for 1 h in a reductive atmosphere (5% H₂, balance Ar) followed by 2 h in an oxidative atmosphere (5% O₂, balance Ar). The

samples were pelletized (50-70 mesh size) and loaded into a quartz tube of dimensions 4 x 6.35 mm^2 (ID x OD) that was placed in an electric furnace. Prior to conducting the H₂ temperature program reaction (TPR), the sample was subjected to 30 sccm of Ar flow at 250°C to remove any adsorbed gases over the Pt. The set-up was then cooled to room temperature, and the H₂-TPR experiment was initiated using a feed gas of 1 vol% H₂ (balance Ar) at a constant flowrate (30 sccm). The temperature was increased from 38 to 800°C with a ramp rate of 10°C/min. The gases were detected using a mass-spectrometer (HIDEN analytic, HPR 20).

2.2.6 Materials characterization

Scanning electron microscopy (SEM) images were obtained using a Zeiss Leo 1525 Gemini FEG instrument. Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku Smartlab Diffractometer using a Cu K α source (40kV, 30mA, $\lambda = 1.54$ Å) in the range of 2 $\theta = 5$ - 50 degrees with 0.02-degree increments. The collected patterns were compared using a reference MFI pattern obtained from the International Zeolite Association (IZA) structure database.

Elemental analysis of the core-shell catalyst was performed using two techniques: X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray (EDX) spectroscopy. XPS measurements were performed on a PHI Model 5700 X-Ray Photoelectron Spectrometer equipped with a standard achromatic Al K α X-ray source (1486.6 eV) at 300W, a concentric hemispherical analyzer, and a neutralizer. EDX measurements were conducted using a JEOL SM-31010/METEK EDAX system at 15kV and 15 mm working

distance. The core-shell structure was further confirmed by time of flight – secondary ions mass spectrometry (ToF-SIMS). Samples were held in place using double-face carbon tape. The sample holder was attached to the transfer arm by means of a bayonet fitting, which was then introduced in the load lock chamber until the vacuum pumping reached 5.0×10^{-10} ⁶ mbar, ensuring an appropriate detection limit. For analysis, a positive high mass resolution depth profile was performed using ToF-SIMS NCS, which combines a ToF-SIMS instrument (ION-TOF GmbH, Münster, Germany) and an in situ scanning probe microscope (NanoScan, Switzerland) at the Shared Equipment Authority (Rice University). A bunched 30 keV Bi³⁺ ions (with a measured current of 0.2 pA) was used as the primary probe for analysis (scanned area = $100 \times 100 \ \mu m^2$), and sputtering was performed using Cs^+ ions at 2 keV with a typical current of ca. 105 nA and a rastered area of $300 \times 300 \,\mu\text{m}^2$. The beams were operated in non-interlaced mode, alternating 3 analysis cycles and 80 sputtering cycles (corresponding to 65.54 s) followed by a pause of 5 s for the charge compensation with an electron flood gun. An adjustment of the charge effects has been operated using a surface potential. During the depth profiling, the cycle time was fixed to 90 μ s (corresponding to m/z = 0 – 738 amu mass range).

The measurements of Pt dispersion were carried out using a 3Flexi Chemi Micromeritics apparatus. The analysis gas selected was CO. Multiple measurements were done on same batch of catalyst; this was also supplemented by measurements on a different batch.

2.3. Results and discussion

2.3.1 Validation of core-shell synthesis

As described in this Section, characterization of the catalyst particle with several techniques collectively validated the successful synthesis of the core-shell Pt/Al₂O₃@Cu/ZSM-5 catalyst. Figure 4(a) shows the SEM micrographs at different stages of synthesis, which reveal the formation of a layer of zeolite crystallites on the external surface of the alumina particles. After in situ seeding (step 2), changes in the surface morphology of core particle catalyst are observed, which may have occurred during the growth of the silicalite-1 layer onto the particles. The seeds with an overcoat of silicalite-1 served as protection against Al leaching of the alumina particles as well as nucleation sites for ZSM-5 during the secondary growth procedure (step 3). Figure 4(d) shows the assynthesized core-shell catalyst after repeated secondary growth stages with no free/excess ZSM-5 crystals observed, indicating growth occurred solely on the exterior shell of the seeds. To approximate the shell thickness, the as-synthesized catalyst was crushed, and from SEM images of the crushed particles (Figure 4(e)), the average shell thickness was approximated to be $1 - 1.5 \mu m$. To confirm the core-shell structure, several characterization methods were used in combination, as discussed below.



Figure 4. SEM at different stages of synthesis: (a) Core: Pt(0.05)-Al₂O₃; (b) In situ seeding: Seeded core, P(0.05)-AS; (c) First *in situ* secondary growth (incomplete surface coverage); (d) Second *in situ* secondary growth (complete surface coverage with ZSM-5 shell); (e) Shell thickness indicated by arrow (thickness ≈ 1.2 µm)

Figure 5 shows the powder XRD patterns for samples at different stages of synthesis: the original Pt/Al₂O₃ core (P(0.05)-A), the intermediate seeded core (P(0.05)-AS), and the final core-shell (CS) catalyst. These patterns are compared to a reference for H-ZSM-5 (MFI framework) obtained from the International Zeolite Association (IZA) database. While there is little to no detectable characteristic ZSM-5 peaks in patterns of core and seeded core samples, the presence of well-pronounced peaks in the case of the core-shell catalyst indicates the presence of MFI type zeolite. It was previously noted (Figure 4(d)) that there is no observable free/excess ZSM-5 crystals post multiple

secondary growth; thus, the MFI peaks can be attributed to the growth of a ZSM-5 shell around the core.



Figure 5. Powder XRD patterns for the core-shell, seeded core (P(0.05)-AS), and core (Pt(0.05)-A). The MFI framework structure of ZSM-5 was indexed according to a reference pattern for H-ZSM-5 provided by the IZA structure database.

Elemental analysis of the core-shell catalyst was performed using a combination of X-ray photoelectron spectroscopy (XPS) and Energy dispersive X-ray (EDX) to determine the Si-to-Al ratio (SAR). EDX probes a greater depth into the catalyst particle (ca. 1 μ m), thereby assessing the bulk Si/Al ratio, whereas XPS is a surface sensitive technique with shorter penetration depth of ca. 10 nm that assesses the outer rim of the particle. Using both of these techniques, the Si/Al ratio was found to be ca. 30 for the core-shell (CS) particles. As described later, EDX detected no Pt, which indicates that EDX probing is confined to the shell. The similar Si/Al ratio measurements using XPS and EDX also suggests an absence of Al zoning in the shell. A more comprehensive analysis of surface composition

by XPS was used to determine the Si/Al ratio at different stages of synthesis (Figure 6). The gradual decrease in Al concentration with a subsequent increase in Si concentration as the synthesis progresses indicates the coverage of the core with a shell of zeolite, which was earlier confirmed by XRD to be ZSM-5. Furthermore, EDX was also employed to determine the fraction of Cu introduced into the ZSM-5 shell via Cu ion-exchange (ca. 2.9%) and to confirm that there is no detectable Pt in the shell. Finally, as describe earlier, CS particles were crushed to enable measurement of the determining the shell thickness using SEM. We used EDX to analyze the exposed core. The EDX characterization indicated no Cu in the core. This is evidence that the Cu does not migrate to the core.



Figure 6. (Bottom) Scanning electron micrographs at different stages of synthesis: Core of Pt(0.05)-Al₂O₃, seeded core of P(0.05)-AS, P(0.05)-AS-S1, CS. (Top) XPS analysis at different stages of synthesis reveals changes in the Si and Al atomic concentrations at the surface.



Figure 7. (a) Depth profile of the catalyst particle composition as measured by ToF-SIMS, plotted as a function of fractional intensity with sputter time of elements Al (black squares) and Si (red circles). (b) Surface mapping of a core-shell catalyst

In order to obtain further evidence of the core-shell structure, time of flight secondary ion mass spectroscopy (ToF-SIMS) depth profiling was performed to generate a depth profile of elemental composition. In Figure 7(a), the fractional intensity of each element (Si and Al) is plotted as a function of sputter time. There exists a direct correlation between sputter time and depth, such that the longer the sputter time, the deeper the probe into the catalyst particle. As sputter time increases, we observe an increase in the fractional intensity of Al and a concomitant decrease of Si, which indicates the transition from the shell of the particle (Si-rich layer) to the core (Al-rich interior). At sputtering times beyond 2600 s the Al and Si intensities remain constant, indicating that the sputtering has reached the core (Pt/Al₂O₃), as indicated by the dashed line. A surface mapping of the core-shell catalyst (Figure 7(b)) with respect to Si and Al ions reveals a homogenous composition (i.e., uniform color), thus validating the complete coverage of the Al₂O₃ core with a zeolite shell. The dark areas represent the shadow cast by ionizing beam. This is due to the rough surface ZSM-5 surface formed over the core, which can be seen in the SEM images.

Furthermore, during the ToF-SIMS depth-profiling no Pt was detected in the shell which confirmed earlier EDX measurements. As mentioned above, EDX analysis of crushed particles showed no Cu in the exposed core.

2.3.2 Steady state NH₃ oxidation

The synthesized core-shell (CS) catalyst was evaluated in a quartz tubular fixedbed reactor. The bed contained 0.18 g of CS catalyst with a particle size ranging from 40 to 50 μ m (mesh size 325). The gas feed containing 500 ppm NH₃, 5 vol% O₂, and balance Ar was delivered at a flowrate of 1000 sccm (GHSV of ca. 280k h⁻¹). Figure 8(a) shows the steady-state NH₃ conversion versus catalyst bed temperature profile for the CS catalyst. We observed that the light-off, defined as the temperature giving ~20% conversion (T₂₀), occurs around 220°C. Complete NH₃ conversion was achieved at around 300°C. For temperatures up to 275°C, non-N₂ products (i.e., N₂O, NO, and NO₂) were not detected, implying 100% N₂ selectivity. As the temperature was increased above 275°C, the emergence of N₂O, NO, and NO₂ were detected in succession. The combined yield of NO, N₂O and NO₂ was less than 10% over the entire temperature range (200 – 500°C). The N₂ yield attained a maximum of 94% at ~310°C, which decreased to ca. 91% at 500°C, at which point the major byproduct was NO.

Figure 8(b) shows the NH₃ conversion profile for the Pt/Al_2O_3 powder sample (P(0.05)-A) for the same reaction conditions. Comparing this data to that of the CS catalyst (Figure 8(a)) reveals similar qualitative trends, but quite different quantitative results. Specifically, NH₃ oxidation light-off over the P(0.05)-A catalyst occurs at a much higher

temperature (T₂₀= 300°C) and the byproduct concentrations are much higher. Complete conversion is achieved at 400°C, the maximum N₂ yield is remarkably low (45% at 325°C), the maximum N₂O yield is 20% at 360°C, and the maximum NO yield at 500°C is approximately 85%.



It is evident from a direct comparison of the two catalysts that the presence of the

Figure 8. Steady state NH₃ oxidation as a function of temperature for (a) core-shell (CS) and (b) Pt(0.05)/Al₂O₃ powder (Conversion: open symbol, Yield: closed symbol, 0.18 g catalyst in fixed bed. Feed : 500 ppm NH₃, 5% O₂, balance Ar, 1000 sccm.

Cu/ZSM-5 shell around the Pt/Al₂O₃ core has a significant beneficial impact on the coreshell activity and selectivity. The high N₂ selectivity obtained with the CS catalyst over a wide range of temperatures demonstrates the desired selective reduction of NOx (NO and NO₂) by NH₃ in the Cu/ZSM-5 shell. This occurs by design and resembles the performance of the dual-layer ASC [21,23,24]. The Pt/Al₂O₃ core catalyzes the oxidation of NH₃ to a mixture in the order N₂, N₂O, NO, and NO₂ with increasing temperature, as seen in Figure 8(b). The overall reactions occurring in the Pt-Al₂O₃ core are as follows:

$$4 NH_3 + 3 O_2 \rightarrow 2 N_2 + 6 H_2 O, \qquad (2-1)$$

$$2 NH_3 + 2 O_2 \rightarrow 1 N_2 O + 3 H_2 O,$$
 (2-2)

$$4 NH_3 + 5 O_2 \rightarrow 4 NO + 6 H_2O \tag{2-3}$$

and
$$4 NH_3 + 7 O_2 \rightarrow 4 NO_2 + 6 H_2O_2$$
. (2-4)

The undesired oxidation products NO and NO₂ react with counter-diffusing NH₃ in the Cu-ZSM-5 shell, through selective SCR chemistry (R5-R8) forming N₂ [22,30]. The selective catalytic reduction reactions occurring in the Cu-ZSM-5 shell are as follows:

$$4 NH_3 + 4 NO + O_2 \rightarrow 4 N_2 + 6 H_2O, \tag{1-5}$$

$$2 NH_3 + NO + NO_2 \rightarrow 2 N_2 + 3 H_2O,$$
 (1-6)

$$4 NH_3 + 3 NO_2 \rightarrow 3.5 N_2 + 6 H_2O \tag{1-7}$$

and
$$4 NH_3 + 3 O_2 \rightarrow 2 N_2 + 6 H_2 O_1$$
. (1-8)

The reader is referred to earlier works on NH₃ oxidation and NH₃-based SCR for more detail.

In contrast, the moderate decrease in the NH₃ oxidation light-off temperature is an unexpected, albeit desirable, outcome of the CS construct. To our knowledge, a decrease in light-off temperature of this magnitude has not been reported previously in ASC studies. At low temperature, the Cu/ZSM-5 shell does not have sufficient activity to explain the

results. Thus, the origin of the activity increase resides with the Pt/Al_2O_3 core, which is discussed in greater detail in Section 3.4.

2.3.3 Comparison between core-shell and physical mixtures

To examine the benefit of the core-shell architecture, a series of experiments were carried out with a physical mixture of Pt/Al₂O₃ and Cu-ZSM-5 particles. In order to enable a meaningful comparison to the CS catalyst, the catalyst composition and properties were fixed. Notably, particles of pure ZSM-5 were prepared with the same Si/Al ratio and crystallite size (i.e., particle diameter equal to the thickness of the shell) as the CS catalyst. The control sample of ZSM-5 for the physical mixture was synthesized using the method described in Section 2.1.3, with the absence of an alumina core. The pure H-ZSM-5 crystals used as a control sample in the physical mixture were characterized by XRD, SEM and XPS (Si/Al ~ 12.3, Cu/Al ~ 0.35, Cu wt %: 3.4). The Cu loading in the zeolite was fixed at 2.9 wt% while the Pt loading of the Pt/Al₂O₃ was kept at 0.05 wt%. A blend of these two catalytic components was prepared by physically mixing the Pt/Al₂O₃ and Cu/ZSM-5 samples. Mixtures containing three overall mass fractions of Cu/ZSM-5 were prepared and are denoted herein as P(0.05)A + x Cu-Z, where x = 0, 10, and 20 wt%. For each experiment, the reactor tube was filled with a total mass of 0.18 g of catalyst and identical protocols were followed. For the samples analyzed, the Pt-containing material was as follows: $0.18g Pt/Al_2O_3$ for sample P(0.05)-A, 0.16 g Pt/Al_2O_3 for sample CS and sample P(0.05)A + 10% Cu-Z, and 0.14 g Pt/Al₂O₃ for sample P(0.05)A + 20% Cu-Z. It is noted that the CS catalyst had an estimated mass fraction of ca. 10 wt% Cu/ZSM-5 based on a core particle diameter of 40 μ m and a shell thickness of 1.5 μ m, along with the assumed densities of 3.7 and 1.8 g/cm³, respectively.

In Figure 9(a) we compare the steady state NH₃ conversion for the CS catalyst relative to the P(0.05)A, P(0.05)A + 10%Cu-Z, and P(0.05)A + 20%Cu-Z samples. The T₂₀ for the three physical mixtures varies from ca. 275°C for the P(0.05)A + 20%Cu-Z mixture to ca. 290°C for the P(0.05)A and P(0.05)A + 10%Cu-Z mixtures. These temperatures are significantly higher than the T₂₀ value of ca. 220°C for the CS catalyst. In addition, complete NH₃ conversion occurs at much lower temperature (i.e., ~300°C for CS vs. 400°C for the other three samples). The explanation for these differences is discussed in greater detail later.



Figure 9. Steady state NH₃ oxidation over different samples showing (a) NH₃ conversion, (b) N₂ yield, (c) NO yield, (d) N₂O yield, (e) NO₂ yield, and (f) N₂ selectivity. 0.18g in fixed bed. Feed conditions: 500 ppm NH₃, 5% O₂, balance Argon, 1000 sccm.

Figure 9(b) shows the N₂ yield for the same four samples. The lowest N₂ yield is obtained with P(0.05)A, which is expected given the absence of Cu-ZSM-5. That is, the presence of Cu/ZSM-5 provides SCR activity to convert NH₃ and NO to N₂. The N₂ selectivity of the four samples (Figure 9(f)) indicates an increase in selectivity with the addition of Cu/ZSM-5. The N₂ selectivity for the Pt-only sample approaches zero as the temperature is increased to 500°C due to the formation of byproducts (NO, N₂O, and NO₂). The N₂ selectivity of the samples containing 10 and 20 wt% Cu-ZSM-5 approach 36 and 54%, respectively. A maximum N₂ yield of ca. 52% is obtained for 20 wt% Cu-ZSM-5, which exceeds that for 10 wt% Cu/ZSM-5 (Y_{N2} \approx 48%). The maximum N₂ yield occurs at essentially the same temperature (ca. 310°C) for the three physical mixtures. This reflects the similar amount of Pt/Al₂O₃ resulting in roughly the same NH₃ conversion (Figure 9(a)) and NO yield (Figure 9(c)).

A direct comparison of the P(0.05)A + 10%Cu-Z and CS samples is informative as each has the same amount of Pt/Al_2O_3 and Cu-ZSM-5. The CS catalyst has a much higher N_2 selectivity compared to the physical mixture, as shown in Figure 9(f). The N_2 selectivity is maintained at ~92% at 500°C compared to ~36% at the same temperature for the physical mixture containing 10% Cu-Z. The CS catalyst selectivity is also higher than the physical mixture having twice the amount of Cu/ZSM-5 (P(0.05)A + 20%Cu-Z). This conveys the importance of the direct proximity of bifunctional catalysts achieved with the CS architecture whereby the products generated in the Pt/Al₂O₃ core (NO + NO₂) diffuse into the contiguous shell to react with counter-diffusing NH₃ on the Cu sites of ZSM-5. In contrast, for the physical mixture, NO + NO₂ generated in the Pt/Al₂O₃ particles must diffuse to Cu/ZSM-5 particles through the interstitial regions of the fixed bed. Reaction with NH₃ then requires co-diffusion of NH₃ and NO + O₂ (standard SCR), NO + NO₂ (fast SCR), or NO₂ (slow SCR) into the Cu/ZSM-5 crystallite. At higher temperature, the SCR reaction may be diffusion limited, and, as a result, the less efficient process leads to inferior performance, such as a higher NOx fraction leaving the catalyst unreacted. Alternatively, it may be stated that the CS catalyst has a higher selectivity for N₂ compared to the physical mixture. The Cu/ZSM-5 shell in direct contact with the Pt/Al₂O₃ core enables efficient contact and reaction of NH₃ with generated NO + NO₂.

2.3.4 Ammonia oxidation light-off

Figure 9(a) shows that the CS catalyst has a considerably lower light-off temperature at an equivalent Pt loading as the Pt(0.05)-Al₂O₃ (P(0.05)-A) sample, which is without a zeolite shell. This result is seemingly counterintuitive. For instance, in prior dual-layer ASC studies the Fe- or Cu-zeolite (ZSM-5 or SSZ-13) top layer was shown to increase N₂ selectivity at the expense of NH₃ conversion [22]. Those studies along with our findings presented here reveal that Pt/Al₂O₃ is highly active towards NH₃ oxidation, but poorly selective towards N₂, with N₂O and NO being the main products at intermediate and high temperature, respectively. The SCR top layer catalyzes the selective lean reduction of NH₃ with NO + NO₂ generated in the underlying Pt/Al₂O₃ layer. In addition to providing the SCR activity, the top layer introduces a resistance to diffusion of reacting species from the feed gas. Thus, for the CS catalyst, its Cu/ZSM-5 shell with a known low NH₃ oxidation activity, should constitute a mass transfer barrier for the underlying Pt/Al₂O₃

core. The unexpected finding of a higher NH_3 oxidation activity, therefore, most likely has its origin in the Pt/Al_2O_3 component of the CS catalyst.

We examined this finding in more detail given its potential importance in increasing the activity of the catalyst. In these experiments we compared the steady state NH₃ oxidation activity of the CS catalyst to four samples: two without a ZSM-5 shell having different Pt loadings (samples P(0.05)-A and P(0.15)-A), one obtained after silicalite-1 seeding (sample P(0.05)-AS with a Pt loading of 0.05 wt%), and one with only one step of secondary growth of ZSM-5 (P(0.05)-AS-S1). Assessment of samples P(0.05)-AS and P(0.05)-AS-S1 (using the same feed conditions as previous experiments) allowed for the decoupling of Cu/ZSM-5 shell contributions from those of Pt to the overall catalytic performance.

Figure 10(a) compares the light-off curve of the CS sample to those of P(0.05)-A and P(0.15)-A. The light-off temperatures (T₂₀) are approximately 300, 240, and 220°C for Pt(0.05)/Al₂O₃, Pt(0.15)/Al₂O₃, and CS, respectively. The data reveal that an increase in Pt loading from 0.05 to 0.15 wt% lowers the light-off temperature by ca. 60°C. Of more interest is that the CS catalyst has an even lower light-off temperature (220°C) than the higher Pt loading sample despite having a 0.08 mg Pt compared to 0.27 mg Pt for the P(0.15)-A sample. This underscores the higher activity of the CS sample. A comparison of the N₂ yields (Figure 10(b)) indicates the high selectivity of the CS catalyst relative to others. The P(0.15)-A catalyst, owing to its higher Pt loading, has a larger N₂ generation peak compared to P(0.05)-A, but then dips down to zero as temperature is increased due to

the generation of NOx. It was also checked if the catalyst performance is affected by the presence of water vapor in the feed. P(0.05)-A, P(0.05)-AS and CS samples were tested in 500 ppm NH₃, 5% O₂, 5% H₂O, 8% CO₂ and balance Argon at 1000 sccm. The addition of H₂O to the feed has a negligible impact on the performance of the catalyst samples. More comprehensive reaction testing is being done to assess the performance of CS samples in the presence of SO₂, SO₂+H₂O in the feed which will be reported later.



Figure 10. Steady state NH₃ oxidation over CS, P(0.05)-A and P(0.15)-A with 0.05, 0.15, 0.05 wt% Pt, respectively. Comparisons are made for (a) NH₃ conversion (b) N₂ yield. 0.18 g in fixed bed. Feed: 500 ppm NH₃, 5% O₂, balance Ar, 1000 sccm.

Here we use P(0.05)-A as a reference to compare its light-off curve with those of P(0.05)-AS and P(0.05)-AS-S1 (Figure 11(a)) to assess the impact of silicalite-1 on catalyst activity. The data in Figure 11(a) reveal a distribution of light-off curves in the order of decreasing T_{20} (in brackets): P(0.05)-A (300°C), CS (225°C), P(0.05)-AS (210°C), and P(0.05)-AS-S1 (190°C). There are two notable trends in this figure. First, the decreasing light-off temperature of the non-CS samples clearly indicates an enhancement of the NH₃ oxidation activity from the core-shell catalyst synthesis. Second, the higher light-off

temperature for CS compared to P(0.05)-AS and P(0.05)-AS-S1 shows the detrimental effect of the Cu/ZSM-5 shell on the oxidation activity of the underlying $Pt(Al_2O_3)$ core.



Figure 11. Steady state NH₃ oxidation over: P(0.05)-A, P(0.05)-AS, P(0.05)-AS-S1 and CS. Reaction data are plotted for (a) NH₃ conversion and (b) N₂ yield. Feed conditions: 500 ppm NH₃, 5% O₂, balance Ar, 1000 sccm and 0.18 g of catalyst.

The presence of the Cu/ZSM-5 shell provides SCR activity but inhibits the diffusion of NH₃ to the underlying Pt/Al₂O₃ core and NO + NO₂ in the opposite direction from the core. As such, while the hydrothermal synthesis apparently increases the intrinsic activity of Pt, the actual growth of the shell layer leads to a formidable diffusion barrier. The net effect is a decrease in the NH₃ conversion at temperatures below 250°C. On the other hand, as the temperature is increased beyond the light-off for each of these samples, the CS catalyst demonstrates a much higher selectivity due to the reduction of NO in the shell. The two non-CS samples are effective in oxidizing NH₃ but are only selective to N₂ over a narrow range of temperature.

SEM images (Figure 2) support this explanation. Figure 4(b) shows that after the growth of silicalite-1, the surface of the Pt/Al₂O₃ particles has some particles which are

likely small particles of silicalite-1 that serve as seeds for ZSM-5 growth. The fact that powder XRD of this seeded core sample, P(0.05)-AS, reveals little to no MFI diffraction peaks is expected due to the minimal quantity (< 3 wt%) of silicalite-1 relative to the core. The presence of Si on the surfaces of Al₂O₃, however, is confirmed by XPS (Figure 6). After the first seeded growth, the resulting particles are sparsely covered with patches of ZSM-5 (Figure 4(c)). The distinct ZSM-5 peaks start to develop after this stage of synthesis as shown in Figure 3. The second secondary treatment of P(0.05)-AS-S1 leads to nearly complete coverage of the core particle with a ZSM-5 shell (Figure 4(d)). The corresponding powder XRD pattern shows strong MFI peaks confirming the crystallinity of the shell, which is measured to be $1 - 1.2 \mu m$ in thickness. The presence of a nearly continuous shell around the core constitutes a diffusion barrier as discussed above [22,30,32]. As a result, the light-off increases from 185°C for the case of P(0.05)-AS-S1 having sparse ZSM-5 coverage to 220°C for the core-shell catalyst having a complete coverage of ZSM-5 (shell).

An intriguing finding is that the hydrothermal steps to grow silicalite-1 and ZSM-5 enhance the intrinsic Pt oxidation activity. Two successive hydrothermal treatments result in a reduction in the NH₃ oxidation light-off temperature. Identifying the root cause of this unexpected but intriguing result is of interest given the ramifications for improved ASC performance. A modification of Pt morphology and particle size, among other physicochemical properties, is likely responsible for the change in catalyst activity.

One logical explanation is a reduction in the Pt particle size. A higher dispersion of the Pt would mean a higher exposed active surface and a higher oxidation rate, which as a result, can lead to increased activity. For this reason, dispersion measurements were carried out for the Pt(0.05)/Al₂O₃ particles before, P(0.05)-A, and after, P(0.05)-AS, the hydrothermal silicalite-1 growth step. Both samples had the same concentration of Pt on Al₂O₃ (0.05 wt%), with Pt dispersion measurements of $45 \pm 2\%$ for P(0.05)-A and $42 \pm$ 1% for P(0.05)-AS. Thus, prolonged exposure to the growth solution resulted in a minor decrease in the Pt dispersion. An estimate of the Pt crystallite size is 2.4 nm for the P(0.05)-A particle and 2.6 nm for the seeded P(0.05)-A particle was obtained using chemisorption measurements with CO as analysis gas. A slight drop in the Pt dispersion of the core-shell catalyst would be expected to lower the catalyst activity; however, the opposite result was observed. This clearly rules out particle size reduction as the responsible cause and a different explanation is needed.

It has been reported previously in the literature that metal-catalyzed oxidation reactions may occur at a higher rate on larger crystallites than smaller ones. Pt-catalyzed NO oxidation to NO₂ is such an example [40,41]. The behavior is attributed to the formation of Pt oxide, which is less active for NO oxidation than metallic Pt. The propensity to form Pt oxide increases when the crystallite size is small. This is particularly prevalent in the presence of NO₂. The presence of excess O₂ and the possible formation of NO and NO₂ are favorable conditions for Pt oxide formation. Indeed, Pt oxide begins to form at 100°C [42,43] and is stable up to 470°C on a γ -Al₂O₃ support. The catalytic activity varies with the presence of Pt in different oxidation states; thus it is important to understand the effect of Pt oxides on catalyst activity with respect to NH₃ oxidation.

For this reason, H₂ temperature programmed reduction (H₂-TPR) was carried out to determine the nature and extent of Pt oxide formation. For instance, a comparison of H₂-TPR profiles for different samples might provide evidence for the role of the Pt oxide. To this end, H₂ TPR was performed for Al₂O₃, Pt(0.05)/Al₂O₃ (or P(0.05)-A) and the seeded core (P(0.05)-AS). The feed conditions were 1 vol% H₂ (with Ar balance) at a flow rate of 30 sccm and a temperature ramp rate of 10°C/min up to 800°C (Figure 12(a)). The catalysts were pelletized to 50-70 mesh size, and 100 mg of sample was used for testing. With the small amount of Pt (26 µmoles in a 100 mg sample) it was difficult to detect H₂ consumption with the mass spectrometer for the given feed. Instead, H₂O generation peaks could be detected during the analysis.



Figure 12. H₂ temperature programmed reduction. (a) Temperature profile used for each experiment with a ramp rate of 10° C/min. (b – d) H₂O generation peaks detected by mass spectrometry for (b) Al₂O₃, (c) P(0.05)-A, Pt/Al₂O₃ (d) P(0.05)-AS.

Figures 12(b - d) show the H₂O production as a function of time over the three samples. The peak at 745°C, which is present for all samples, is the contribution from the γ -Al₂O₃ support (Figure 12(b)). The commercial γ -Al₂O₃ support contains 3 wt% La₂O₃ to improve thermostability. The peak at 745°C is attributed to H₂-TPR contribution from La_2O_3 [44]. The P(0.05)-A sample has a peak at 375°C in addition to the peak at 745°C (Figure 12(c)). In contrast, the P(0.05)-AS sample has a H_2O peak appearing at a lower temperature of 250°C (Figure 12(d)). Huizinga et al., [45] showed an increased stability of Pt oxide over γ -alumina, compared to alternative supports such as TiO₂ or SiO₂. In that work, H₂-TPR over Pt/TiO₂ showed that Pt oxide species decompose at lower temperature compared to Pt/γ -Al₂O₃, which suggests that alumina stabilizes surface Pt oxide. We invoke similar reasoning for the core-shell particles. For example, the formation of H₂O peaks at lower temperature for P(0.05)-AS compared to P(0.05)-A indicates a lower stability (or higher reactivity) of Pt oxides during reduction by H₂. An interesting observation may be drawn from Figure 12(c), i.e., the appearance of H₂O happens at nearly the same temperature range of the NH₃ oxidation light-off on the CS catalyst (~ 250° C; see Figure 9(a)). The H₂O generation for P(0.05)-A starts at 360°C and reaches a maximum at $375^{\circ}C$ (Figure 11(c)). The higher H₂O generation temperature for P(0.05)-A compared to the seeded core reveals that Pt oxides are more stable in the P(0.05)-A sample compared to P(0.05)-AS (seeded core).

From the H_2 -TPR experiments the effect of the support on the stability of these oxides is evident. Yao et al., [46] showed an increase in H_2 reduction temperature with decrease in Pt weight percent (or increase in Pt dispersion). This was attributed to the

presence of smaller crystallite size with increase in Pt dispersion. However CO chemisorption measurements showed similar Pt dispersion (particle size) for catalyst samples P(0.05)-A and P(0.05)-AS. This rules out particle size dependence on the drop in H_2 reduction temperature for P(0.05)-AS. We propose the alternative explanation that during the hydrothermal synthesis step a thin layer of silicalite-1 is deposited onto the Pt/Al₂O₃ surface. The presence of the thin layer alters the Pt binding to the γ -Al₂O₃ support, which in turn destabilizes any oxides that form on the Pt crystallites during oxidation. Indeed, Yazawa et al., [47] reported an increasing activity of Pt at a given dispersion as the metal support was changed. Specifically, the turnover frequency of Pt decreased in the sequence Pt/SiO_2 - Al_2O_3 > Pt/Al_2O_3 > Pt/MgO. This order follows the acid strength of these oxides (i.e., $SiO_2-Al_2O_3 > Al_2O_3 > MgO$). An increasing acidity of the support suppresses the formation of Pt oxides. Studies have shown that the activity of Pt catalysts decreases with Pt oxidation [47–49]. The formation of a thin layer of silicalite-1 over the surface of the core appears to increase the acidity. This suppresses the formation of Pt oxides, which leads to a higher activity of the seeded core.

2.3.5 Effect of shell thickness on N₂ selectivity

As described earlier, ammonia slip catalyst consists of an oxidation function (Pt- Al_2O_3) and a NOx reduction function (Cu-Zeolite). The oxidation function is highly active towards ammonia oxidation but poorly selective towards N₂ selectivity. The SCR function plays the important role in improving the N₂ selectivity for ammonia slip catalysts. In the case of dual layer ASC samples, Shrestha et al., [22] showed the dependence of N₂ selectivity with the SCR layer thickness. Increasing the thickness of SCR layer improves

the selectivity but is accompanied by decreased NH₃ conversion owing to the increased diffusional resistance.



Figure 13. Steady state NH₃ oxidation over core-shell catalysts with varying shell thickness
(a) NH₃ conversion (open symbol), N₂ selectivity (closed symbol). SEM micrograph for core-shell catalysts with (b) shell thickness ~ 0.5 microns – CS-0.5 (c) shell thickness ~ 1.2 microns – CS-1.2.

To examine the effect of shell thickness on N₂ selectivity, two core-shell catalysts samples were synthesized by adjusting the hydrothermal synthesis duration: CS-0.5 with shell thickness 0.5 μ m and CS-1.2 with shell thickness 1.2 μ m. The thickness was obtained from SEM imaging as shown in Figure 13(b) and 13(c). In both the cases, the core was P(0.05)-A having a Pt loading of 0.05 wt%. The Cu/ZSM-5 shell was prepared to have a Cu loading of ~3 wt% in the shell. Each of the samples was evaluated under steady state conditions using 500 ppm NH₃, 5 vol% O₂ and balance Argon at 1000 sccm flowrate. The fixed bed contained 0.18 g of catalyst. Figure 13(a) shows the steady state NH₃ conversion and N₂ selectivity for samples, CS-0.5 and CS-1.2. The NH₃ conversion is negligibly affected by the variation in the shell thickness. In contrast, the N₂ selectivity is significantly impacted. For both catalysts the data show a general trend of decreasing N₂ selectivity with increasing temperature between 200 and 500°C. This trend is a result of increasing generation of NOx. However, the decrease in N₂ selectivity is steeper for the CS-0.5 sample; i.e., from 100% to a limiting value of 70% for CS-0.5 compared to 90% for CS-1.2 sample. Thus, the thicker shell is beneficial in improving the N_2 selectivity at higher temperature where the NH₃ conversion is 100%. The thicker Cu-ZSM-5 shell provides a longer diffusion length enabling additional Cu sites for SCR to occur, resulting in a higher N_2 selectivity.

2.3.6 Aging effects on catalyst stability

The catalyst samples P(0.05)-A, P(0.05)-AS and CS were hydrothermally aged in a fixed bed reactor at a temperature of 550°C in presence of 5% O₂, 5% H₂O, 8% CO₂ and balance Argon, maintaining a total flowrate of 1000 sccm. The catalyst performance was evaluated at discrete time of 0 h (fresh catalyst – post degreening) and 10 h (aged catalyst). Figure 14 reports the NH₃ conversion (Figure 14(a)) and N₂ selectivity (Figure 14(b)).



Figure 14. Experimental results of steady state (a) NH₃ conversion, (b) N₂ selectivity for P(0.05)-A, P(0.05)-AS, CS samples as a function of temperature at different aging time. 0.18 g in fixed bed. Aging conditions: 5% O₂, 5% H₂O, 8% CO₂ balance Argon, 1000 sccm, 10 h, 550°C.

NH₃ **conversion:** The steady state reaction measurements showed a negligible change in the light off temperature for all the three catalyst samples. In contrast, for P(0.05)-A showed a decrease in NH₃ conversion at higher temperature regime (T > 315° C) after aging, while P(0.05)-AS and CS catalysts showed negligible effect.

Aging of catalyst at elevated temperatures results in loss of exposed metal surface which is detrimental to catalytic activity. A decrease in exposed metal surface (Pt dispersion) would result into an increase in the light-off temperature. However, this trend was not observed in the experiments, which suggests the aging conditions did not lead to sintering of the Pt particles. In the case of sample P(0.05)-A, the negligible impact on lower temperature activity but a drop in conversion at high temperature suggests a change in morphology of Al_2O_3 support impacting the mass transport. This trend was observed in a study by Dhillon et al., [50] where Pt/Alumina was coated onto a monolith with longer aging period. The results showed negligible impact in light off temperature even after 253 h of aging, but a significant drop in conversion at higher temperature. It was shown upon hydrothermal aging, the BET surface area dropped which is consistent with change in morphology of alumina particles Furthermore, Dhillon et al., [50] showed the formation of Al(OH)₃, gibbsite, after hydrothermal aging using DRIFTS and SEM analyses. It was proposed that hydrothermal aging produces a surface layer on γ -Al₂O₃ crystallites, in form of Al(OH)₃ constricting the meso-pores. This results in decrease in pore size, in turn reducing the diffusional flux and high temperature conversion.

The catalytic activity of CS samples did not change after hydrothermal aging as shown in Figure 14(a). In order to get a better understanding, aging was done on the seeded core sample (P(0.05)-AS). The activity of P(0.05)-AS remained unchanged after 10 h of hydrothermal aging both in low and high temperature regimes. This indicates the Pt has not sintered after hydrothermal aging as discussed in the previous paragraph but also the morphology of catalyst particles was not affected by the hydrothermal aging in contrast with P(0.05)-A. The seeding process of core (P(0.05)-A) results in deposition of Silicalite-1. This might inhibit the formation of the aforementioned Al(OH)₃. As a result, the pore size is not affected which is translated into negligible change in catalytic performance at high temperature.

N₂ selectivity: The N₂ selectivity of both core (P(0.05)-A) and P(0.05)-AS was unaffected by aging conditions as reported in Figure 14(b). This suggests that intrinsic reactions rates do not change after hydrothermal aging. Even in the case of CS sample, the N₂ selectivity was not affected to a great extent, we could only see a slight drop of < 2%in N₂ selectivity at T > 250°C after 10 h of aging. This suggests that SCR shell of Cu-ZSM-5 is stable even after hydrothermal aging carried out at 550°C in presence of 5% H₂O.

2.3.7 Application of active seeded core to dual layer ammonia slip catalyst

In the Section 3.4 we described the increased activity of the core-shell catalyst for NH₃ oxidation. The core-shell catalyst exhibits a light-off characteristic similar to that of the Pt/Al₂O₃ catalyst having three times higher Pt loading (Figure 10(a)). The shifting of the light-off towards lower temperatures is attributed to the increased stability of Pt in the

metallic state. The lower light-off temperature in the presence of low Pt loading can be seen as an opportunity to improve the activity of the dual layer ammonia slip catalyst.

To examine this in more detail, a modified dual layer ammonia slip catalyst comprised of a seeded core (P(0.05)-AS) as the base layer and a top Cu-SSZ-13 layer was washcoated on a monolith and its performance was compared to a conventional dual layer ASC washcoated monolith. To this end, we compared three dual layer ASC samples each having the same overall Cu-loading (2.90 g/ft³ of monolith). The samples were evaluated under steady state conditions using 500 ppm NH₃, 5 vol% O₂ and balance Ar at 332Kh⁻¹ GHSV. The thicknesses of each layer (top and bottom) were fixed in order to preserve any diffusional effects. As seen in Figure 15, the ASC samples are denoted by Pt(x)-Cu(y), where *x* represents Pt loading in g/ft³ of monolith and *y* stands for Cu-SSZ-13 loading in g/ft³ of monolith. Two samples with different Pt loadings (1.5 and 0.50 g/ft³ of monolith) are denoted as Pt(1.5)-Cu(2.90) and Pt(0.5)-Cu(2.90), respectively. The third ASC was modified by washcoating the base layer with seeded core Pt/Al₂O₃ (P(0.05)-AS) at a loading of 0.50 g/ft³ and is denoted by Pt(0.5)-AS-Cu(2.9).



Figure 15. Schematic diagram of the washcoated monoliths, top SCR layer and base PGM layer. (top) Conventional dual layer ASCs: Pt(1.5)-Cu(2.90) and Pt(0.50)-Cu(2.90) (bottom) Modified dual layer ASC: Pt(0.50)-AS-Cu(2.90), washcoated with seeded core in base layer.

Figure 16 compares the steady state NH₃ oxidation performance for the three monolith samples. The light-off temperature at 50% conversion (T₅₀) for are respectively 285, 375 and 285°C for Pt(1.5)-Cu(2.90), Pt(1.5)-Cu(2.90), and Pt(0.5)-AS-Cu(2.90) (Fig. 16(a)). An increase in the Pt loading from 0.5 g/ft³ to 1.5 g/ft³ lowers the light-off by 90°C. This is clearly a result of the higher Pt loading. On the other hand, the ASC sample with the seeded core Pt/Al₂O₃ layer with a loading of 0.5 g/ft³ exhibits a conversion and light-off trend very similar to that of the Pt(1.5)-Cu(2.9) sample having 3-fold higher Pt loading. It is noted that for each of the samples the NH₃ conversion does not reach 100% at high temperature. This is a result of mass transfer limitations at the very high space velocity.

These findings show that the same enhanced activity of the modified Pt/Al_2O_3 can be exploited in the dual layer ASC design, as it was in the core-shell catalyst shown earlier.

The product distribution results are encouraging. Figure 16(b) compares the N₂ selectivity for the three samples. For each of the samples the N₂ selectivity is 100% at low temperature, conditions for which the bottom PGM layer is highly selective to N_2 . At T > 210°C, the N₂ selectivity starts to drop for each sample [23,31,50,51]. The departure from 100% N_2 is due to the formation of N_2O at intermediate temperature (Figure 16(d)). The N₂ selectivity minimum is 80, 90 and 82% for Pt(1.5)-Cu(2.90), Pt(0.50)-Cu(2.90) and Pt(0.50)-AS-Cu(2.90), respectively. Comparing Pt(0.50)-Cu(2.90) and Pt(0.5)-AS-Cu(2.90), the highest N₂ selectivity is obtained for the lowest Pt loading. This may be due to a difference in the Pt crystallite size [41]. Interestingly, the ASC with the more active modified Pt/Al₂O₃ has a comparable selectivity to that of the conventional Pt/Al₂O₃ catalyst, which has 3-times higher loading. The explanation for this interesting result is not known and warrants further study. The conventional ASC sample (Pt(0.50)-Cu(2.90)), owing to its less active PGM layer, has a relatively high light-off of 375°C for NH₃ oxidation. This results in a lower production of NOx and N_2O compared to the more active modified PGM layer. Thus, a higher N₂ selectivity comes at the cost of a lower NH₃ conversion. On the other hand, the modified ASC sample has a NH₃ oxidation light-off similar to that of the Pt(1.5)-Cu(2.90) ASC sample; however, owing to higher activity, there is higher N₂O yield at intermediate temperatures compared to the conventional ASC

sample with the same Pt loading. Finally, a similar trend for all washcoated samples is seen in Figure 16(c) for the NOx selectivity [36-38].



Figure 16. Steady state NH₃ oxidation over 3 dual layer ammonia slip catalysts: Pt(1.5)-Cu(2.90), Pt(0.50)-Cu(2.90), Pt(0.5)-AS-Cu(2.90). Reaction data for (a) NH₃ conversion, (b) N₂ selectivity, (c) NOx yield, (d) N₂O yield. Feed : 500 ppm NH₃, 5 vol% O₂, balance Ar, GHSV 332Kh⁻¹.

2.4. Conclusions

In summary, we synthesized a bifunctional core-shell catalyst for NH_3 oxidation and tested its performance relative to conventional catalysts in a fixed bed reactor. The core-shell catalyst showed better performance with respect to N_2 selectivity and had a lower light-off when compared to a physical mixture of Pt/Al_2O_3 and Cu-ZSM-5. The higher activity of the seeded core was preserved after washcoating it as the base for the dual layer ASC, showing trends similar to dual layer ASC with thrice the Pt loading, thus increasing NH_3 conversion without having any impact on N_2 selectivity. It was shown that the improved performance of the bifunctional catalyst was attributed to the presence of a shell 54 of Cu-ZSM-5 around the core of Pt/Al₂O₃. The core-shell catalyst exhibited enhanced low temperature activity at the expense of lower PGM loading, while the NOx yield was below 10%. Using H₂-TPR to probe active Pt sites, it was shown that the zeolite synthesis process has a positive impact on Pt-support interactions in the core, leading to the suppression and destabilization of Pt oxides that ultimately increase the activity of core-shell catalysts. With the novel approach of mimicking dual layer ammonia slip catalyst at a single particle level, the requisite loading of expensive metals as active materials can be significantly reduced while maintaining good N_2 selectivity the for entire operating range with significant lowering of NH₃ oxidation light-off.

Chapter 3: Kinetics of NH₃ Oxidation on Pt/Al₂O₃: Rate Enhancement and NH₃ Inhibition

3.1. Introduction

The oxidation of NH₃ over Pt containing catalysts is one of the oldest documented heterogeneous catalytic reactions with its importance spanning HNO₃ production (Ostwald Process) to diesel emission control (Ammonia Slip Catalysts, ASC). The oxidation of NH₃ is exothermic, is especially sensitive to both temperature and NH₃ concentration, and leads to four major N-containing products:

$$4 NH_3 + 3 O_2 \rightarrow 2 N_2 + 6 H_2 O, \tag{3-1}$$

$$2 NH_3 + 2 O_2 \rightarrow 1 N_2 O + 3 H_2 O, \qquad (3-2)$$

$$4 NH_3 + 5 O_2 \rightarrow 4 NO + 6 H_2O \tag{3-3}$$

and
$$4 NH_3 + 7 O_2 \rightarrow 4 NO_2 + 6 H_2O_2$$
. (3-4)

The formation of molecular nitrogen (N₂) dominates at $T < 250^{\circ}$ C, while the main product shifts to NO at temperatures exceeding 350°C. N₂O and NO₂ appears at intermediate temperatures. The complex product distribution is of utmost importance in the aforementioned HNO₃ and emission control applications. For the former, the desired products are NO and NO₂ during the selective oxidation of NH₃ over Pt/Rh catalysts at temperatures over 600°C [52]. For the latter, the desired product is N₂. For both, N₂O is a highly undesired byproduct and potent greenhouse gas. The high operating temperature of the Ostwald process means that the reaction is typically external transport controlled. For
the much lower temperature of the ASC application the reaction kinetics are paramount with pore diffusion and external mass transfer becoming more important during and beyond light-off [53]. For these reasons, it is essential that a mechanism and associated kinetic model is developed for NH₃ oxidation over Pt-based catalysts.

Most previous studies of Pt-catalyzed NH₃ oxidation kinetics have involved single crystal Pt, including Pt <111>, Pt <100> and others with various stepped and kinked Pt surfaces [54–63]. Moreover, these studies were conducted under low pressures, in the range of 10^{-9} to 10^{-4} mbar. The experimental studies have been recently complemented by density functional theory (DFT) studies to elucidate mechanistic pathways and structure-activity relationships [62–65]. Scheibe et al., [60] devised a kinetic model for low pressure (10^{-6} to 10^{-3} mbar) NH₃ oxidation over two stepped Pt<111> surfaces, Pt<533> and Pt<443>. The model does not describe the formation of N₂O or other byproducts at high pressure. Rebrov et al., [61] developed a reactor model of atmospheric pressure NH₃ oxidation on Pt-Al₂O₃ in microreactor and which accounted for mass transport processes. The microkinetic model was based on single Pt crystals with reactions taking place over Pt<100>. Kraehnart and Baerns [58,59] did extensive studies of NH₃ oxidation over Pt foil in micro-structured quartz reactor at pressures of 10^{-2} atm based on the Pt<100> crystallite used in model development.

The aforementioned HNO₃ and NH₃ slip processes involve NH₃ oxidation at atmospheric pressure and utilize technical polycrystalline Pt catalysts. Thus while low pressure studies of Pt single crystals provide fundamental insight, the catalysis occurs on a distribution of crystal planes and is coupled with transport processes. As a result, the kinetics therefore are a weighted contribution from surfaces of varying activity, along with the potential contribution from pore diffusion and external transport processes. Pt form surface oxide at the high O₂ partial pressures [45,62,66–68]. Some progress has been made for these more realistic situations. The study by Scheuer et al., [69] successfully applied the microkinetic scheme of Kraehnart et al., [58] to simulate the atmospheric pressure reaction system over a Pt-Al₂O₃ washcoated monolith. The parameters of the model were modified to give a good fit with the experimental data.

Despite these advances, a systematic kinetic study of NH₃ oxidation over Pt is needed. In particular, the kinetic models developed to date do not adequately predict the intrinsic dependence of the NH₃ oxidation rate on NH₃ concentration. The aforementioned studies of Scheuer et al., [69], Shrestha et al., [22], and Dhillon et al., [50] employ the dualsite scheme framework developed by Kraehnart et al., [70]. Shrestha et al., [71] applied the aforementioned dual-site microkinetic model to the simulation of dual-layer NH₃ slip catalysts containing either Fe- or Cu-zeolite SCR top layer and a Pt-Al₂O₃ base layer. Recent work by Dhillon et al., [72] evaluated dual layer catalysts with modified porosity for enhanced conversion and "hybrid" layered catalysts comprising a mixed Cu/SSZ-13 + Pt-Al₂O₃ base layer and a thin Cu/SSZ-13 top layer. The dual-site scheme predicts a NH₃ oxidation rate that has a NH₃ reaction order between 0 and 1.

In the current study, we show through kinetics measurements and modeling in the current study, at sufficiently high concentration the rate becomes negative order in NH₃.

The data reveal the presence of a rate maximum and a NH₃ reaction order varying between 1 and -1.6 suggesting the competitive adsorption between reactants NH₃ and O₂. The experiments also show an unexpected activity dependence on the extent of ball milling of the Pt-Al₂O₃ catalysts which we show to be a result of mechanical modification of the exposed crystalline facets. The microkinetic scheme developed and analyzed earlier by Rebrov et al., [61] and Baerns et al., [73] is extended to capture the presence of maximum-rate and variation in rate order with respect to NH₃. In addition, the scheme captures the product distribution over different Pt concentration and wide temperature ranges, 180 – 500°C. This is also able to explain the increase in activity for the ball-milled and monolith catalysts. Validation of the scheme is accomplished through successful prediction of Pt-Al₂O₃ particles and washcoated monoliths over a range of conditions.

3.2. Experimental

3.2.1 Catalyst synthesis

Table 1 lists the powder and washcoated catalysts used in this study. Herein the synthesis of the catalysts is described. The Pt-Al₂O₃ catalyst powder, denoted as Pt(x)-Al₂O₃ (where *x* is the weight percent of Pt), was synthesized by incipient wetness impregnation using chloroplatinic acid hexahydrate as the precursor. The γ -Al₂O₃ powder was dispersed in a quartz glass boat and an aqueous solution of the Pt complex was added dropwise uniformly over the particles. The volume of the aqueous solution was calculated based on the pore volume of alumina powder (0.5 cm³/g). 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. Pt-Al₂O₃ with 0.07 wt.% and 0.15 wt.% were

synthesized (Pt(0.07)-Al₂O₃ and Pt(0.15)-Al₂O₃). The Pt-Al₂O₃ powder catalysts were evaluated in a fixed bed reactor. The samples were reduced with 2% H₂ and balance Argon for 1 h at 500°C to eliminate any chlorine precursor, followed by degreening with 5% O₂ and balance Argon at 500°C for 6 h. The powder sample was kept in an oxidizing atmosphere containing 5% O₂ and balance Ar at 650°C for 30 min before commencement of reaction testing.

Samples	Туре	Pt[wt%] in Al ₂ O ₃	Pt dispersion [%]
Pt(0.07)-Al ₂ O ₃	Pt/Al ₂ O ₃ , Un-milled, 40-50 microns	0.07	45
Pt(0.07)-Al ₂ O ₃ -20h- BM	Pt/Al ₂ O ₃ , Bal-milled for 20 h	0.07	42
Pt(0.07)-Al ₂ O ₃ -50h- BM	Pt/Al ₂ O ₃ , Bal-milled for 50 h	0.07	40
Al ₂ O ₃ -20h-BM + Pt(0.07)	Al ₂ O ₃ ball-milled for 20 h, followed by Pt addition		44
Pt-3.2	Pt/Al_2O_3 washcoated onto monolith, 3.2 g/ft ³ of Pt in monolith or 1.5 g/in ³ of Pt/Al_2O_3 in washcoat 400 cpsi, 0.5 cm	0.15	25

Table 2. Composition and nomenclature of catalyst samples.

A separate Pt(0.15)- Al_2O_3 slurry to be used for washcoating onto the monolith reactors was prepared by adding deionized water and boehmite solution to a $Pt(0.15)/Al_2O_3$ catalyst powder (mass ratio Pt- Al_2O_3 :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 < 10 µm.

3.2.2 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 the prepared Pt-Al₂O₃ slurry for 30 s and excess slurry was blown with air for 10 s. The monolith was then dried in an oven at 120°C for 2 h; the dipping procedure was repeated to get the required loading. The coated monolith was dried overnight in an oven at 120°C, followed by calcination at 550°C for 5 h with a temperature ramp rate of 0.5° C/min. The washcoated monolith was then reduced with 2% H₂ and balance Argon for 1 h at 500°C to eliminate any chlorine, followed by degreening (activation) 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 performance testing. The prepared samples had a Pt-Al₂O₃ washcoat (wc) loading of 1.5 g wc/in³monolith, which corresponds to a Pt monolith loading of 3.2 g/ft³ monolith.

3.2.3 Bench scale reactor setup

Catalytic activity and performance measurements were carried out in both fixed bed and monolith reactors in an overall set-up that is described elsewhere [40]. A quartz tube (OD 12.8 mm OD, 8.1 mm ID) containing the catalyst sample was placed in an electric furnace equipped with a programmable temperature controller. For powdered Pt/Al₂O₃ sample, the catalyst was packed at the axial midpoint of the quartz tube, with quartz wool on either end of the bed. Whereas, the washcoated monolith sample was wrapped in FiberfraxTM ceramic paper and fitted inside a quartz tube (O.D. 1.27 cm and I.D. 0.81 cm). The thermocouple junction was positioned in the axial and radial midpoint of the catalyst for both fixed-bed and monolith reactors. The feed gas flows were metered by MKS mass flow controllers. The compressed gases purchased from Matheson Inc. had research grade purity. The concentrations of outlet gases from the reactor were analyzed by a FTIR (Thermo-Nicolet Nexus 470; Nicolet Analytical Instruments) equipped with OMNIC software. The system total pressure inside was maintained at 760 Torr by using a globe valve positioned downstream of the FTIR. The steady state N₂ yield reported in this paper is calculated by difference using an overall nitrogen balance.

3.2.4 Steady state reaction experiments

All flow lines were heated to 150° C by electrical heating tape to prevent condensation and/or adsorption of H₂O and NH₃ onto the tube surfaces. All lines were flushed with Ar for 1 h before collecting background spectra. After taking the background spectra, 500 ppm NH₃ in 10 vol. % O₂ and balance Ar were directed through a reactor bypass line to measure the feed concentration of NH₃ for reference. The flow was then switched to the reactor side, and reaction performance was tested at steady state in the temperature range from 150 to 500°C. Once the gas concentrations remained constant for about 30 min, the steady state data was collected.

The steady-state reaction rates with respect to NH₃ were measured for varying NH₃ concentrations ranging from 10 ppm to 20000 ppm at different temperatures with fixed 10 vol. % O₂ in the feed. The reaction-rate measurements were taken for both fixed-bed and monolith reactors once steady-state was reached. All measurements were done in the kinetic regime, confirmed using the Weisz-Prater criterion for assessing intrusion by pore diffusion [74].

3.2.5 Catalyst characterization

Powder X-ray diffraction (XRD) was conducted with a Rigaku Smartlab diffractometer using a Cu K α source (40 kV, 30 mA, $\lambda = 1.54$ Å) in the range of $2\theta = 10-70^{\circ}$ with 0.02 degree increment. The Pt dispersion measurements were made using a 3Flexi Chemi Micromeritics apparatus. The adsorbing gas was CO. Multiple measurements were done on the same batch of the catalyst; this was also supplemented by measurements on a different batch. Properties and nomenclature of the catalysts used in this study are provided in Table 1.

3.3. Model Description

3.3.1 Reactor Models

A one-dimensional, heterogeneous fixed bed reactor model was used to simulate reaction in the powder-in-tube reactor. The two phases described in the model are the intraparticle and the interstitial phase. The gas flow is laminar based on the low particle Reynolds number (Re ~ 1). Concentration gradients in the radial direction (r) are neglected due to the small tube diameter of 8.1 mm. Dispersion is ignored in the axial (z) direction due to larger convective flow compared to diffusive transport (axial Pe ~ 370). Isothermal conditions are assumed due to the negligible heat effects from the low NH₃ feed concentration (mostly < 1 vol.%) and low NH₃ conversion. The Appendix section A4 provides an estimate of the adiabatic temperature rise for typical conditions. For 1% NH₃ and 10% conversion the temperature rise is estimated to be 8.5°C. Along with the assumption of axially-uniform heating, an energy balance is not needed.

With these assumptions in mind, the following model equations are used. The interstitial fluid phase includes accumulation, axial convection, and fluid-to-particle mass transfer terms is given by,

$$\frac{\partial x_{f,j}}{\partial t} = -\langle u \rangle \frac{dx_{f,j}}{dz} + k_{me,j} a_v \big(x_{s,j|r=0} - x_{f,j} \big). \tag{3-5}$$

Here the mass transfer coefficient $k_{me,i}$ is given by

$$k_{\rm me,j} = \frac{Sh_e D_{\rm f,j}}{4R_{\Omega 1}},$$
 (3-6)

where $R_{\Omega 1}$ is the hydraulic radius and $D_{f,j}$ is the species i diffusivity in the interstitial region of the catalyst bed, calculated as a function of temperature using the Lennard-Jones formulation, $D_{f,j} = a(T/T_0)^{1.75}$. The intraparticle fluid phase balance includes accumulation, intraparticle diffusion, and reaction terms is given by,

$$\frac{\partial x_{p,j}}{\partial t} = \frac{D_{ej}}{r^2} \frac{d}{dr} \left[r^2 \frac{dx_{p,j}}{dr} \right] + \frac{1}{C_{Tm}} \left[\sum_{r=1}^{rxn} \vartheta_{kr} R_r \left(T, \theta, x_{pj} \right) \right], \tag{3-7}$$

where R_r is net rate of formation of component 'j' in reaction r, ϑ_{jr} is the stoichiometric coefficient of species 'j' in reaction r, C_{Tm} is total molar concentration, and D_{ej} is the species j effective diffusivity in the mesopores of the particle. Due to the small pores of the Al₂O₃ with a nominal diameter ~10 nm, D_{ej} represents the Knudsen diffusivity with a temperature dependence of T^{0.5}. Finally, the surface species balances include accumulation and net rate of formation of species k is given by

$$\frac{\partial \theta_k}{\partial t} = \frac{1}{C_{st}} \left[\sum_{r=1}^{rxn} \vartheta_{kr} R_r (T, \theta, x_{pj}) \right], \tag{3-8}$$

with the coverages of adsorbed species (θ_k) and vacant sites summing to unity. The reaction rate expression (R_r) are provided in Table 6.

In the above equations, $x_{f,j}$ and $x_{p,j}$ 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-particle interface. $R_{\Omega 1}$ and a_v are the hydraulic radius (ratio of cross-sectional area to parameter) and external surface area at fluid-particle interphase per unit reactor volume. $\langle u \rangle = \frac{F}{\varepsilon_b * A}$ is average interstitial velocity through the bed which is a function of volumetric flowrate (F), bed porosity (ε_b) and reactor cross-sectional surface area (A). C_{st} is the total active site density (mol/m³ catalyst bed) of Pt in the fixed-bed.

Boundary and initial conditions are as follows:

$$x_{f,j}(t) = x_{f,j}^{in}(t)$$
 at $z = 0$, (3-9)

$$k_{mej}(x_{f,j} - x_{s,j}) = -D_{ej} \frac{\partial x_{p,j}}{\partial r}\Big|_{x_{p,j} = x_{s,j}} \text{ at } r = R$$
(3-10)

and
$$\frac{\partial x_{p,j}}{\partial r} = 0$$
 at $r = 0$. (3-11)

The model comprising eqns. (1) - (4) were discretized in the axial and radial directions. The differential equation MATLAB code 'ODE15s' was used to solve these

equations. Typically the time integration was conducted for 2000 s in order to reach steady state. The modeling parameters for the fixed bed reactor modeling is listed in the Table 3.

A single channel monolith model adopted from earlier work [50,69] was used to simulate the washcoated catalyst performance for Pt-catalyzed NH₃. The 1 + 1 D model was previously applied to simulate NH₃ oxidation reaction over Pt-Al₂O₃ washcoated monolith reactor [50]. The model assumes isothermal operation, fully-developed laminar flow through the channel, no axial dispersion, and constant physical properties. As mentioned earlier, while NH₃ oxidation is highly exothermic the adiabatic temperature rise is small as a result of the low NH₃ feed concentration. Isothermal conditions preclude the need for energy balance.

The developed reactor model consist three sets of transport equations (i) fluid phase mass balances, (ii) solid phase mass balances, and (iii) surface species includes convective flow in the axial direction and transverse mass transfer from the fluid phase to the washcoat is given by,

$$\frac{\partial x_{f,j}}{\partial t} = -\langle u \rangle \frac{\partial x_{f,j}}{\partial z} - \frac{k_{me,j}(Z)}{R_{\Omega 1}} (x_{f,j} - x_{s,j}).$$
(3-12)

The species 'j' washcoat balances of account for radial transport and consumption/generation by chemical reaction:

$$\varepsilon_{wc} \frac{\partial x_{wc,j}}{\partial t} = D_{e,j} \frac{\partial^2 x_{wc,j}}{\partial y^2} + \frac{1}{c_{Tm}} (\sum_{r=1}^{rxn} \vartheta_{jr} R_r(T, \theta, x_{wc,j})).$$
(3-13)

The surface species balances are given by

$$\frac{\partial \theta_k}{\partial t} = \frac{1}{C_{Pt}} \left(\sum_{r=1}^{rxn} \vartheta_{kr} R_r(T, \theta, x_{wc,j}) \right).$$
(3-14)

Here, $x_{f,j}$ and $x_{wc,j}$ are cup-mixing mole fraction of species 'j' in fluid and solid phase, respectively, while $x_{s,j}$ is mole fraction of species 'j' at fluid-washcoat interface. $k_{me,j}$ is external mass transfer coefficient. ε , $D_{e,j}$, $R_{\Omega 1}$ 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 the cross-sectional average velocity through monolith channel. R_r and ϑ_{jr} are the reaction rate and stoichiometric coefficient of species 'j'. C_{Pt} is the total active site density (mol/m³ washcoat) of Pt in the washcoat and C_{Tm} is total molar concentration. θ_k is fractional surface coverage of species 'k'. Boundary conditions are as follows:

$$x_{f,j}(t) = x_{f,j}^{in}(t)$$
 at $z = 0$, (3-15)

$$k_{me,j}(z)(x_{f,j} - x_{s,j}) = -D_{e,j} \frac{\partial x_{wc,j}}{\partial y}\Big|_{x_{wc,j} = x_{s,j}} \text{ at } y = 0$$
 (3-16)

and
$$\frac{\partial x_{wc,j}}{\partial y} = 0$$
 at $y = R_{\Omega 2}$. (3-17)

Where
$$k_{\text{me},j} = \frac{Sh_e D_{f,j}}{4R_{\Omega 1}}$$
. (3-18)

 $D_{f,j}$ is the diffusivity of the species 'j' in the fluid phase, calculated as a function of temperature using the Lennard-jones formulation, $D_{f,j} = a(T/T_o)^b$. The ratio of the fluid and effective diffusivity for each species is given by

$$\frac{D_{\mathrm{f},j}}{D_{\mathrm{e},j}} = \frac{\tau}{\varepsilon},\tag{3-19}$$

where τ is tortuosity of washcoat and ε is washcoat porosity. The effective diffusivity estimation using Eq. (19) is ascribed to the simple transport model based on the washcoat average porosity and tortuosity. The diffusion regime (bulk, Knudsen or both) determines the order of temperature dependence of effective diffusivity; b ~ 1.75 for bulk and 0.5 for Knudsen. In Eqn. (18), $D_{f,j}$ 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 the channel develops fully within 5% length of the monolith. The value of the external Sherwood number (Sh_e) for a square channel, is taken as position independent. The modeling parameters for the monolith reactor modeling is listed in the Table 4 with diffusivities provided in Table 5.

Parameter	Value			
R	50e–6m			
RΩ1	11е–6m			
<u></u>	1.22(T/273.15)(m/s)			
εb	0.45			
L	0.3e–2 m			
C _{Tm}	$(12187.3/T) \text{ mol/m}^3$			
Cet	0.6 mol exposed Pt/(m ³ of			
Csi	catalyst bed)			
She	3.1608			

Table 3. Fixed bed modeling parameters

Table 4. Monolith modeling parameters

Parameter	Value			
а	1.1e–3m			
R _{Ω1}	0.268e–3m			
R _{Ω2}	15e–6m			
<u></u>	$0.49(T/273.15)(a/(a-2R_{\Omega 2}))(m/s)$			
3	0.4			
τ	10.5			
L	0.5e–2 m			
C _{Tm}	(12187.3/T) mol/m ³			
Cent	$3.2 \text{ mol exposed Pt/(m^3 of}$			
	washcoat)			
She	3.608			

Table 5. Bulk diffusivities of reactants and products in gas phase

D _{f,NH3}	$1.2 \text{ x} 10^{-9} \text{ T}^{1.75}$
D _{f.NO}	$1.2 \text{ x} 10^{-9} \text{ T}^{1.75}$
D _{f,N2O}	$0.8 \text{ x} 10^{-9} \text{ T}^{1.75}$
D _{f,N2}	$1.3 \text{ x} 10^{-9} \text{ T}^{1.75}$
D _{f,NO2}	$0.8 \text{ x} 10^{-9} \text{ T}^{1.75}$
D _{f,O2}	$1.1 \text{ x} 10^{-9} \text{ T}^{1.75}$

3.3.2 Microkinetic schemes

2.

In this study three schemes are applied for NH₃ oxidation on Pt-Al₂O₃ particles (fixed-bed reactor) and Pt-Al₂O₃ washcoat (monolith reactor). The three schemes are so named "BA", "AA" and "BA + AA" to reflect the types of active sites that are involved in the NH₃ adsorption and first reaction step with adsorbed O. Scheme BA is a dual-site mechanism involving 'b' and 'a' sites, Scheme AA is a single-site mechanism involving 'a' sites, while Scheme BA + AA is combination of the BA and AA schemes. From a molecular standpoint, the 'b' top sites and 'a' hollow sites strictly involve the Pt <111> crystal plane. While we recognize that the Pt crystallites have more than just the <111>exposed crystal planes, below we show that the observed kinetics are consistent with the co-existence of single- and dual-site NH₃ oxidation pathways. For reference, Figure 17 lists all of the reactions spanning the three schemes while the rate expressions are listed in Table

	- [R1	NH ₃	+ b	- *	NH ₃ -b	AA
		R2	NH₃-b	+ 1.50-a		$N-a + 1.5H_2O + 0.5$	<u>ia</u> + b
		R3	O ₂	+ 2a	₽	20-a B	4
		R4	N-a	+ O-a		NO-a	
		R5	NO	+ a	-	NO-a	
		R6	2N-a			N ₂ + 2a	
		R7	NO-a	+ 0-a	-	NO ₂ -a + a	
		R8	NO-a	+ N-a		$N_2O + 2a$	
		R9	NO_2	+ a	-	NO ₂ -a	
		R10) NH₃	+ a		NH ₃ -a	
		R11	l NH₃-a	ı + 1.50-a		$N-a + 1.5H_2O + 1.5$	ia
- ici	rokir	netic :	Schem	— — - es			
BA : NH ₃ adsorbing on site 'b' [Box AA]							
			5	5			

Figure 17. Microkinetic models with elementary reaction steps for NH₃ oxidation.

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Scheme BA follows from the work of Kraehnart et al., [70], adopted by Scheuer et al., [69] and extended by Shrestha et al., [71] and Dhillon et al., [50]. Here NH₃ and O₂ adsorption occur on independent, but adjacent sites. The scheme, depicted by Box BA in Fig. 17, assumes that NH₃ adsorption (R1) occurs on site 'b', steps (R3) through (R11) occur on site 'a' and step R2 occurs on both sites; i.e., reaction between NH₃-b and O-a.

Scheme AA considers that both NH₃ and O₂ adsorption/desorption occur on single site type 'a' as represented by Box AA in Figure 17. The difference in this scheme compared to the BA scheme is the elimination of the NH₃ adsorption/desorption on site 'b'. As a result, reaction only occurs between species on the 'a' sites. Thus, reaction R11 involving NH₃ and O adsorbed species replaces R2. To this end, site-competition between NH₃ and O₂ is introduced.

Scheme BA + AA is a combination of the BA and AA schemes and is represented by Box BA + AA in Fig. 17. This scheme involves both 'a' and 'b' sites and in that sense is similar to the BA scheme. On the other hand, instead of NH₃ only adsorbing/desorbing on/from site 'b' and reacting with adsorbed O on site 'a', NH₃ adsorption/desorption occurs on site 'a' as well. Thus, the scheme includes both reaction steps R2 and R11.

Reaction between adsorbed NH₃ and O represented by R2 and R11 lump together several elementary reactions, earlier described by Kraehnert et al., [58,70] and Ma et al., [63]. In general, NH₃ conversion proceeds through the breaking of one or more N-H bonds through oxidation; i.e.,

$$NH_{3}-a + O-a \rightarrow NH_{2}-a + OH-a,$$
 (3-20)

$$NH_2-a + O-a \rightarrow NH-a + OH-a,$$
 (3-21)

$$NH-a + O-a \rightarrow N-a + OH-a,$$
 (3-22)

along with decomposition followed by oxidation; i.e.,

$$NH_{3}-a + a \rightarrow NH_{2}-a + H-a, \qquad (3-23)$$

$$NH_2-a + a \rightarrow NH-a + H-a,$$
 (3-24)

$$NH-a + a \rightarrow N-a + H-a$$
 (3-25)

and
$$H$$
- $a + O$ - $a \rightarrow OH$ - a . (3-26)

In turn, these steps are followed by H₂O formation and desorption:

$$OH-a + OH-a \rightarrow H_2O-a + O-a,$$
 (3-27)

$$OH-a + H-a \rightarrow H_2O-a + a$$
 (3-28)

and
$$H_2O$$
- $a \leftarrow \rightarrow H_2O + a.$ (3-29)

The remaining steps in the microkinetic scheme involve the formation of N_2 (R6), N_2O (R8), NO (R4, R5), and NO₂ (R7, R9) shown in figure 17.

Estimation of unknown kinetic parameters (pre-exponential factors, activation energies) entails tuning the monolith model containing one of the microkinetic schemes (AA, BA, BA + AA) in a fit of selected data. In this study an initial set of kinetic parameters were taken from the previous studies of Shrestha et al., [71] and Dhillon et al., [50]. These were adjusted to predict NH₃ conversion and product distribution as a function of catalyst temperature, for both fixed-bed and monolith reactors, depending on the catalyst type (powder, washcoat). Validation of the tuned kinetics was accomplished by simulating experimental data obtained for different Pt loadings and feed flowrates but not included in the data set used for tuning. The parameter estimation was done in such a way that kinetic parameters associated with reactions R3 - R9 were kept nearly constant in each of the three models, while parameters for reactions R1, R2, R10 and R11 were adjusted to give satisfactory fits of the data.

The final set of estimated kinetic parameters for $Pt-Al_2O_3$ (unmilled), $Pt-Al_2O_3$ (milled) and $Pt-Al_2O_3$ washcoat monolith are listed in Table 6.

Micro-Kinetics		Un-milled Pt-Al ₂ O ₃		Monolith/Ball-milled Pt- Al ₂ O ₃		Pote expression (Pr)	
			А	Ea (KJ/mole)	А	Ea (KJ/mole)	Kate expression (KI)
DI	R1f	$NH_3 + b \rightarrow NH_3-b$	59	0	59	0	$k_{1f}C_{pt}X_{NH3}\theta_bC_{Tm}T$
KI	R1b	$NH_3-b \rightarrow NH_3+b$	66000	106.60	66000	106.60	$k_{1b}C_{pt} heta_{NH3-b}$
F	R2	$\mathrm{NH_{3}\text{-}b} + 1.5\mathrm{O}\text{-}a \xrightarrow{} \mathrm{N}\text{-}a + 1.5\mathrm{H_{2}O} + 0.5a + b$	3E13	151.70	3E14	132	$k_2 C_{pt}^2 \theta_{NH3-b} \theta_{O-a}$
R	R3f	$O_2 + a \rightarrow 2O-a$	65	0	65	0	$k_{3f}C_{pt}^2X_{O2}\theta_a^2C_{Tm}T$
K3	R3b	2O-a → O_2 +a	7.4E11	125.02	7.4E11	125.02	$k_{3b}C_{pt}^2\theta_{O-a}$
F	R4	N-a + O-a → NO-a + a	6E15	137.50	6E15	131.32	$k_4 C_{pt}^2 \theta_{N-a} \theta_{O-a}$
R5 -	R5f	$NO + a \rightarrow NO-a$	290	0	290	0	$k_{5f}C_{pt}X_{NO}\theta_aC_{Tm}T$
	R5b	NO-a \rightarrow NO + a	7E19	173	7E19	150	$k_{5b}C_{pt} heta_{NO-a}$
F	R6	2N-a → N ₂ + 2a	2E16	110	2E16	110	$k_6 C_{pt}^2 \theta_{N-a}^2$
D7	R7f	NO-a + O-a → NO ₂ -a + a	8E13	139	8E13	105.4	$k_{7\mathrm{f}}C_{pt}^{2} heta_{NO\text{-a}} heta_{O\text{-a}}$
K/	R7b	NO_2 -a + a \rightarrow NO-a + O-a	9.2E09	77.12	9.2E09	77.12	$k_{7b}C_{pt}^2\theta_{NO2-a}\theta_a$
F	28	$NO-a + N-a \rightarrow N_2O + a$	4.5E18	138	3E19	127.50	$k_{8}C_{pt}^{2} heta_{NO-a} heta_{N-a}$
DO	R9f	$NO_2 + a \rightarrow NO_2-a$	0	0	0	0	$k_{9f}C_{pt}X_{NO2}\theta_aC_{Tm}T$
R9	R9b	NO_2 -a $\rightarrow NO_2$ + a	1E13	120	1E13	120	$k_{9b}C_{pt} heta_{NO2-a}$
D 10	R10f	$NH_3 + a \rightarrow NH_3$ -a	39	0	39	0	$k_{10f}C_{pt}X_{NH3}\theta_{a}C_{Tm}T$
K10	R10b	NH_3 -a \rightarrow NH_3 + a	150000	50	150000	35	$k_{10b}C_{pt} heta_{NH3-a}$
R	.11	NH ₃ -a + 1.5O-a → N-a + 1.5H ₂ O + 1.5a	1.1E14	152.70	1.1E14	110	$k_{11}C_{pt}^2\theta_{NH3-a}\theta_{O-a}$

Table 6. Pt catalyzed NH₃ oxidation reactions

Microkinetic models \rightarrow *Model BA: R1 – R9; Model AA: R3 – R11; Model AA + BA: R1 – R11*

3.4. Results and Discussion

This section presents the experimental results spanning the rate measurements with catalyst samples including powders (unmilled or milled) and washcoated monoliths, along with light-off experiments with the monoliths. In addition, kinetic modeling and parameter estimation results are discussed with catalyst synthesis effects and mechanistic implications discussed. Finally, monolith reactor simulations are presented and discussed.

3.4.1 Reaction rate measurements

The steady state NH₃ oxidation rate was measured for unmilled Pt((0.07)-Al₂O₃ particles in the fixed bed reactor setup. The bed contained 0.22 g of Pt((0.07)-Al₂O₃ with particle size in the range of 40-50 µm. The NH₃ feed concentration was varied over the range 10 – 1000 ppm, while the O₂ was fixed at 10 vol.% and the diluent Argon was adjusted to maintain a fixed total flow rate (500 sccm or 1000 sccm). Rate measurements were made for NH₃ concentration as low as 10 ppm at the higher flow rate and were conducted at three different temperatures; 235, 240 and 245°C. The turnover frequency (TOF, 1/s) was determined by dividing the measured rate (mol NH₃ consumed/g cat s) by the exposed Pt loading (mol Pt/g cat) using the measured Pt dispersion (45%) and loading (0.07 wt.%).

Figure 18(a) shows the steady reaction rate as a function of NH_3 feed concentration (ppm) measured at a flow rate of 500 sccm. In order to access the lower NH_3 concentration the flow rate was doubled to 1000 sccm; these data are shown in Fig. 18(b). Figs. 18(a) and (b) show that the TOF is a nonmonotonic function of the NH_3 concentration: TOF exhibits a maximum at the intermediate NH_3 concentration of ~500 ppm. To the left of the maximum the rate is positive-order in NH_3 while to the right the rate is negative-order in NH_3 due to self-inhibition. The maximum TOF occurring at 500 ppm of NH_3 does not change within the 235 to 245°C temperature range.



Figure 18. Turn over frequency (TOF) of NH₃ oxidation as a function of NH₃ concentration for Pt(0.07)-Al₂O₃ at (a) 500 sccm (b) 1000 sccm flow-rates (c) Reaction order (n) with respect to NH₃ concentration at 1000 sccm (d) Apparent activation energy (E_a) of NH₃ oxidation over Pt(0.07)-Al₂O₃ 100 ppm of NH₃.

The reaction order with respect to NH₃ molar concentration (C_{NH3}) is indicated in the ln(TOF) versus ln(C_{NH3}) plot, Fig. 18(c). The convex shape of the rate curves reveals a monotonic decreasing dependence of the NH₃ reaction order with increasing C_{NH3}. At low NH₃ concentration (10 ppm to 80 ppm) the order approaches ~0.9 while at high NH₃ concentration (700 – 1000 ppm) the order approaches -1.2. The order is in the range ~ \pm 0.2 for NH₃ concentrations between 300 – 700 ppm. The apparent activation energy (E_a) was estimated from rate measurements at four temperatures at a NH₃ feed concentration of 100 ppm , giving a value of 153 kJ/mole (Fig. 18(d)). The reaction rate measurements presented thus far are for unmilled Pt-Al₂O₃ catalyst in the fixed bed reactor. We decided to confirm the steady state rate dependence on NH₃ concentration and temperature for the washcoated monolith. As described earlier, the washcoat had a Pt loading of 0.15 wt.% and a volumetric Pt loading of 3.2 g/ft³ on the 0.5 cm long substrate. The Pt dispersion was measured to be 25%. The rate was measured over a wide range of NH₃ concentrations (10 – 25000 ppm) in an excess of O₂ (10 vol. %) O₂ with balance Argon at a flow rate of 1000 sccm.

Fig. 19(a) shows the TOF as a function of NH₃ concentration at 190, 200 and 210°C. The TOF increases with NH₃ concentration, reaching a maximum at ~10000 ppm NH₃, beyond which the rate drops. This same trend is evident for each of three temperatures. The TOF variation for the lower NH₃ concentration between 10 to 2000 ppm is shown in Fig. 19(b). The nonmonotonic TOF dependence on NH₃ concentration is retained for the monolith-supported Pt-Al₂O₃ washcoated catalyst; i.e., compare data to Pt-Al₂O₃ powder in Fig. 18. However, there is a noted quantitative difference in the TOF magnitude as well as the NH₃ concentration giving the maximum rate, $C_{NH3,m}$. Specifically, the monolith catalyst has a maximum TOF of ~25 1/s at 210°C compared to 0.06 1/s for the powder catalyst in fixed bed reactor at 245°C. Furthermore, $C_{NH3,m}$ shifts from ~10000 ppm for the former to ~500 ppm for the latter. That is, the positive order regime extends to

a much higher NH_3 concentration. The higher TOF for the $Pt-Al_2O_3$ washcoat clearly indicates a much higher activity than that of the $Pt-Al_2O_3$ powder.



Figure 19. Turn over frequency (TOF) of NH₃ oxidation as a function of NH₃ concentration for Pt washcoated monolith samples (a&b) and 20 h ball-milled Pt(0.07)-Al₂O₃ tested in fixed bed reactor (c&d) (e) Reaction order (n) with respect to NH₃ concentration for ball-milled Pt(0.07)-Al₂O₃ sample (f) Apparent activation energy (Ea) of NH₃ oxidation over Pt(0.07)-Al₂O₃ at 100 ppm of NH₃.

The higher activity for the Pt-Al₂O₃ monolith compared to unmilled Pt-Al₂O₃ powder is an unexpected and interesting finding. Clearly, in the kinetically-controlled regime the intrinsic rate should be independent of the reactor type at the same conditions, such as NH₃ concentration and temperature. On the other hand, the assumption of kinetic controlled reaction might need to be re-evaluated due to, for example, the presence of intraparticle diffusion limitations for the powder, and as a result, the measured apparent rate would be lowered by diffusional gradients (in the positive-order w/r NH₃ regime). To check this potential cause for the difference in rates, we assessed the extent of diffusional

limitations for the unmilled powder catalyst using the Weisz-Prater criterion [74] using the measured (by SEM) average particle size of ~50 μ m. In contrast, the particle size of the milled catalyst is in the range of 1 – 10 μ m. The analysis reveals that the maximum Weisz-Prater modulus has a value of ~10⁻⁴ for unmilled and 10⁻² for milled Pt-Al₂O₃, thereby ruling out diffusion limitations and ensuring kinetic control for the Pt-Al₂O₃ powder.

With pore diffusion limitations ruled out as the root cause for the much higher NH₃ oxidation rate with the milled catalyst, other factors must be considered. As described earlier, the Pt(0.07)/Al₂O₃ particles were ball-milled with ceramic beads for 20 h, followed by sieving to remove any large particles or agglomerates. This was necessary to enable improved adhesion of the catalyst slurry to the monolith during the coating step. The particle size was reduced from 50 μ m to < 10 μ m as a result of ball-milling. We conclude that the higher activity of the washcoated Pt-Al₂O₃ is attributed to the milling step during slurry preparation. The impact of milling process is investigated in more detail later.

To check the generality of finding while retaining the particulate form of the catalyst, we examined the kinetics of the milled catalyst powder, denoted by Pt(0.07)-Al₂O₃-20h-BM. The differential rate was measured in the fixed-bed reactor under similar conditions as the monolith catalyst; i.e., total flow rate of 1000 sccm, 10 v.% O₂, balance Ar, and $C_{NH3} = 10$ to 25000 ppm. Fig. 19(c), with the expanded low concentration region shown in Fig. 19(d), shows the steady state rate (TOF, 1/s) as a function of C_{NH3} . The data were collected at three catalyst temperatures, 170, 180 and 190°C. While the existence of a TOF maximum is consistent with what was obtained for the unmilled Pt(0.07)-Al₂O₃

powder (Figs. 16(a), 16(b)), the milled Pt(0.07)-Al₂O₃-20h-BM sample results more closely resemble those of the monolith catalyst; compare Figs. 19(c) and 19(d) to Figs. 19(a) and 19(b). The TOF variation in the lower C_{NH3} range between 10 and 2000 ppm shown in Fig. 19(d) has the same convex/concave transition at $C_{NH3} \sim 400$ ppm. Further, the magnitude of the TOF for the milled powder and washcoated monolith are much closer in magnitude, considerably exceeding the TOF for the unmilled catalyst. Again, these findings point to milling being responsible for the catalyst activity enhancement.

Fig. 19(e) shows the reaction order plot for the milled catalyst powder. The dependence of the NH₃ reaction order has a more complex dependence on C_{NH3} than does the unmilled catalyst (Fig. 18(c)). The order is ~ 0.3 at low range of NH₃ concentration from 100 ppm to 700 ppm, increases to ~1.45 for 900 – 6000 ppm, and decreases to zero at 10000 ppm. Beyond the maximum the order becomes more strongly negative, decreasing to a value of ~ - 1.6. The apparent activation energy (E_a) was estimated at 100 ppm, giving a value of 121 kJ/mol as shown in Fig. 19(f). This value is 32 kJ/mole less than that of the unmilled Pt(0.07)-Al₂O₃ catalyst, which confirms in part the higher activity of the monolith and milled catalysts. In section 4.5 we continue with our investigation of the enhanced activity obtained through milling.

3.4.2 Microkinetic scheme simulation and parameter estimation

The reaction-rate measurements for the three catalyst types – unmilled powder, milled powder, and milled washcoat, exhibit a nonmonotonic TOF dependence on the NH_3 concentration. The existence of a rate maximum implies the presence of active site-competitive adsorption between NH_3 and O_2 . Further, the changing reactor order dependence as a function of NH_3 concentration suggests an important feature of the reaction mechanism. In this section we describe the ability of the three microkinetic schemes to address these features. Ultimately our aim is to develop a unifying scheme that predicts the rate data for all three catalyst types.



Figure 20. Comparison of the 3 microkinetic model predictions versus experimental data with respect to steady state NH₃ oxidation (a, d, g) & TOF (b, c, e, f, h, i) over 3 catalysts, Row 1: Pt(0.07)-Al₂O₃ in fixed bed reactor, Row 2 : 3.2 g/ft³ of Pt washcoated over Monolith, Row 3 : 20 h ball-milled Pt(0.07)-Al₂O₃ in fixed bed reactor.

We first consider the unmilled Pt(0.07)-Al₂O₃ catalyst. The dual-site BA microkinetic scheme which was applied in the previous studies by Shrestha et al., [71] and Dhillon et al., [50] considers that NH_3 and O_2 adsorption are independent and noncompetitive. These studies applied the kinetic scheme developed by Kraehnert and Baerns [70]. As described earlier, the dual-site basis is not consistent with the maximum rate observed for each of the three catalysts. In fact, it is an oversimplification to think that only the Pt<111> crystal plane would be present. That said, we used the BA scheme as that starting point given its ability to predict the conversion and product distribution over a wide range of temperature [50]. The kinetic parameters for steps R1-R9 were estimated to give a fit of the steady state NH₃ oxidation light-off curve shown in Fig. 20(a), making sure these parameters fit the product distribution of the NH₃. As expected, the BA scheme is incapable of predicting a maximum in the NH_3 oxidation rate given the absence of site competition. As shown in Fig. 20(b), the tuned scheme predicts a constant reaction-rate (TOF) as a function of varying NH₃ concentration, matching the measured rate maximum at 500 ppm for 235, 240 and 245°C. Again, this is an expected result due to the lack of competitive adsorption feature of the dual-site scheme.

The presence of a maximum rate (TOF) suggests the presence of competitive adsorption of NH_3 and O_2 . Microkinetic scheme AA considers a single-site denoted by 'a' for both NH_3 and O_2 adsorption and no site 'b'; i.e., site competition. As we did for the BA scheme, we used the same set of kinetic parameters for reaction steps R3 – R9 (Fig 17, Table 2). Then the kinetic parameters of step R10 (NH_3 adsorption/desorption) and step R11 (surface reaction between NH_3 -a and O-a) were adjusted to get a good fit of the light-

off data (Fig. 20(a)) and reaction rate data at 235°C (Fig. 18(b)). This process of tuning was followed throughout. The tuned scheme does a good job in predicting the rate maximum at ~500 ppm as well as the NH₃ inhibition regime beyond the maximum for the three temperatures shown in Fig. 20(b); i.e., 235, 240 and 245°C. Further, the AA scheme accurately predicts the steady state NH₃ oxidation light-off (Fig. 20(a)) along with the dependence of the TOF on NH₃ concentration for the unmilled catalyst (Figs. 20(b) and (c)).

Similar results were obtained with the milled catalyst. The steady state NH₃ oxidation light-off curve is shown for the Pt-Al₂O₃ washcoated monolith in Fig. 20(d) and for the powder catalyst in Fig. 20(g). The feed gas contained 500 ppm of NH₃, 10 vol.% O₂ and balance Argon delivered at 1000 sccm. The BA scheme does a good job predicting the steady state NH₃ conversion and product distribution versus temperature. The scheme also does well in predicting the TOF dependence for $C_{NH3} < 200$ ppm at 210°C for the monolith (Fig. 20(e)) and 190°C for the milled powder (Fig. 20(h)). However, scheme fails to predict the TOF at higher C_{NH3} rates. The TOF vs. C_{NH3} shows the predicted shift from first- to zeroth-order in NH₃ consistent with the saturation of 'b' sites. The data on the other hand show a shift to higher rate consistent with the emergence of a second reaction pathway.

While the BA scheme cannot predict the rate maximum and fails at high NH_3 concentrations, the AA scheme fails at low NH_3 concentration. To illustrate, we fixed kinetic parameters for steps R3 - R9 from the BA scheme while tuning the parameters for

steps R10 and R11 to get a good fit of the light-off and reaction rate data. The results are mixed. The AA scheme does a poor job in predicting the steady-state NH₃ oxidation light-off curve at the low NH₃ concentration of 500 ppm as seen in Figs. 20(d) (washcoated monolith) and 20(g) (milled powder in fixed bed). The scheme also under predicts the TOF at lower NH₃ concentration shown in Figs. 20(e). There is a mechanistic explanation for this feature: At low NH₃ concentration site 'a' is blocked by O₂. Without the ability to adsorb noncompetitively on site 'b', the rate is under predicted. However at higher C_{NH3} the higher rate frees up 'a' sites for NH₃ adsorption and reaction. At even higher values blocking of O₂ adsorption by NH₃ occurs, leading to rate maximum and eventual decline (Figs. 20(b), 21(b)).

As discussed earlier, the BA dual-site scheme presumes that the supported Pt catalyst behaves as if only the Pt<111> plane comprising the 'b' and 'a' sites are present. This is contrary to supported Pt catalysts which typically have several exposed facets. As a result, the rate is a composite contribution of the activities of those facets. For this reason, the dual-site BA + AA scheme introduced in Section 3.2 presumes that the NH₃ adsorbs on 'a' and 'b' sites and reacts with O adatoms on 'a' sites. The competitive adsorption and reaction of NH₃ and O₂ enables a rate maximum while the dual-site pathway enables a non-competitive reaction consistent with the aforementioned Pt<111> mechanism. Kinetic parameters for schemes BA and AA were used as initial estimates; R1 + R2 and R10 + R11, respectively. The remaining parameters from common steps (R3 – R9) were fixed. After iterations in the R1, R2, R10 and R11 parameters a few of the "fixed" parameters in R3-R9 were adjusted to get the final fit.

The results of this approach, shown in Fig. 20, were successful. Scheme BA + AA captures the presence of the TOF maximum at 500 ppm for each of the three temperatures and two flow rates (see Figs. 20(b) and 20(c)). Fig. 20(b) shows that the BA + AA scheme does a better job of predicting the rate at lower NH₃ concentration while at higher concentrations the BA + AA and AA nearly coincide. This indicates that the BA pathway becomes important at low C_{NH3} . Further, only scheme BA + AA is able to predict the precise location of the maximum for the milled catalyst samples. In the Appendix (Section A2) an analytical treatment of the BA + AA scheme assuming surface reaction control shows that a noncompetitive (BA) and competitive (AA) NH₃ oxidation paths are necessary to predict the rate maximum location shift.

In accounting for NH₃ adsorption on the 'a' and 'b' sites, the BA + AA scheme is able to predict the measured rates at extremes in NH₃ concentration. At low NH₃ concentration adsorption on site 'b' avoids inhibition by O₂ while at high NH₃ concentration there is competition leading to NH₃ inhibition. The kinetic parameters estimated from a fit of the unmilled Pt(0.07)-Al₂O₃ catalyst were used as initial estimates. The R1, R2, R10 and R11 parameters were then tuned to fit the steady state NH₃ oxidation light-off curve for the Pt-Al₂O₃ washcoated monolith (3.2 g Pt/ft³ loading). Finally, a few of the "fixed" parameters in R3-R9 were tweaked to get the final fit. A good fit of the steady state NH₃ oxidation light-off is shown in Fig. 20(d) while Fig. 20(e) shows the model-predicted TOF as a function of the NH₃ concentration. The rate data for very low NH₃ concentrations is predicted quite well. Finally, the scheme also captures the difference in slope of curves in Fig. 20(e) from 0 – 100 ppm and > 100 ppm which further underscores its effectiveness. The scheme also predicts the TOF maximum at 10000 ppm for each of the temperatures as shown in Fig. 20(f).

Earlier we showed the similarity in the rates obtained with the milled $Pt-Al_2O_3$ powder and $Pt-Al_2O_3$ washcoated monolith catalysts. The same kinetic parameters estimated from the fit of the monolith catalyst were used to simulate the fixed-bed catalyst data as shown in Figs. 20(g), 20(h), and 20(i). The BA + AA scheme is clearly able to predict the temperature and NH₃ concentration dependence.



Figure 21. Comparison of the three microkinetic models for Milled Pt(0.07)- Al_2O_3 catalyst. The TOF vs C_{NH3} is divided into two regions, (a) Enlarged Region for lower C_{NH3} from 0 to 1200 ppm (b) for the entire range of C_{NH3} .

Fig. 21 compares the TOF predictions of the three schemes over a range of NH_3 concentrations for the milled Pt(0.07)- Al_2O_3 at 190°C. Schemes AA and BA + AA both do well in predicting the TOF vs. C_{NH3} between ~1000 and 20000 ppm. This reflects the fact that the reaction is dominated by competitive adsorption and reaction on the single 'a' sites. In contrast, scheme BA vastly under predicts the TOF since the site 'a' pathway is

prohibited. On the other hand, scheme BA does a good job of predicting the very low C_{NH3} (< 200 ppm) behavior evident in Fig. 21(a) while scheme AA fails.



Figure 22. Reactant species site coverage as a function of Ammonia concentration superimposed with reaction rate variation (TOF) for (A) Un-milled Pt(0.07)-Al₂O₃ (B) 20 h ball-milled Pt(0.07)-Al₂O₃. [lines – site coverages, dashed lines – reaction rate (TOF)]

The microkinetic scheme predicted surface coverages of the reacting species provide insight into the impact of the operating conditions. A deeper understanding of the differences in three schemes can be obtained by examining the model predicted species coverages over a range of NH₃ concentrations for the milled and monolith catalysts. While the predicted coverages are not verified by measurements, they are useful in explaining certain features such as the existence of different rate controlling regimes. Figure 22 shows the surface coverages of the primary species as a function of NH₃ concentration for the unmilled Pt(0.07)-Al₂O₃ and milled (20 h) Pt(0.07)-Al₂O₃ catalyst at 240 and 190°C, respectively. Also shown is the predicted TOF, which was shown earlier to predict well the experimental data (Figs. 20(b) and 20(i)). Fig. 22(a) shows that the NH₃ coverage on site

b, θ_{NH3-b} , increases sharply from the origin to 1, indicating that these sites are filled at rather low NH₃ concentration. The coverage of O adatoms on the 'a' sites, θ_{O-a} , approaches 1 as $C_{NH3} \rightarrow 0$. That the TOF increases with C_{NH3} in this regime shows that the oxidation occurs through reaction between NH₃ adsorbed on the 'b' sites since the high coverage of O blocks NH₃ adsorption on 'a' sites. As C_{NH3} is increased from 0, the NH₃ coverage on 'a' sites, θ_{NH3-a} , increases as θ_{O-a} decreases due to O consumption. By $C_{NH3} \sim 500$ ppm θ_{NH3-a} exceeds θ_{O-a} while TOF reaches a maximum and proceeds to decrease. At this point the reaction becomes inhibited by NH₃ which blocks O₂ dissociative adsorption. As θ_{NH3-a} increases, θ_{O-a} decreases showing the competition. For example, θ_{NH3-a} varies from ~0.45 at 100 ppm of NH₃ to 0.18 at 900 ppm of NH₃. Similar trends are seen in Fig. 22(b), indicating that the same shift in NH₃ oxidation pathways occurs on the milled catalyst. The main difference is a much higher turnover rate and a sharper demarcation between the two kinetic regimes.

An additional difference between the unmilled and milled catalysts is the magnitude and location of the rate maximum. A comparison of Figs. 22(a) and 22(b) indicates that the rate maximum occurs at a much higher NH_3 concentration; i.e., ~10,000 ppm for the milled catalyst compared to ~500 ppm for the unmilled catalyst. Thus the positive-order w/r NH_3 regime extends over a much wider range of NH_3 concentrations. This feature actually is clear evidence for the existence of two different oxidation pathways.

3.4.3 Model validation – steady state NH3 oxidation

The tuned BA + AA scheme was validated by comparing the model predictions with the measured NH₃ conversion and product distribution for three catalysts, shown in Fig. 23; namely, unmilled Pt(0.07)-Al₂O₃ (fixed bed), Pt – 3.2 (monolith), and milled Pt(0.07)-Al₂O₃-20h-BM (fixed bed). The conditions used correspond to a feed containing 500 ppm of NH₃, 10 vol.% O₂ and balance Argon at a flow-rate of 1000 sccm. Light-off was observed at 305, 240, and 215°C for the three catalysts, respectively. As a reminder, the kinetic parameters for the milled and monolith catalysts are identical. Overall, the experimental data are predicted well for each of the catalysts, including the light-off temperature and product yields. With increasing temperature the onset of the byproducts N₂O, NO and NO₂ were detected in succession, well captured by the model. The onset temperatures and maxima of the N₂ and N₂O yields are also well predicted. For the milled Pt and monolith catalysts, the N₂ yield is higher than the unmilled Pt-Al₂O₃. This interesting result suggests that the milling process exposes more selective crystal planes, a



Figure 23. Steady state NH₃ oxidation over 3 catalyst samples (a) Fixed bed: Pt(0.07)-Al₂O₃ (b) Monolith: Pt-3.2 (c) Fixed bed: Pt(0.07)-Al₂O₃-20h-BM. Feed conditions: 500 ppm NH₃, 10% O₂, balance Ar at 1000 sccm. [symbols – experiments, lines – model]

Based on the above discussion, the BA + AA scheme accurately captures the lightoff characteristics and the TOF dependence on the NH₃ concentration. The apparent activation energy (E_a) for R2, R11 for unmilled is 152 kJ/mol, ~30 kJ/mol higher than that of milled Pt-Al₂O₃ and monolith catalysts. The estimated E_a obtained from scheme tuning clearly predicts the higher activity for monolith and ball-milled catalysts due to the lower energy barrier. Further model validations are provided in the Appendix (Section A3).





Figure 24. NH₃ concentration at maximum reaction rate for 0.07, 0.15 & 0.45 weight % of Pt in Al₂O₃ support at 240°C, 0.20 g of un-milled Pt/Al₂O₃ tested in fixed bed reactor. Feed conditions: NH₃, 10% O₂, balance Ar, 1000 sccm. [symbol – experimental data, line – model]

The effect of Pt loading was examined for the unmilled $Pt-Al_2O_3$ catalyst evaluated in the fixed bed reactor. The reaction rate was measured for three Pt loadings; 0.07, 0.15 and 0.45%, each at 240°C, and each in the amount of 0.2 g. The NH₃ feed concentration was varied in 10 vol.% O₂, balance Argon, with the gas mixture flowing at a rate of 1000 sccm. The corresponding model predictions are shown. Fig. 24 shows the NH₃ concentration at the maximum measured TOF, $C_{NH3,m}$, as a function of Pt loading $C_{NH3,m}$ increases monotonically with the Pt loading; specifically, $C_{NH3,m} = 500$, 850 and 1100 ppm for 0.07, 0.15 and 0.45 wt.% loading, respectively. The trend is attributed to the increase in the Pt site density that accompanies with the increase in Pt loading. As the number of sites increase the NH₃ concentration at maximum shifts to higher values. This expands the positive-order regime. This trend is consistent with the earlier discussion related to the milled Pt(0.07)-Al₂O₃ and washcoated monolith exhibiting maximum at 10,000 ppm. It is interesting to note that the rate maximum occurs at 50% coverage of NH₃ on site 'a'.

3.4.5 Effect of milling

The steady state rate measurements (comparing Fig. 18(a & b) and Fig. 19(a)) and light-off experiments in Fig. 25 reveal an interesting increase in activity for the milled washcoated catalyst (Pt – 3.2). As described earlier, the monolith washcoated was prepared by dipping the substrate into a Pt-Al₂O₃ slurry. The slurry preparation included a milling step, conducted for 20 h. Indeed, the only difference between the catalyst particles and monolith catalyst is the ball milling step. The total moles of Pt in both milled and unmilled samples is ~ 3.6 x 10⁻⁷ moles Pt with a Pt dispersion of 45%. For the monolith catalyst with a volumetric loading of 3.2 g Pt /ft³ monolith catalyst is ~ 3.1 x 10⁻⁸ moles. Thus, the milled and unmilled Pt(0.07)-Al₂O₃ powder catalysts have about 10 times more Pt compared to the monolith catalyst. Despite this difference, the monolith has a demonstrably higher overall activity. This is seen by comparing the reaction rates (TOF) for the unmilled

Pt(0.07)-Al₂O₃ and the Pt – 3.2 monolith catalyst. At the same flowrate of 1000 sccm, the maximum TOF for the unmilled Pt(0.07)-Al₂O₃ is 0.055 s⁻¹, obtained at 500 ppm NH₃ and 245°C. This is considerably lower than the maximum TOF of ~23 s⁻¹ at 10000 ppm NH₃ and 210°C for the monolith catalyst. Thus, the impact of the milling is to extend the positive-order NH₃ regime to much higher concentration. The higher activity of the monolith is reflected in the estimated E_a of ~121 kJ/mole, which is ~32 kJ/mole lower than estimated E_a for the unmilled catalyst.

Additional experiments were conducted to quantify and understand the impact of ball-milling on the catalytic activity. A set of steady state NH₃ oxidation experiments was carried out over four different catalysts in the fixed bed reactor. The Pt loading was kept fixed at 0.07 wt.%. The first catalyst was unmilled Pt(0.07)-Al₂O₃. The second and third catalysts were ball-milled for two different durations of 20 and 50 h; these are designated as Pt(0.07)-Al₂O₃-20h-BM and Pt(0.07)-Al₂O₃-50h-BM. For the fourth sample the Al₂O₃ particles were ball-milled for 20 h, followed by the addition of Pt by wet impregnation; designated by Al₂O₃-20h-BM + Pt(0.07). A total mass of 0.2 g of the catalyst was loaded into the fixed bed reactor for each. The comparison experiments were conducted using the same feed comprising 500 ppm NH₃, 10 vol.% O₂, balance Argon, delivered at 1000 sccm.

Fig. 25 compares the NH₃ oxidation light-off curves for each of the four samples. These data show two groups of light-off curves; the higher temperature pair has a T50 of \sim 305°C while the lower temperature pair has a T50 of \sim 205°C. The higher lightoff temperature data were obtained for the two less active catalysts, Pt(0.07)-Al₂O₃ and Al₂O₃-
20h-BM + Pt(0.07). The lower light-off temperature data were obtained for the two more active catalysts, $Pt(0.07)-Al_2O_3-20h-BM$ and $Pt(0.07)-Al_2O_3-50h-BM$. These results show unequivocally that milling of the Pt-Al_2O_3 increases the activity. The two lower activity catalysts were either not milled or milled prior to impregnation of the Pt.



Figure 25. Steady state NH₃ oxidation over 4 catalyst samples Pt(0.07)-Al₂O₃: Un-milled, Al₂O₃-20h-BM + Pt(0.07): 20 h ball-milled Alumina followed by Pt impregnation, Pt(0.07)-Al₂O₃-X-BM: Ball-milled Pt(0.07)-Al₂O₃ for X = 20h, 50h tested in fixed bed reactor. Feed: 500 ppm NH₃, 10% O₂, balance Ar at 1000 sccm.

The obvious impact of ball milling is a reduction in the particle size of the Al_2O_3 . SEM measurements revealed a 5-fold reduction in the particle size, from ~50 µm to ~10 µm. This suggests that the increase in activity is a result of a reduction in intraparticle diffusion limitations. However, as previously discussed, the Weisz Prater analysis indicated negligible pore diffusion limitations for both the unmilled and milled Pt-Al₂O₃. Were diffusion limitations the root cause, then the activity of the sample in which the milling and Pt impregnation were done in succession would have shown a similar enhancement in rate as the sample in which milling was conducted after impregnation. One logical explanation towards increased activity is a reduction in the Pt particle size or increase in Pt dispersion. It is known that milling of a catalyst sample can alter the dispersion of the active species. A higher dispersion of Pt would mean a higher exposed active surface and a higher oxidation rate, which as a result can lead to increased activity. However, the Pt dispersion measurements do not indicate this to be a large factor (Table 1). The Pt dispersion for the unmilled Pt(0.07)-Al₂O₃ and milled samples (Pt(0.07)-Al₂O₃-20h-BM, Pt(0.07)-Al₂O₃-50h-BM) varied only marginally; 45 % to 42%. In fact, the dispersion decrease should lead to a decrease in rate, but in fact the rate increased. This clearly rules out particle size reduction as the responsible cause, and a different explanation is needed.

It has been reported in the literature that the various crystalline planes of Pt have different reactivity [63,75]. Studies by Zeng et al., [75] and recently by Ma et al., [63] discuss the structure sensitivity effects of NH₃ oxidation over Pt. Ma et al., [63] compared the reactivity of Pt<211> and Pt<111>, which Zeng et al., [73] compared the reactivity for Pt foil, Pt<533>, Pt<865>, Pt<433> and Pt<100>. Hence, we decided to look if the milling process leads to change in crystal plane structure of Pt which can have an impact on reactivity of milled Pt-Al₂O₃ samples. In order to detect such changes in crystal planes during the milling process, powder X-ray diffraction (XRD) was done over unmilled and ball-milled Pt-Al₂O₃ powder samples. In these experiments the Pt loading was increased from 0.07 to 7 wt.% to improve the signal-to-noise of the peaks associated with Pt.

Figure 26 shows the powder XRD patterns for the following samples: , γ -Al₂O₃ support, unmilled Pt(7)-Al₂O₃, and ball-milled Pt(7)-Al₂O₃-20h-BM. We were able to detect specific Pt facets and Pt oxide species. Note that for each sample, (γ -Al₂O₃ unmilled Pt(7)-Al₂O₃ ball-milled Pt(7)-Al₂O₃-20h-BM), the powder XRD diffraction pattern was obtained after averaging over 5 individual rounds of XRD diffraction experiments. This was done to confirm the changes in peak heights of the Pt crystal planes and not just any experimental error.

The three peak assignments follow from the literature [76–80]; Pt<111> at 39°, Pt<200> at 46° and PtO₂<211> at 57°. The detection of different Pt crystal planes, <111> and <200>, along with oxides of Pt in the form of PtO₂<211> suggests the potential root cause for the milling-induced activity enhancement. A comparison of the unmilled and milled Pt(7)-Al₂O₃ samples reveals a decrease in the peak height intensity of the Pt<111> and an increase in the peak height of PtO₂<211>. A smaller increase in Pt<200> is also noted. An increase in peak height is indicative of an increase in the fraction of the particular crystal plane.

The XRD data suggest that ball milling of the Pt-Al₂O₃ results in a decrease in the fraction of Pt<111> and an increase in the fraction of PtO₂<211> planes. Apparently, the ball milling serves to modify the shape and crystallinity of the nanometer sized Pt crystallites on the Al₂O₃ surface, an unexpected but interesting finding. The ball milling also leads to increase in the Pt oxide. The sustained collisions of the hard quartz beads with the Pt-Al₂O₃ particles over a period of 20 h may result in a localized Pt crystal phase

transformation and oxide formation on the stepped Pt<211> surface. While the decrease in the Pt<111> and increase in Pt<200> is not likely to impact the catalytic activity, the formation of $PtO_2<211>$ may do so. We expand on this point next.



Figure 26. Powder X-ray diffraction patterns for Pt(7)-Al₂O₃ (un-milled), Pt(7)-Al₂O₃-20h-BM (20 h ball-milled) and γ-Al₂O₃ (support)

If we are to attribute the milling-induced formation of $PtO_2 < 211$ > to the observed activity increase, then we need to evaluate its stability. Ma et al., [63] and Zheng et al., [73] have reported on the different NH₃ oxidation activities of Pt crystal planes. Zheng et al., [73] also showed the that Pt<865>, Pt<533>, Pt<433> crystal planes steps and kinks to be more active compared to single plane of Pt<111>, Pt<100>. In their DFT study, Ma et al., [63] showed under NH₃ slip conditions that the stepped Pt<211> plane has a much lower activation energy of 51.3 kJ/mole than Pt<111> (239 kJ/mole). Perhaps related is our finding that upon milling there is a decrease in the less active Pt<111> and an increase

in the more active Pt<211>, albeit the latter in the form of PtO₂<211>. It is well known that the catalytic oxidation activity of metallic Pt is higher than that of PtO₂. Further Pt oxides begin to form at 50°C [42,76,81] and are stable up to 470°C on a γ -Al₂O₃ support.



Figure 27. H₂ temperature programmed reduction. (a) Temperature profile used for each experiment with a ramp rate of 10°C/min. (b – d) H₂O generation peaks detected by mass spectrometry for: (b) Al₂O₃; (c) P(0.07)-Al₂O₃ unmilled; (d) P(0.07)-Al₂O₃-20h-BM, 20 h ball milled Pt/Al₂O₃.

In order to evaluate the stability of the PtO_2 we carried out H_2 temperature programmed reduction (H₂-TPR) on both unmilled and milled catalysts; specifically, Pt(0.07)-Al₂O₃ and 20 h milled Pt(0.07)-Al₂O₃, along with the γ -Al₂O₃ support as reference The feed conditions were 1 vol% H₂ (with Ar balance) at a flow rate of 30 sccm and a temperature ramp rate of 10°C/min up to 800°C (Fig. 27(a)). For each experiment 100 mg of sample was used. Due to the small amount of Pt (35 µmoles in a 100 mg sample) it was difficult to detect H₂ consumption with the mass spectrometer for the given feed. Instead, H_2O generation peaks could be detected during the analysis. Figs. 27(b) - 27(d) show the H_2O production as a function of time over the three samples. The peak at 745°C, which is present for all samples, is the contribution from the γ -Al₂O₃ support. The commercial γ -Al₂O₃ support contains 3 wt% La₂O₃ to improve thermostability. The peak at 745°C is attributed to H₂-TPR contribution from La₂O₃ [44]. The P(0.07)-Al₂O₃ sample has a peak at 375°C in addition to the peak at 745°C (Fig. 27(c)). In contrast, the P(0.05)-AS sample has a H₂O peak appearing at a lower temperature of 265°C (Fig. 27(d)). The H₂O peaks appearing in the TPR profile indicates the temperature at which PtO₂ are reduced by H₂ to Pt(0). The formation of H₂O peaks at 265°C for milled Pt-(0.07)-Al₂O₃ compared to 375°C for un-milled Pt(0.07)-Al₂O₃. This indicates a lower stability of the PtO₂ on the milled Pt(0.07)-Al₂O₃. Metal-support interactions (MSI) are known to play an important role in determining the stability of Pt oxides. Huizinga et al., [45] showed that Pt oxide supported on γ -Al₂O₃ has a higher stability than on TiO₂ or SiO₂. In that work, H₂-TPR over Pt/TiO₂ showed that Pt oxide species decompose at lower temperature compared to Pt/γ -Al₂O₃, which suggests that alumina stabilizes the oxide particles. In the case of milling, the large ~50 μ m Pt-Al₂O₃ particles are broken down to <10 μ m Pt-Al₂O₃ particles. The process of milling the $Pt-Al_2O_3$ leads to Pt crystallite transformations and the creation of new grain boundaries for γ -Al₂O₃ support [82–84]. From the H₂-TPR experiments, we can clearly see the lowering of the Pt oxide reduction temperature which indicates the altering of the metal support interactions between the Pt and γ -Al₂O₃ support. The milling of γ -Al₂O₃ support modifies the metal-support interaction which leads to an easier destabilization of Pt oxides

upon milling, exposing metallic Pt which is more active towards NH₃ oxidation. This combined with the effect of Pt crystallite transformation towards more stepped crystalline planes would explain the increase in activity of the ball-milled Pt-Al₂O₃ catalysts and Pt – 3.2 monolith catalysts. The E_a as determined from kinetic experiments, for unmilled Pt(0.07)-Al₂O₃ is 153 kJ/mole while 121 kJ/mol for ball-milled Pt(0.07)-Al₂O₃ catalysts. The decrease of 32 kJ/mole in E_a after milling can hence be related to closely related effects of destabilization of Pt oxides and crystalline transformations.

3.5. Conclusions

In summary, we were able to show the variation of reaction rate as a function of NH_3 concentration for Pt-Al₂O₃ catalysts in presence of excess oxygen. We also showed the reaction order varies from positive to negative-order with zero order reaction at maximum reaction rate. We compared three microkinetic schemes; a dual-site, single-site, and combined dual-site and single-site. It was found that only the combined scheme is able to capture the trends of the rate, light-off curve, and product distributions, revealing that there exists a site competition between NH_3 and O_2 in the reaction mechanism. Using the scheme proposed in this work we were able to explain the impact of site-competition using reactant species coverages. The maximum NH_3 rate takes place at 50% NH_3 coverage at site 'a'. It was also shown that ball-milling of Pt-Alumina leads to increase in activity and using XRD it was ascertained that this is due to the structural changes happening to Pt crystallites due to the impact of milling process.

Chapter 4: Simulation of selective oxidation of NH₃ in a Pt/Al₂O₃@Cu-ZSM-5 core-shell catalyst

4.1. Introduction

The adoption of ammonia (NH₃) based selective catalytic reduction (SCR) for the control of NO_x (x = 1, 2) emissions from diesel and other lean burn vehicles follows its successful deployment for stationary source emissions . Catalysts typically employed in stationary source applications are mixed metal oxides of V, Ti, and/or W [29], whereas the catalysts developed for vehicles tend to be metal-exchanged zeolites. NOx is reduced over Cu- or Fe-exchanged zeolites (BEA, ZSM-5, SSZ-13) through the standard (R1), fast (R2), and slow (R3) pathways [19]. The selective catalytic reduction (SCR) catalyst selectively reduces NOx to N₂ over Cu or Fe exchanged zeolites proceeds through the standard (4-1), fast (4-2), slow (4-3) and NH₃ oxidation (4-4) mechanisms:

$$4 NH_3 + 4 NO + O_2 \rightarrow 4 N_2 + 6 H_2O, \tag{4-1}$$

$$2 NH_3 + NO + NO_2 \rightarrow 2 N_2 + 3 H_2O,$$
 (4-2)

$$4 NH_3 + 3 NO_2 \rightarrow 3.5 N_2 + 6 H_2 O \tag{4-3}$$

and
$$4 NH_3 + 3 O_2 \rightarrow 2 N_2 + 6 H_2 O_2$$
. (4-4)

The reaction steps (R1 - R3) are the main SCR reaction mechanism [21,23-26,51,85,86] that makes the SCR unit a robust technology in meeting the strict emission restrictions. However, the NH₃ oxidation (4-4) taking place at high temperature over the metal exchanged zeolites, is an unwanted side reaction leading to the consumption of much needed reducing agent NH₃. As a result, the requisite NH₃/NOx ratio is slightly over unity in order to mitigate with consumption of NH₃ via reaction 4-4, which is most prominent at higher temperature on Cu-exchanged zeolites. This along with transient operating conditions of variable engine load, exhaust temperature leads to unavoidable release of unreacted NH₃ from SCR unit [27,28]. This led to the development of Ammonia slip catalyst (ASC), responsible for converting NH₃ to N₂ as the final unit in a modern diesel vehicle emission system.

The state-of-the-art ASC has a dual-layer architecture comprised of a base Pt/Al_2O_3 (PGM) layer and a top Cu-zeolite (SCR) layer to selectively oxidize NH_3 to N_2 . The base PGM layer oxidizes the NH_3 to a mixture of N_2 , N_2O , NO, and NO_2 , in that order, with increasing temperature through the following reactions (4-5 – 4-8) :

$$4 NH_3 + 3 O_2 \rightarrow 2 N_2 + 6 H_2 O, \tag{4-5}$$

$$2 NH_3 + 2 O_2 \rightarrow 1 N_2 O + 3 H_2 O, \tag{4-6}$$

$$4 NH_3 + 5 O_2 \rightarrow 4 NO + 6 H_2O \tag{4-7}$$

and
$$4 NH_3 + 7 O_2 \rightarrow 4 NO_2 + 6 H_2O$$
. (4-8)

In the dual-layer system, the undesired products NO and NO₂ react with counter-diffusing NH₃ in the top Cu-zeolite layer, through selective NO/NO₂ reduction chemistry (4-1 – 4-4) to form N₂ [22,30]. This dual-layer architecture proves to be efficient in converting to NH₃ to N₂ [22]. The presence of top SCR layer improves N₂ selectivity, but it does so at

the expense of NH_3 conversion given that SCR layer adds a diffusion barrier. The impact of increasing thickness of the top SCR layer was studied extensively by Shrestha et al., [22] who showed a monotonic decrease in NH_3 conversion. Other challenges associated with ASC technology, is the need to improve the low-temperature activity of NH_3 oxidation with minimal Pt loading and reactor size without affecting the N_2 selectivity. There is a need to develop highly active, selective and robust ammonia slip catalysts that can tolerate the demanding diesel exhaust environment.

To that extent different strategies can be employed to reduce the diffusion resistance offered by the top SCR layer and mitigate the challenges mentioned above. Dhillon et al., [32] demonstrated a pore-forming method to reduce the diffusional resistance in the top layer which led to 15 % improvement in NH₃ oxidation activity without having any detrimental impact in N₂ selectivity. Another approach used by Dhillon et al., [72], Shrestha et al., [22] is to optimize the washcoat architecture of having a mixed (PGM + SCR) bottom layer and a thin top SCR layer. Using this approach, the resulting hybrid ASC did a good job in improving the NH₃ conversion due to thin top SCR layer. This study also showed that washcoat structure is an important parameter in design of ASC.

The above two approaches are based on decreasing diffusion resistance by pore formation or by modifying the washcoat structure. The third approach is to develop a new catalyst in order to meet the challenges associated with ammonia slip catalyst. In our recent work, Ghosh et al., [87] synthesized a bifunctional core-shell catalyst for selective NH_3 oxidation to N_2 that emulate the dual layer monolith. The core-shell catalyst Pt/Al₂O₃@Cu/ZSM-5 was designed with an oxidation catalyst as its core (Pt/Al₂O₃) and a NOx reduction catalyst (Cu/ZSM-5) as its shell. The core-shell catalyst showed better performance with respect to N₂ selectivity and had a lower light-off when compared to a physical mixture of Pt/Al₂O₃ and Cu-ZSM-5. The core-shell catalyst exhibited enhanced low temperature activity at the expense of lower PGM loading, while the NOx yield was below 10%. The enhanced activity of the Pt/Al₂O₃ catalyst is attributed to a modification of the reducibility of oxides of Pt crystallites owing to the overgrowth of silicalite-1 (seeded core) and ZSM-5 layers in the core-shell configuration. With the approach of mimicking dual layer ammonia slip catalyst at a single particle level, the requisite loading of expensive metals can be reduced by 2/3rd while maintaining good N₂ selectivity the for entire operating range with significant lowering of NH₃ oxidation light-off.

The model decouples the chemistry and kinetics in the Pt/Al₂O₃ core and Cu-ZSM-5 SCR shell. We evaluate the NH₃ oxidation kinetics of the Silicalite -1 seeded Pt/Al₂O₃ core (P(0.05)-AS) using the microkinetic scheme developed in the Chapter 3.]. The model for the Cu-ZSM-5 SCR powder catalyst uses a global reaction scheme following the one developed by Olsson et al. [88].We also show a method to measure the intracrystalline diffusivities in zeolite by using an active core (PGM) and inert shell (Na-ZSM-5). The diffusivities were used in development of the SCR model in Cu-ZSM-5 powder sample. We then incorporate the NH₃ oxidation kinetics over Pt and SCR kinetics over Cu along with reactor model to simulate the ammonia oxidation data over Pt/Al₂O₃@Cu-ZSM-5 core-shell in a fixed bed reactor. We use the model to converge on the optimal Pt loading and shell thickness, resulting in further enhancement of NH₃ oxidation activity of the coreshell catalyst, while still preserving high N_2 selectivity of > 90% in the entire temperature range.

4.2. Experimental Section

4.2.1 Catalyst Synthesis

The nomenclature and composition of all catalyst samples tested in this study are listed in Table 1. The first step is the addition of Pt to commercial grade γ -Al₂O₃ (Puralox SCFa 140/L3, Sasol) using incipient wetness impregnation. In the second step, *in situ* seeding of the Pt/Al₂O₃ particle with silicalite-1 (MFI type zeolite) nanocrystals is conducted. This is followed by the third step involving secondary growth of a ZSM-5 shell onto the seeded core. Finally, the fourth step focuses on metal incorporation by Cu ion exchange with the protonated ZSM-5 shell. The detailed process of synthesizing the CS catalyst has been described in our previous work [87].

Abbreviation	Туре	Cu-ZSM5 [wt%] in total catalyst ^(a)	Pt[wt%] in Al ₂ O ₃
CS	Core-shell, Pt/Al ₂ O ₃ @Cu/ZSM-5	10	0.05
P(0.05)-A	Pt/Al ₂ O ₃	0	0.05
P(0.05)-AS	Seeded core	0	0.05
P(0.05)-AS-S1	Sample after first stage of secondary growth	0	0.05
CS-Na	Core-Shell, Pt/Al ₂ O ₃ @Na/ZSM-5	0	0.05

 Table 7. Composition and nomenclature of catalyst samples

4.2.2 Bench scale reactor setup

Catalytic activity and performance measurements were carried out in both fixed reactors in an overall set-up that is described elsewhere [87]. A quartz tube (OD 12.75 mm and ID 10.5 mm) containing the catalyst sample was placed in an electric furnace equipped

with a programmable temperature controller. The catalyst was packed at the center of the quartz tube with quartz wool on either end of the bed. The thermocouple end point was positioned in the middle of the catalyst bed both radially and axially. The feed gas flows were metered by MKS mass flow controllers, and the gases used in our work were purchased from Matheson Inc. The concentrations of outlet gases from the reactor were analyzed by a FTIR (Thermo-Nicolet Nexus 470; Nicolet Analytical Instruments) with OMNIC software. The pressure inside the flow lines was maintained at 760 Torr by using a globe valve positioned downstream of the FTIR. The steady state N₂ yield reported in this paper is calculated by difference using an overall nitrogen balance.

4.2.3 Steady state reaction experiments

All flow lines were heated to 150° C by electrical heating tape to prevent condensation and/or adsorption of H₂O and NH₃ onto the tube surfaces. All lines were flushed with Ar for 1 h before collecting background spectra. After taking the background spectra, 500 ppm NH₃ in 10 vol. % O₂ and balance Ar were directed through a reactor bypass line to measure the feed concentration of NH₃ for reference. The flow was then switched to the reactor side, and reaction performance was tested at steady state in the temperature range from 150 to 500°C. Once the gas concentrations remained constant for about 30 min, the steady state data was collected.

The steady-state reaction rates with respect to NH_3 were measured for varying NH_3 concentrations ranging from 10 ppm to 20000 ppm at different temperatures with fixed 10 vol. % O₂ in the feed. The reaction-rate measurements were taken for both fixed-bed and

monolith reactors once steady-state was reached. All measurements were done in the kinetic regime, confirmed using the Weisz-Prater criterion for assessing intrusion by pore diffusion [21].

4.2.5. NH₃ adsorption and temperature programmed desorption (TPD)

The transient adsorption and temperature programmed desorption of NH_3 were carried out on powder Cu-ZSM-5 samples in fixed bed reactor to quantify NH_3 storage. 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., [89] and Dhillon et al., [90], the steps included:

Step 1: At 0 min, only Ar flowing at 100°C.

Step 2: At 5 min, inlet NH3 (355 ppm) started, fixing temperature at 100 °C.

Step 3: At 100 min, inlet NH3 turned-off and temperature maintained at 100 °C.

Step 4: At 110 min, inlet NH3 remained off and temperature ramped-up to 550 °C with 10 °C/min.

The inlet NH₃ of 355 ppm diluted with balance argon and the space velocity was maintained at 1000 sccm for these transient experiments. The time lag between inlet flow controller and outlet FTIR was measured by running an experiment through a blank quartz tube without catalyst, which was subtracted while doing quantification.

4.2.6 Materials characterization

Scanning electron microscopy (SEM) images were obtained using a Zeiss Leo 1525 Gemini FEG instrument. Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku Smartlab Diffractometer using a Cu K α source (40kV, 30mA, $\lambda = 1.54$ Å) in the range of 2 $\theta = 5$ - 50 degrees with 0.02-degree increments. The collected patterns were compared using a reference MFI pattern obtained from the International Zeolite Association (IZA) structure database.

Elemental analysis of the core-shell catalyst was performed using two techniques: X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray (EDX) spectroscopy. XPS measurements were performed on a PHI Model 5700 X-Ray Photoelectron Spectrometer equipped with a standard achromatic Al K α X-ray source (1486.6 eV) at 300W, a concentric hemispherical analyzer, and a neutralizer. EDX measurements were conducted using a JEOL SM-31010/METEK EDAX system at 15kV and 15 mm working distance. The characterization results are discussed in Appendix section (A9).

4.3. Model Description

4.3.1 Reactor Model

A one-dimensional, heterogeneous fixed bed reactor model was used to simulate reaction in the powder-in-tube reactor. The two phases described in the model are the intraparticle and the interstitial phase. The gas flow is laminar based on the low particle Reynolds number (Re \sim 1). Concentration gradients in the radial direction (r) are neglected due to the small tube diameter of 8.1 mm. Dispersion is ignored in the axial (z) direction

due to larger convective flow compared to diffusive transport (axial Pe ~ 370). Isothermal conditions are assumed due to the negligible heat effects from the low NH_3 feed concentration (mostly < 1 vol.%) and low NH_3 conversion. Along with the assumption of axially-uniform heating, an energy balance is not needed.

With these assumptions in mind, the following model equations are used. The interstitial fluid phase includes accumulation, axial convection, and fluid-to-particle mass transfer terms is given by

$$\frac{\partial x_{f,j}}{\partial t} = -\langle u \rangle \frac{dx_{f,j}}{dz} + k_{me,j} a_{\nu} (x_{s,j|r=0} - x_{f,j}).$$
(4-9)

Here the mass transfer coefficient $k_{me,j}$ is given by

$$k_{\text{me},j} = \frac{Sh_e D_{f,j}}{2R_1}.$$
 (4-10)

where R_1 is the radius of the catalyst particle, She is the particle level Sherwood number calculated using Frössling correlation [41], a_v is external surface area at fluid-particle interphase per unit reactor volume and $D_{f,j}$ is the species i diffusivity in the interstitial region of the catalyst bed, calculated as a function of temperature using the Lennard-Jones formulation, $D_{f,j} = a(T/T_o)^{1.75}$. $\langle u \rangle = \frac{F}{\varepsilon_b A}$ is the average interstitial velocity through the bed which is a function of volumetric flowrate (F), bed porosity (ε_b) and reactor cross-sectional surface area (A). For a spherical Cu-ZSM-5 particle of radius 'R', the transport and SCR reactions within the particle is described as the intraparticle fluid phase balance equation (4-11), which includes accumulation, intraparticle diffusion, and reaction terms is given by

$$\frac{\partial x_{p,j,scr}}{\partial t} = \frac{D_{ej,scr}}{r^2} \frac{d}{dr} \left[r^2 \frac{d x_{p,j,scr}}{dr} \right] + \frac{1}{c_{Tm}} \left[\sum_{r=1}^{rxn} \vartheta_{kr} R_{r,scr} \left(T, \theta, x_{pj,scr} \right) \right].$$
(4-11)

For the case of core-shell ASC particle, the intraparticle fluid phase balance for core and the shell includes accumulation, intraparticle diffusion, and reaction terms:

$$Core: \frac{\partial x_{p,j,pgm}}{\partial t} = \frac{D_{ej},pgm}{r^2} \frac{d}{dr} \left[r^2 \frac{dx_{p,j,pgm}}{dr} \right] + \frac{1}{c_{Tm}} \left[\sum_{r=1}^{rxn} \vartheta_{kr} R_{r,pgm} (T, \theta, x_{pj,pgm}) \right] (4-12)$$

and Shell:
$$\frac{\partial x_{p,j,scr}}{\partial t} = \frac{D_{ej,scr}}{r^2} \frac{d}{dr} \left[r^2 \frac{dx_{p,j,scr}}{dr} \right] + \frac{1}{c_{Tm}} \left[\sum_{r=1}^{rxn} \vartheta_{kr} R_{r,scr} \left(T, \theta, x_{pj,scr} \right) \right].$$
(4-13)

The subscripts 'pgm' and 'scr' distinguish the common terms in the equations. The microkinetics and species adsorbed/reacting over platinum is represented by the subscript 'pgm'. The reactions and species over Cu sites is represented by the subscript 'scr'. R_r is net rate of formation of component 'j' in reaction r, ϑ_{jr} is the stoichiometric coefficient of species 'j' in reaction r, C_{Tm} is total molar concentration. There exists two type of diffusion regimes, $D_{ej,scr}$ intra-crystalline diffusivity in the zeolite shell or a zeolite particle and $D_{ej,pgm}$ as Knudsen diffusivity within the alumina core. Due to the 10 nm pore size for the Al₂O₃ core, $D_{ej,pgm}$ represents the Knudsen diffusivity with a temperature dependence of T^{0.5}. $D_{ej,scr}$ is the species j intra-crystalline diffusivity in the pore network of the zeolite particle. The pore size of ZSM-5 is in the range of ~ 0.5 nm and cannot be represented by Knudsen diffusivity. The diffusivity of species within the zeolite will be experimentally determined which has been described in Section 4.2 of the paper.

Finally, the surface species balances include accumulation and net rate of formation of species k :

$$\frac{\partial \theta_k}{\partial t} = \frac{1}{c_{pt}} \left[\sum_{r=1}^{rxn} \vartheta_{kr} R_{r,pgm} (T, \theta, x_{pj,pgm}) \right]$$
(4-14)

and
$$\frac{\partial \theta_k}{\partial t} = \frac{1}{C_{Cu}} \left[\sum_{r=1}^{rxn} \vartheta_{kr} R_{r,scr} (T, \theta, x_{pj,scr}) \right].$$
 (4-15)

In the above equations, $x_{f,j}$ and $x_{p,j}$ 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-particle interface. C_{pt} is the total active site density (mol/m³ catalyst bed) of Pt in the fixed-bed. C_{Cu} is the total active site density (mol/m³ of catalyst bed) of Cu in the fixed bed determined from the NH₃ uptake and TPD experiments.

Boundary and initial conditions are as follows:

$$x_{f,j}(t) = x_{f,j}^{in}(t)$$
 at $z = 0$, (4-16)

$$k_{mej}(x_{f,j} - x_{s,j}) = -D_{ej} \frac{\partial x_{p,j,scr}}{\partial r}\Big|_{x_{p,j,scr} = x_{s,j}} \text{ at } r = R_1,$$
(4-17)

$$-D_{ej,scr} \frac{\partial x_{p,j,scr}}{\partial r}\Big|_{x_{p,j},scr=x_{s,j}} = -D_{ej} \frac{\partial x_{p,j,pgm}}{\partial r}\Big|_{x_{p,j,pgm}=x_{s,j}} \quad \text{at } r = R_2$$
(4-18)

$$x_{p,j,scr}\Big|_{r=R2-} = x_{p,j,Pt}\Big|_{r=R2+}$$
 at $r = R_2$ (4-19)

and
$$\frac{\partial x_{p,j,pgm}}{\partial r} = 0$$
 at $r = 0$. (4-20)

Equation 4-16 represents the Dirichlet inlet boundary condition. Equations 4-17 and 4-20 represent the flux balance at fluid-particle interface and no-flux boundary condition at the center of the particle. Equation 4-18 represents the equation of continuity at core-shell interface. R_1 is the radius of the core-shell catalyst, with R_2 being the radius of the core.

The model comprising of the above equations were discretized in the axial and radial directions. The differential equation MATLAB code 'ODE15s' was used to solve these equations. Typically the time integration was conducted for 2000 s in order to reach steady state. The modeling parameters for the fixed bed reactor modeling is listed in the as Table 8-10.

Parameter	Value		
R1	21.2 μm		
RΩ1	11 μm		
R2	20 µm		
Shell thickness: R1-R2	1.2 μm		
<u></u>	1.22(T/273.15)(m/s)		
εb	0.45		
L	0.3e–2 m		
C _{Tm}	$(12187.3/T) \text{ mol/m}^3$		
C	0.6 mol exposed Pt/(m ³ of		
Cpt	catalyst bed)		
Con	1220 moles of Cu/(m ³ of		

Table 8. Parameters used in the model

Table 9. Diffusivity of gases in fluid phase

		00
$D_{f,NH3}$	$1.2 \times 10^{-5} T^{1.75}$	
D _{f,NO}	$1.2 \text{ x}10^{-9} \text{ T}^{1.75}$	
D _{f,N2O}	$0.8 \text{ x}10^{-9} \text{ T}^{1.75}$	
D _{f,N2}	$1.3 \text{ x}10^{-9} \text{ T}^{1.75}$	
D _{f,NO2}	$0.8 \text{ x}10^{-9} \text{ T}^{1.75}$	
D _{f,O2}	1.1 x10 ⁻⁹ T ^{1.75}	

Knudsen diffusivity within the Al₂O₃ core, here $T^{0.5}$

Table 10. Estimated intracrystalline diffusivity of gases in ZSM	[-5
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T [K]	Estimated intra-crystalline diffusivity [m ² /s]				
	NH3	NO	N2O	NO2	N2
453	8.07E-10	2.1E-10	2.58E-10	1.94E-10	2.83E-10
473	1.32E-09	3.15E-10	2.6E-10	2.55E-10	4.78E-10
503	1.25E-09	7.38E-10	4.8E-10	4.69E-10	9.7E-10
533	2.09E-09	1.12E-09	9.26E-10	5.76E-10	1.45E-09
573	2.41E-09	1.53E-09	1.26E-09	1.23E-09	1.65E-09
623	3.09E-09	1.42E-09	1.17E-09	1.15E-09	1.35E-09
673	3.58E-09	2.25E-09	1.86E-09	1.82E-09	2.33E-09
723	8.6E-09	4.64E-09	3.83E-09	3.75E-09	6.7E-09
773	8.51E-09	4.69E-09	5.29E-09	5.17E-09	6.63E-09

4.3.2 Kinetic models over Pt and Cu

The kinetic model incorporated with reactor model has already been successfully applied in our previous study of NH₃ oxidation kinetics over Pt/Al₂O₃ catalysts from Chapter 3. The model was an extension of previous work done by Rebrov et al., [61,91], Scheibe et al., [60], Kraehnart et al., [58], Scheuer et al., [69] and Shrestha et al., [22]. The study showed the variation of reaction rate as a function of NH₃ concentration for Pt-Al₂O₃ catalysts in presence of excess oxygen. The study also showed the variation of reaction order from positive to negative order with zero order at maximum reaction rate. Detailed modeling studies showed that a dual site kinetic scheme was able to capture the trends of rate, light-off curve and product distribution, revealing a site competition between NH₃ and O₂ in reaction mechanism. In the current study, the model is extended to the case of Silicalite-modified catalyst, P(0.05)-AS. Two different active sites are defined in the micro-kinetic reaction scheme, 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 adsorption/desorption of both NH_3 and O_2 which induces site competition along with other reactions as shown in the scheme. The reaction schemes with along with kinetic parameters are listed in Table 11.

Micro-Kinetics		Seeded core: P(0.05)-AS		Pate expression (Pr)	
		А	Ea (kJ/mole)	Rate expression (RI)	
R-1 R-1b	$NH_3 + b \rightarrow NH_3-b$	59	0	$k_{1f}C_{pt}X_{NH3}\theta_{b}C_{Tm}T$	
	R-1b	$NH_3-b \rightarrow NH_3 + b$	66000	106.60	$k_{1\mathrm{b}}C_{pt} heta_{NH3-\mathrm{b}}$
R-2		$\mathrm{NH_{3}\text{-}b} + 1.5\mathrm{O}\text{-}a \mathrm{N}\text{-}a + 1.5\mathrm{H_{2}O} + 0.5a + b$	3E14	128	$k_2 C_{pt}^2 \theta_{NH3-b} \theta_{O-a}$
R-3 R-3	R-3f	$O_2 + a \rightarrow 2O-a$	65	0	$k_{3f}C_{pt}^{2}X_{O2}\theta_{a}^{2}C_{Tm}T$
	R-3b	2O-a → O_2 +a	7.4E11	125.02	$k_{3b}C_{pt}^{2} heta_{0-a}$
R-4		N-a + O-a → NO-a + a	6E15	131.32	$k_4 C_{pt}^2 heta_{N-\mathrm{a}} heta_{O-\mathrm{a}}$
R-5 -	R-5f	$NO + a \rightarrow NO-a$	290	0	$k_{5f}C_{pt}X_{NO}\theta_aC_{Tm}T$
	R-5b	NO-a \rightarrow NO + a	7E19	150	$k_{5\mathrm{b}}C_{pt} heta_{NO ext{-a}}$
R-6		2N-a → N ₂ + 2a	2E16	110	$k_6 C_{pt}^2 \theta_{N-a}^2$
R-7 R7f	R7f	NO-a + O-a → NO ₂ -a + a	8E13	105.4	$k_{7f}C_{pt}^2 heta_{NO-a} heta_{O-a}$
	R7b	NO ₂ -a + a → NO-a + O-a	9.2E09	77.12	$k_{7b}C_{pt}^2 heta_{NO2-a} heta_a$
R-8		NO-a + N-a → N ₂ O + a	3E19	127.50	$k_{8}C_{pt}^{2} heta_{NO-a} heta_{N-a}$
D O	R-9f	$NO_2 + a \rightarrow NO_2-a$	0	0	$k_{9f}C_{pt}X_{NO2}\theta_aC_{Tm}T$
R-9	R-9b	NO_2 -a $\rightarrow NO_2$ + a	1E13	120	$k_{ m 9b}C_{pt} heta_{NO2- m a}$
R-10 -	R-10f	$NH_3 + a \rightarrow NH_3$ -a	39	0	$k_{10f}C_{pt}X_{NH3}\theta_{a}C_{Tm}T$
	R-10b	NH_3 -a $\rightarrow NH_3$ + a	150000	35	$k_{10b}C_{pt} heta_{NH3-a}$
R·	-11	NH ₃ -a + 1.5O-a → N-a + 1.5H ₂ O + 1.5a	1.1E14	105	$k_{11}C_{pt}^2\theta_{NH3-a}\theta_{O-a}$

Table 11. Reaction scheme and kinetic parameters for P(0.05)-AS, seeded core

The reaction steps over Cu-ZSM-5 involves a series of 8 reaction steps. This reaction scheme has been adopted from the study done by Olsson et al., [88] for Cu-ZSM-5. The reaction scheme involves NH₃ adsorption/ desorption, NH₃ oxidation, NO oxidation, standard SCR, fast SCR and NO₂ SCR reaction steps. The kinetic parameters were estimated through a fit of experimental data for transient NH₃ uptake, TPD, steady state NH₃ oxidation, NO oxidation, Standard SCR and Fast SCR. The details of the parameter estimation for the individual reaction steps will be described later in the results

and discussion section. The final set of estimated kinetic parameters is provided in Table 12.

Reaction		Cu-ZSM-5		Determine (Dr)
		А	Ea (kJ/mole)	Kate expression (Kr)
R1	$NH_3 + S \rightarrow NH_3-S$	53	0	$k_{1f}C_{Cu}X_{NH3}\theta_{S}$
R2	$NH_3-S \rightarrow NH_3 + S$	8E+12	$143.5*(1-0.93*\theta_{NH3-S})$	$k_{1b}C_{Cu} heta_{NH3-S}$
R3	$2\mathrm{NH_3-S} + 1.5\mathrm{O2} \xrightarrow{} \mathrm{N_2} + 3\mathrm{H_2O} + 2\mathrm{S}$	4E+12	170	$k_2 X_{02} C_{Cu} \theta_{NH3-S}$
R4	$NO + 0.5O_2 \rightarrow NO_2$	5E+04	39	$k_{3f}X_{02}^{1/2}X_{NO}$ - $k_{3b}X_{NO2}$
R5	$4\mathrm{NH_3-S} + 4\mathrm{NO} + \mathrm{O_2} \xrightarrow{} 4\mathrm{N_2} + 6\mathrm{H_2O} + 4\mathrm{S}$	2E+11	67	$k_4 C_{Cu} X_{NO} \theta_{NH3-S}$
R6	$2NH_3-S + NO + NO_2 \rightarrow 2N_2 + 3H_2O + 2S$	8.5E+15	62	$k_5 C_{Cu} X_{NO} X_{NO2} \theta_{NH3-S}$
R7	$4\mathrm{NH_3-S} + 3\mathrm{NO_2} \xrightarrow{} 3.5\mathrm{N_2} + 6\mathrm{H_2O} + 4\mathrm{S}$	2E+09	120	$k_6 C_{Cu} X_{NO2} \theta_{NH3-S}$
R8	$2NH_3-S+2NO_2 \rightarrow N_2+N_2O+3H_2O+2S$	3.7E+03	59	$k_7 C_{Cu} X_{NO2} \theta_{NH3-S}$

Table 12. Reaction scheme and kinetic parameters for Cu/ZSM-5

4.4. Results and Discussions

4.4.1 Steady state ammonia oxidation and reaction – rate measurements

The synthesized seeded core, P(0.05)-AS was evaluated in a quartz tubular fixed bed reactor. The bed contained 0.018 g of the catalyst with a particle size of 40 -50 microns. The gas feed containing 500 ppm of NH₃, 10 vol % O₂, balance Argon was delivered at 1000 sccm. The Pt weight percent in the Alumina is 0.05 wt %. Figure 28(a) shows the steady state ammonia oxidation profile versus catalyst bed temperature for the catalyst sample. The light-off for NH₃ oxidation occurs at 210°C and reaches 100 % conversion by 225°C. This is consistent with our previous study from Chapter 3 at same reaction conditions. The maximum N₂ yield is 77% achieved at 225°C, and then it drops down with increase in reaction temperature. The maximum N₂O yield is 20% at 250°C, and the maximum NO yield at 500°C is approximately 78%. The maximum NO₂ yield at 500°C reaches a maximum of ~ 20 % for the P(0.05)-AS.



Figure 28. Steady state NH₃ oxidation over (a) Fixed bed: P(0.05)-AS, TOF of NH₃ oxidation for P(0.05)-AS at (b) 1000 sccm, (c) Reaction order (n) with respect to NH₃ concentration at 1000 sccm (d) Apparent activation energy (E_a) of NH₃ oxidation over P(0.05)-AS, 100 ppm of NH₃. [symbols: experiment, solid lines: simulation]

The steady state NH₃ oxidation was complemented with a measurement of steady state NH₃ oxidation rate kinetics over P(0.05)-AS with same quantity of catalyst in the fixed bed reactor. The rate was measured over a wide range of NH₃ concentrations (10 – 25000 ppm) in an excess of O₂ (10 vol. %) O₂ with balance Argon at a flow rate of 1000 sccm. The reaction rate was measured at three different temperatures: 160, 170 and 180°C.

The turnover frequency (TOF, 1/s) was determined by dividing the measured rate (mol NH_3 consumed/g cat s) by the exposed Pt loading (mol Pt/g cat) using the measured Pt dispersion (42%) and loading (0.05 wt.%). The seeded core, P(0.05)-AS catalyst has a lower light off, compared to 305°C for P(0.05)-A tested at same reaction conditions. A detailed comparison of this has been provided in the Appendix (section A10).

Figure 28(b) shows the steady reaction rate as a function of NH₃ feed concentration (ppm) measured at a flow rate of 1000 sccm. The data indicates that the TOF is a nonmonotonic function of the NH₃ concentration. The TOF increases with NH₃ concentration, reaching a maximum at ~ 10000 ppm NH₃, beyond which the rate starts to drop. The TOF reaches a maximum ~ $1s^{-1}$, $2s^{-1}$ and $4s^{-1}$ at 160, 170 and 180°C respectively. The rates almost double with delta T increments of 10°C. To the left of the maximum the rate is positive-order in NH₃ while to the right the rate is negative-order in NH₃ due to self-inhibition. The reaction order with respect to NH₃ molar concentration (C_{NH3}) is indicated in ln(TOF) vs ln(C_{NH3}) plots as shown in Figure 28(c). The order is ~ 0.3 at low range of NH₃ concentration from 100 ppm to 700 ppm, increases to ~1.3 for 900 – 6000 ppm, and decreases to zero at 10000 ppm. Beyond the maximum the order becomes more strongly negative, decreasing to a value of ~ - 1.3. The apparent activation energy (E_a) was estimated at 100 ppm, giving a value of 114 kJ/mol as shown in Fig. 28(d).

The non-monotonic behavior with varying reaction order as a function of NH₃ concentration and the self-inhibition effect is consistent in with the work done previously [18] over Pt/Alumina catalysts. The seeded core, P(0.05)-AS performs more like milled

 Pt/Al_2O_3 samples studied in the previous work in Chapter 3. Both the milled Pt/Al_2O_3 samples and P(0.05)-AS have similar light off, with P(0.05)-AS being slightly more active. The trends and magnitude of the TOF are similar as well. A comparison between milled P(0.05)-A and P(0.05)-AS has been provided in the Appendix (section A11). The kinetic model developed earlier, has been applied to model the seeded core, P(0.05)-AS for the purpose of this study.

A fixed bed reactor model was used to estimate the kinetic parameters by fitting the steady state ammonia oxidation data in Figure 28(a). The pre-exponential factor and Activation energies were varied to fit the simulation results with experimental data. The kinetic parameters reported for milled Pt/Al_2O_3 catalysts in our previous study in Chapter 3, was used as initial values. Modifying the kinetic parameters for reaction steps, R2 and R11 were sufficient to fit the simulation to light-off/product distribution of Ammonia oxidation over seeded core, P(0.05)-AS. The estimated kinetic parameters are shown in Table 2. The solid lines in Figure 28(a) represents the simulated data. This model is able to predict light off characteristics of ammonia oxidation with the subtle trend in appearance of products and maximum yields.

The validation of the estimated kinetic parameters was done by comparing the experimentally obtained kinetic data over P(0.05)-AS with model prediction represented as solid lines in Figure 28(b). The kinetic parameters estimated were kept fixed for the purpose of model validation. We can see the model is able to predict the non-monotonic trend of reaction rate (TOF) for all the three temperatures, 160, 170 and 180°C. The model

is also successful in predicting the C_{NH3max} as 10000 ppm or the concentration of ammonia where maximum rate (TOF) takes place.

Now that we have estimated kinetic parameters of seeded core, P(0.05)-AS we move ahead to model the steady state ammonia oxidation for the CS catalyst. We take a sequential approach to determine the SCR kinetics taking place in the shell of Cu-ZSM-5. But before we can move ahead with the determination of SCR kinetics, we need to determine of diffusivity of gases in the zeolite shell. The effect of diffusional resistance is quite prominent. The added diffusional resistance, although has a detrimental impact on NH₃ light off, but it also leads to the improvement of N₂ selectivity in presence of Cu in the ZSM-5 shell providing SCR activity. Hence, it quite important that we know the diffusivity of gases within the zeolite shell. In the next section we describe a method that encompasses the tandem use of experiment and modeling to determine intra-crystalline diffusivities of the following gases: NH₃, N₂, NO, NO₂, N₂O.

4.4.2 Estimation of Diffusivity through ZSM-5 shell

The diffusivity of reacting species through the porous layers is an important factor that impacts activity and selectivity of the catalyst. Work done by Votsmeier et al., [92], Metkar et al., [23] showed diffusion limitations in washcoat can significantly decrease the NH₃ conversion. Shrestha et al., [22] reported a monotonic decrease in NH₃ conversion with increased thickness in top Cu-SSZ-13 layer, attributed to the diffusional barrier of the top layer. Dhillon et al., [72] further showed by optimizing the washcoat architecture, of having a mixed bottom layer and a thin SCR layer on the top can be effective in increasing NH₃ activity in form of decreased diffusional limitation. The studies were done over dual layer ammonia slip catalyst, with bottom PGM layer and top SCR layer being washcoated over the monolith surface. The SCR layer washcoated onto surface of monolith is not a dense zeolite layer, hence this diffusional resistance can be modeled by using the concept of effective diffusivity due to the presence of macropores within the washcoat. However in the present case of core-shell catalyst, the shell is a dense zeolite layer hence a much robust approach must be taken to determine the diffusivity of these gases in the intracrystalline pores of zeolite. Nevertheless, the work done over dual layer ammonia slip catalysts show the importance of diffusivity and the effect it can have on activity and selectivity.

The dense zeolite shell around the core of Pt/Al₂O₃ belongs to a class of ZSM-5 framework. The ZSM-5 crystallites in the shell layer have an anisotropic pore system with zig-zag and straight intracrystalline pores. ZSM-5 has a pore size of around 0.53 nm. Due to the narrow pore size, the diffusion in the intracrystalline pores of ZSM-5 shell falls into a different regime of configurational diffusion [93]. This is an activated process with energy of activation arising from the steric hindrance. In order to accurately account for the diffusivity of reacting species in the dense zeolite shell of core-shell catalyst we carried out an experiment with the core-shell catalyst comprising of an active Pt/Al₂O₃ core and inert Na-ZSM-5 shell. The Si/Al ratio of ZSM-5 as measured from XPS/EDX was 30. The activity of ZSM-5 shell was suppressed by ion-exchanging it with Na+ ions. The thickness of the shell from SEM images was found to 1.2 microns. The Pt loading within the core for both the catalyst samples was fixed at 0.05 wt % of Pt. The NH₃ oxidation activity of seeded

core (P(0.05)-AS) and Pt(0.05)/Al₂O₃@Na-ZSM-5(CS-Na) was examined to determine the effect of the dense zeolite layer over the core. The dense Na-ZSM-5 shell serves as a diffusional barrier which would enable the estimation of diffusivity of reacting species within the zeolite pores by integrating mathematical model to simulate the experimental data.



Figure 29. Steady state NH₃ oxidation with comparison of conversion and product yields between P(0.05)-AS and CS-Na in fixed bed reactor (a) NH₃ conversion (b) N₂ yield (c) NO yield (d) N₂O yield (e) NO₂ yield. [symbols: experiment, solid lines: simulation]

The catalysts were evaluated in a quartz tubular fixed bed reactor. The bed containing 0.18 g of the catalyst was evaluated in a gas feed containing 500 ppm NH₃, 10 vol % O₂ and balance Argon delivered at a flow-rate of 1000 sccm. Figure 29(a) shows the comparison of light-off curves for P(0.05)-AS and CS-Na catalysts. The light off temperatures of both the catalysts are as follows: 210°C for P(0.07)-AS and 240°C for CS-Na. The difference in conversion becomes quite apparent as we increase the temperature.

In this regime, the diffusivity of gases within the zeolite shell starts playing an important role. The increasing light-off temperature clearly shows the impact of added diffusional resistance in form of a dense ZSM-5 zeolite shell. Similar trends were also observed in the product distribution while comparing them with the Seeded core catalyst. The N₂ generation peak shifts by 50°C for the CS-Na catalyst. There is a drop in maximum yield from 75 % for P(0.07)-AS to 60% for CS-Na catalyst as show in Figure 29(b). This trend is also visible for NO, N₂O and NO₂ generation as shown in Figures 29 (c-e). The increase in light-off temperature, shift in product generation peaks can now be used to extract diffusivity of these gases in ZSM-5 shell.



Figure 30. Estimated gas diffusivities with activation energy for (a) NH_3 (b) N_2 (c) NO (d) N_2O (e) NO_2

The diffusivity estimation was carried out as follows. First steady state NH₃ oxidation data for seeded core (P(0.05)-AS) operating at 1000 sccm was fitted using the reactor model. The microkinetic parameters estimated earlier were used to model this data. Now keeping the microkinetic scheme and parameters to be constant, we moved ahead to model the steady state ammonia oxidation data for the CS-Na catalyst with equivalent Pt loading of 0.07 wt % and has 1.2 micron thick Na-ZSM-5 shell. Using the reactor model described in previous section for the core-shell particles, with shell here being inert adding only to the diffusional resistance. The effect of intra-crystalline diffusivity of gases in ZSM-5 shell was captured in $D_{ej,scr}$ term as,

$$Na - ZSM - 5 \ shell: \ \frac{\mathrm{d}x_{pj,scr}}{\mathrm{d}t} = \frac{D_{ej,scr}}{r^2} \frac{\mathrm{d}}{\mathrm{d}r} \left(r^2 \frac{\mathrm{d}x_{pj,scr}}{\mathrm{d}r} \right), \tag{4-20}$$

where $D_{ej,scr}$ is the diffusivity of species 'j' in the zeolite shell. This particle level species mass balance equation does not have any reaction term due to the inertness of Na-ZSM-5 shell towards ammonia oxidation. The initial guess for $D_{ej,scr}$ was taken as the Knudsen diffusivity for the gases. The Diffusivity parameter ($D_{ej,scr}$) was varied at temperatures which had experimental data point to fit the simulation data keeping the kinetic parameters constant. This was done for all the gases at different temperatures. The result of this process is shown in Figure 30. Figure 30 shows the diffusivity parameter estimated for NH₃, NO, NO₂, N₂ and N₂O estimated at temperatures which had experimentally obtained data point in form of Ln D vs 1/T plots. Due to the configurational diffusivity of gases in zeolites, these plots also indicate the diffusivity are an activated process. The individual activation energy of these gases are show in Figures 30 (a – e). The diffusivity as estimated by this method of combining experimental data with tandem modeling are in the range of 10^{-10} to 10^{-9} m²/s with increasing temperature. The activation energy in the range of 20-30 kJ/moles. Table 10 provides the values of the estimated diffusivities of NH₃, NO, NO₂, N₂O and N₂. The diffusivity values of these gases will be used later in the modeling of the core-shell catalyst as an ammonia slip catalyst.

In the next few sections, we use a sequential approach to determine the SCR kinetics taking place in the Cu-ZSM-5 shell of CS catalyst. This approach has been previous applied by Pritpal et al [90], Olsson et al., [88] and Metkar et al., [23].

4.4.3 NH₃ temperature programmed desorption (NH₃-TPD)

The NH₃ TPD experiment was done for 0.18 g of Cu-ZSM-5 powder catalyst in a fixed bed reactor. Using EDX, the Cu weight percent was determined to be 3 wt %. The catalyst was exposed to 355 ppm of NH₃ and balance Argon at 1000 sccm for 95 minutes followed by Argon only flow with a temperature ramp of 10°C/min. Detailed procedure is described in the experimental section. Figure 31 shows the NH₃ TPD profile for the Cu-ZSM-5 catalyst in a fixed bed reactor. There is total uptake of ammonia until 1300 seconds after which ammonia concentration starts to increase until it reaches a complete saturation at 2500 seconds. Thereafter there is no uptake of ammonia. The outlet concentration of ammonia stays constant at 355 ppm until 6000 seconds after which ammonia was turned off and it drops down. Following the protocol as described in experimental section, the temperature ramp was started 10 minutes after NH₃ was turned off. Within the 10 minute period, there was a steady state flow of Argon at 1000 second.

physiosorbed ammonia. The temperature ramp of 10°C/min was applied from 6600 seconds. We can see with the rise in temperature, NH₃ starts to desorb with a single peak. At 315°C, ammonia desorption reaches a peak of 215 ppm after which it fall down as shown in the Figure. The single peak profile shown in the NH₃ TPD profile shows there is a single site for NH₃ adsorption/desorption taking place. Hence for modeling a single site adsorption model sufficient.



Figure 31. Transient NH₃ adsorption and temperature programmed desorption as a function of time in seconds. Experimental data (markers) and model predictions (lines) for Cu-ZSM-5 powder sample in fixed bed reactor with 0.12 g of catalyst.

The kinetic parameters for reactions steps R1 and R2 were estimated by simulating the experimental data shown in Figure 31. The NH₃ adsorption was considered to be nonactivated over the site which is consistent with previous studies [23,88]. The desorption activation energies as determined by fitting the data was found to be, $143.5*(1-0.93*\theta_{NH3}$ s) kJ/moles. This coverage dependent Tempkin type of adsorption has been reported in several literatures [23,88,94]. The site 'S' here is used to represent the adsorption and desorption sites, with coverage of θ_{NH3-S} indicating NH₃ adsorbed on site S. The estimated kinetic parameters are shown in Table 3. The number of sites was fitted which resulted in 1210 moles/m^3 of catalyst bed. The solid line in Figure 31 shows the simulated results which is able to capture the uptake profile and desorption profile. The subtle features at the saturation and desorption peak are captured well by the simulation.



4.4.4 NH₃ oxidation over Cu-ZSM-5

Figure 32. Steady state ammonia oxidation over 0.12 g of Cu-ZSM-5 powder sample in fixed bed reactor. Feed conditions: 500 ppm NH₃, 10 % O₂, Balance Argon for a total flow rate of 1000 sccm. [symbols – experiments, lines – model]

Steady state ammonia oxidation experiments were carried out over 0.12 g of Cu-ZSM-5 powder catalyst in fixed bed reactor. The gas feed containing 500 ppm of NH₃, 10 vol % O2 and balance Argon delivered at a flow-rate of 1000 sccm. Figure 32 shows the steady state ammonia oxidation conversion versus catalyst bed temperature. We observe that the light-off, defined as the temperature at 50 % conversion (T_{50}) occurs at 365°C. A complete conversion of ammonia or a 100 % conversion is reached at 500°C. The light off temperatures, T_{50} for P(0.05)-A is 300°C and T_{50} for seeded core, P(0.05)-AS is 210°C indicating a very high activity towards ammonia oxidation. The comparison of light-off curves is provided in the Appendix (section A10). On the other hand, high light off temperature for Cu-ZSM-5 indicates that the catalyst is not active for ammonia oxidation. Experimental data of ammonia oxidation over Cu-ZSM-5 was used to estimate the kinetic parameters for the step R3, by including the already determined kinetic parameters of reaction steps R1 and R2 from ammonia storage experiments. Figure 32 compares the experimentally obtained ammonia conversion with that of the model predictions. The rate parameters obtained for the reaction steps, R1, R2 and R3 from ammonia TPD and ammonia oxidation experiments were kept constant for subsequent parameter estimation for SCR reactions.

4.4.5 NO oxidation



Figure 33. Steady state NO oxidation over 0.12 g of Cu-ZSM-5 powder sample in fixed bed reactor. Feed conditions: 500 ppm NO, 10 % O₂, Balance Argon for a total flow rate of 1000 sccm. [symbols – experiments, lines – model]

A steady state NO oxidation was carried out over 0.12 g of Cu-ZSM-5 catalyst in fixed bed reactor. The gas feed containing 500 ppm of NO, 10 vol % O₂, balance Argon was delivered at 1000 sccm. NO oxidation is a reversible reaction which is kinetically

limited at low temperatures and equilibrium limited at higher temperatures. The NO₂ production increases and reaches a maximum at 400°C after which it starts to decrease due to thermodynamic constraints as shown in Figure 33. The model of NO oxidation was fitted to the experimental and results are shown as solid lines in Figure 33. The kinetic parameters for reaction R4 were estimated from the model fitting with reverse reaction rate constant for R4 was calculated using equilibrium constant to ensure thermodynamic consistency.

4.4.6 Standard SCR



Figure 34. Steady state NO conversion function of temperature for 0.12 g of Cu-ZSM-5 powder sample in fixed bed reactor. Feed conditions: 500 ppm NH₃, 500 ppm NO, 10 % O₂, balance Ar at 1000 sccm. [symbols – experiments, lines – model]

Steady state SCR experiments were conducted for a feed containing 500 ppm of NH₃ and NO, 10 vol % O₂, balance Argon delivered at a space velocity of 1000 sccm. Figure 34 shows the steady state NO conversion profile versus catalyst bed temperature. The Cu-ZSM-5 catalyst is highly active catalyst, with catalyst achieving 100 % conversion at 300°C. But upon increasing the temperature, to be specific at T > 400°C, the NO conversion starts to drop reaching 77 % at 500°C. This drop NO conversion is due to the
ammonia oxidation side reaction. This trend is quite specific to Cu based catalysts as reported by Metkar et al., [23] and Olsson et al., [88]. Similar work done on Fe-ZSM-5 catalysts done by Metkar et al., [23] showed that Fe based catalysts are less active but on higher temperatures there is no dip in NO conversion. This is because Fe based catalysts have lower reactivity towards ammonia oxidation compared to Cu based zeolite catalysts.

The kinetic parameter estimation for standard SCR reaction was carried out as follows. The reaction steps, R1 – R4, along with standard SCR reaction step R5 was added to the mechanistic sequence to simulate the experimentally obtained data. The parameters for reaction steps, R1-R4 obtained from NH₃ uptake + TPD, NH₃ oxidation and NO oxidation were kept fixed. The reaction step, R5 was estimated by using the experimental data in Figure 34. The figure compares the experimental and model predicted NO conversion during the standard SCR over Cu-ZSM-5 catalyst. The model is able to capture the experimental trends over the entire temperature range.

4.4.7 Fast SCR

Fast SCR is another set of important reaction that takes place in presence of NO₂ along with NH₃, NO and O₂. In presence of NO₂, the rate of NOx reduction is greatly enhanced. The steady state Fast SCR reaction was carried out in equimolar mixture of NO and NO₂. This ratio of NO to NO₂ was chosen as this resulted in maximum efficiency for NOx reduction with highest selectivity for N₂ during NH₃ SCR shown by different studies [88,94–96]. The reaction was carried out over 0.12 g of Cu-ZSM-5 catalyst in fixed bed reactor. The gas feed containing 500 ppm of NH₃, 250 ppm of NO and NO₂, 10 vol % O₂, balance Argon was delivered at 1000 sccm. Figure 35(a) shows the N₂ generation measured

at steady state conditions. Figure 35(b) shows the concentration profile for NH_3 , NO, NO_2 and N_2O measured at steady state condition. This figure clearly show the higher activity of NOx reduction as compared to Standard SCR reaction with more than 90 % conversion at the entire temperature range. The major product from fast SCR reaction as shown in figure is N_2 with negligible formation of N_2O for the entire operating range.



Figure 35. Steady state concentration of species obtained during Fast SCR reaction as function of temperature carried out on 0.12 g of Cu-ZSM-5 powder sample in fixed bed reactor. Feed conditions: 500 ppm NH₃, 250 ppm NO, 250 ppm NO₂, 10 % O₂, balance Ar at 1000 sccm. [symbols – experiments, lines – model]

The kinetic parameters estimation for fast SCR was carried out as follows. The reaction steps R1 - R8 were used to simulate the data. The parameters obtained from earlier analysis for reactions R1 - R5 were kept fixed. The fast SCR step is represented by reaction step R6. Additional reaction steps, R7 and R8 were also taken into the reaction scheme. This group of reaction steps also known as NO₂ SCR was added to reaction scheme as work done by Olsson et al., [88] and Metkar et al. [23] who detected the formation of ammonium nitrates and N₂O at temperatures below 400°C. However this effect was lower

in the Cu based zeolite samples. The kinetic parameters for reaction steps, R6 - R8 were estimated using the experimental data in Figure 35. This figure shows upon estimating the parameters, the model is able to predict the high N₂ formation, high NOx reduction and low N₂O formation for the entire temperature range.

The experiments described above along with simulation were used to estimate the kinetic parameters for NH_3 oxidation, NH_3 SCR (Standard + Fast). The activation energy of 170 kJ/moles estimated for ammonia oxidation is comparable to the results reported in the literature. Kusaka et al., [97] reported an activation energy of 168.6 kJ/mole from a kinetic study done over powder Cu-ZSM-5 catalyst. Work done by Chatterjee et al., [9] also reported an activation energy of 168 kJ/moles. Olsson et al., [88], from his experimental and modeling work estimated the activation energy to be 162 kJ/moles. The estimated activation energy of 67 kJ/moles for standard SCR reaction is a bit lower than reported in literature. Olsson et al., [88] estimated the activation energy to be 85 kJ/moles while Kusaka et al., [97] measured it to be 75 kJ/moles from his kinetic experiments. For the case of fast SCR, the estimated activation energy of 62 kJ/moles was 23 kJ/moles lower than reported by Olsson et al., [19]. The parameters estimated from the above analysis are listed in the Table 12. These kinetic parameters were used to simulate the ammonia oxidation over core-shell catalysts, with core of Pt/Alumina and a shell of Cu-ZSM-5 with SCR activity.

4.4.8 Steady state ammonia oxidation over Pt/Al₂O₃@Cu-ZSM-5

The above described SCR model is combined with a model of seeded Pt/Al_2O_3 catalyzed NH_3 oxidation. The microkinetic modeling of the Pt catalyzed NH_3 oxidation has already been validated in the section 4.1 The model did a good job in predicting the light-off and product distribution for NH_3 oxidation of P(0.05)-AS samples show in Figure 36(a).



Figure 36. Steady state (a) NH₃ conversion (b) N₂ selectivity as a function of temperature carried out over P(0.05)-AS, CS-0.5 & CS-1.2. 0.18 g of catalyst was used in fixed bed reactor. Feed: NH₃, 10 % O₂, balance Ar at 1000 sccm [symbols: experiment, solid lines: simulation]

Next, the model is validated in simulation of CS with different thickness of ZSM-5 shell around the seeded core, P(0.05)-AS. The synthesized core-shell (CS) catalysts was evaluated in a quartz tubular fixed-bed reactor. The bed contained 0.18 g of CS catalyst with a particle size ranging from 40 to 50 μ m (mesh size 325). The gas feed containing 500 ppm NH₃, 10 vol% O₂, and balance Ar was delivered at a flowrate of 1000 sccm. The bed contained 0.18 g of CS catalyst, with Pt loading of 0.05 wt % in the Alumina core and Cu loading of ~ 3 wt % in the ZSM-5 shell. Two CS samples namely, CS-1.2 with a shell thickness of 1.2 microns and CS-0.5 with a shell thickness of 0.5 microns were considered for model validation. In the modeling of CS catalyst, two reaction schemes were considered catering to the NH₃ oxidation(Table 2) reactions taking place over Pt in core and the SCR reactions(Table 3) over Cu in the zeolite shell. Figure 36(a) compares the steady state ammonia conversion experimental(symbols) and predicted(solid lines) results for CS-1.2, CS-0.5 and P(0.05)-AS samples. Without adjusting the estimated kinetic parameters, the reactor model along with kinetics were applied. The model does a good job in predicting the light-off temperatures of both CS-1.2 and CS-0.5 samples. Figure 36(a) shows a significant decrease in NH₃ conversion in the presence of dense ZSM-5 shell. The lightoffs (T₅₀) were observed at 210, 235, 250°C for P(0.05)-AS, CS-0.5 and CS-1.2 respectively. Due to the thicker shell of 1.2 microns around seeded core, P(0.05)-AS, the light off temperature is higher as compared to P(0.05)-AS by 40°C. But for a CS-0.5 sample with 0.5 micron thick ZSM-5 shell, the light off temperature increases by 25°C as compared to CS-1.2. There is a direct proportionality in the diffusion resistance to the thickness of the shell in turn affects the light-off, which the model is able to predict. The importance of the shell thickness can also be studied by comparing the diffusion and reaction time scales. An analysis has been shown in the Appendix (section A12) which shows for temperature as low as 190°C, the conversion becomes diffusion limited process. The analysis shows the change in NH_3 activity and N_2 selectivity if diffusivity within the zeolite shell were changed to Knudsen regime, showcasing the importance of a diffusion limited process required for a good N₂ selectivity. The model also predicts the differences in N_2 selectivity for the three samples as shown in Figure 36(b). The decrease in N_2 selectivity is steeper for the CS-0.5 sample; i.e., from 100% to a limiting value of 70% for CS-0.5 compared to 90% for CS-1.2 sample. Thus, the thicker shell is beneficial in improving the N_2 selectivity at higher temperature where the NH₃ conversion is 100%. The thicker Cu-ZSM-5 shell provides a longer diffusion length enabling additional Cu sites for SCR to occur, resulting in a higher N_2 selectivity. The decrease in N_2 selectivity of P(0.05)-AS is even steeper, dropping down from 100% to 0 % at 500°C. This is due to the increased production of NOx. The model did a good job in predicting the N_2 selectivity for all the three samples. All these results further validates the kinetics obtained for Cu-ZSM-5 and seeded core, P(0.05)-AS.

4.4.9 Optimizing Pt loading and shell thickness for CS catalyst – Using the model



Figure 37. Model predictions for steady state (a) NH₃ conversion at $T = 250^{\circ}C$ (b) N₂ selectivity at $T = 500^{\circ}C$ as a function varying shell thickness & Pt loading for core-shell catalysts . Feed: NH₃, 10 % O₂, balance Ar to give 1000 sccm.

The model can further be utilized to optimize the best combination of Pt loading and shell thickness. Figure 37 shows the model predicted NH_3 conversion at 250°C and N_2 selectivity at 500°C as function of shell thickness. The model is simulated for 500 ppm NH_3 , 10 vol % O₂, balance Argon at 1000 sccm. CS-0.5 and CS-1.2 samples are represented

as symbols in the figure. At the origin of the horizontal axis, if represented as a physical catalyst would be seeded core, P(0.05)-AS with no shell. Moving along the horizontal axis, represents the shell thickness around the seeded core, P(x)-AS or a core-shell catalyst. The Pt loading is denoted by 'x'. The model predicts that with decrease in shell thickness, ammonia conversion increases with drop in N_2 selectivity for a fixed loading of Pt in shell. However it also predicts that on lowering the Pt loading, here from 0.05 wt % to 0.02 wt %, the N₂ selectivity at 500°C increases for a given shell thickness with a slight drop in NH₃ conversion. For example, looking for a shell thickness of 1 micron, the NH₃ conversion drops from 70 % to 65 % but N_2 selectivity at 500°C increases from 89 % to 93 % as we decrease the Pt loading from 0.05 to 0.02 wt %. Another trend that can be seen is for a shell thickness of 1 micron with a Pt loading 0.02 wt % has lower light-off with better N₂ selectivity when compared with CS-1.2 sample with 1.2 micron thick shell and a Pt loading of 0.05 wt %. The N₂ selectivity is 93 % compared to 91 % for CS-1.2. The change in N_2 selectivity is not as prominent when compared to the improvement in the NH_3 conversion. The NH₃ conversion jumps from 50 % at 250°C for CS-1.2 to 65 % for coreshell catalyst with 1 micron shell and 0.02 wt % Pt. The above trend clearly shows the presence of an optimized point where we can further lower Pt loading along with shell thickness without any detrimental impact in NH₃ conversion at lower temperature regime and N₂ selectivity at high temperature. We considered a threshold limit of 90 % N₂ selectivity for the purpose of selecting the optimized parameters. We can see that, for a shell thickness of 0.83 microns with a Pt loading of 0.02 wt % has better performance characteristics. There is no impact in N₂ selectivity. The major improvements can be seen

in NH₃ conversion. The NH₃ conversion at 250°C increases from 50 % to 73 % for the newly optimized CS sample. This is done without addition of any Pt, but by lowering it from 0.05 wt % to 0.02 wt % which further ascertains the advantages of this core-shell structure along with NH₃ oxidation enhancement due to the seeding process.

4.5. Conclusions

In summary, we were able model the NH₃ oxidation carried out over the core-shell, Pt/Al₂O₃@Cu-ZSM-5 catalyst. The reaction parameters were estimated by decoupling the contributions of the seeded core and Cu-ZSM-5 SCR shell. Using kinetic measurements over the seeded core, we were able to show the variation of reaction rate as a function of NH₃ concentration for Pt-Al₂O₃ catalysts in presence of excess oxygen as found in our earlier work [18]. The kinetic parameters for NH_3 oxidation over seeded core were determined by fitting light-off curve and then validated with the kinetic experiments. We also considered the effects of intra-crystalline diffusivity in the zeolite crystals in the SCR shell. We applied the core-shell geometry, with an active PGM core and inert zeolite shell to experimentally determine the diffusivities of gases in the zeolite. This was done by fitting the diffusivity parameter for each gas at a particular temperature to the experimental data of steady-state NH₃ oxidation over the core-shell, Pt/Al₂O₃@Na-ZSM-5 sample, while keeping the kinetic parameters of the core constant. Using the measured diffusivities, the parameters over the Cu-ZSM-5 SCR catalyst were estimated following a sequential approach of fitting the transient NH₃ TPD, steady-state NH₃ oxidation, NO oxidation, standard SCR, fast and NO₂ SCR. The estimated SCR parameters combined with NH₃ oxidation kinetic parameters were combined to finally simulate the steady-state NH₃ oxidation over Pt/Al2O3@Cu-ZSM-5 with great degree of accuracy. Using the model, we were able to further optimize the core-shell catalyst by reduction of Pt loading in the core by more than 50 % and for an optimal shell thickness, we were able to improve the NH_3 oxidation light-off without effecting the N_2 selectivity.

Chapter 5: Conclusions and future work

5.1 Conclusions

The state-of-the-art ASC for selective oxidation of NH_3 is the dual layer washcoated catalyst with bottom Pt/Al_2O_3 and top Cu-SSZ-13 layer. The bottom PGM layer oxidize NH_3 to NO/NO_2 at high temperature while top Cu layer selectively reduce NO/NO_2 to N_2 by counter-diffusing NH_3 . Even though the commercial dual layer ASC does a good job in N_2 selectivity there still exists a lot of challenges. This dissertation study focused on improving the performance characteristic and meeting the challenges of the ammonia slip catalyst (ASC) specifically related to NH_3 oxidation activity, N_2 selectivity and lowering the loading of active catalysts.

In the first part of the study, we developed a core-shell Pt/Al₂O₃@Cu-ZSM-5 shell with the idea of emulating the dual-layer architecture down to the micro-scale level. The core is a Pt/Al₂O₃ catalyst which oxidizes NH₃ and the shell is the Cu-ZSM-5 shell which reduces the NOx to N₂ using SCR chemistry. The synthesis route involved in-situ silicalite-1 seeding of the Pt/Al₂O₃ core with subsequent 2 stages of hydrothermal growth for the complete coverage of the Cu-ZSM-5 shell. The core-shell catalyst showed better performance with respect to N₂ selectivity and had a lower light-off when compared to a physical mixture of Pt/Al₂O₃ and Cu/ZSM-5. The higher activity of the seeded core was preserved after washcoating it as the base for the dual-layer ASC, showing trends similar to dual-layer ASC with thrice the Pt loading, thus increasing NH₃ conversion without having any impact on N2 selectivity. This enhancement in the activity has been attributed to the zeolite synthesis process which lead to suppression and destabilization of Pt oxides

that ultimately increase the activity of the CS catalysts. With the novel approach of mimicking dual-layer ASC at a single particle level, the requisite loading of expensive metals as active materials can be significantly reduced while maintaining good N_2 selectivity for the entire operating range without any detrimental impact on NH₃ oxidation light-off. This study met the earlier objectives set of improving the low temperature NH₃ oxidation activity with low Pt loading while keeping > 90 % N₂ selectivity.

Next, we studied the NH₃ oxidation kinetics over Pt/Al₂O₃ catalysts. The objective of this study was to bridge the gap between experimental rate-measurements done on single Pt crystallites at low pressure contrary to the real world applications where reactions take place on Pt-supported catalysts with various defects and different crystallites at atmospheric pressure. We were able to show the non-monotonic reaction rate as a function of NH₃ concentration for Pt/Al₂O₃ catalysts in presence of excess oxygen. We also showed the variation in reaction order with respect to NH_3 from positive to negative order with zero order reaction at maximum reaction rate. The combined model 'AA + BA' which considered NH₃ adsorption and reaction on both Pt sites was accurate in predicting the variations in TOF and Light-off curves. It was also shown that due to the variation in rate order from positive to negative, there exists a site competition between NH_3 and O_2 . Using the model we were explain the impact of site-competition using reactant species coverages. The maximum NH₃ rate takes place at 50 % NH₃ coverage at site 'a'. It was also shown that ball-milling of Pt-Alumina leads to increase in activity was due to crystalline transformation towards more active stepped planes from XRD studies and destabilization of Pt oxides exposing more active metallic Pt for reactions to take place shown using H₂-TPR experiments.

Finally after understanding the kinetics of NH₃ oxidation over Pt/Al₂O₃ we moved ahead with the modeling and optimization of the core-shell Pt/Al₂O₃@Cu-ZSM-5 catalyst. The reaction parameters were estimated by decoupling the contributions of the seeded core and Cu-ZSM-5 SCR shell. The NH₃ oxidation contribution from the seeded core was mathematically modeled along with rate-kinetic measurements using the microkinetic scheme developed in Chapter 3. We also developed a kinetic and transport model which considered the intra-crystalline diffusivities of gases for zeolites for the SCR reactions taking place over the Cu-ZSM-5 catalyst. The diffusivity of NH_3 , NO, NO₂, N₂O and N₂ were measured by fitting the diffusivity parameter for each gas at a particular temperature to the experimental data of steady-state NH₃ oxidation over the core-shell, Pt/Al₂O₃@Na-ZSM-5 sample, while keeping the kinetic parameters of the core constant. Using the measured diffusivities, the parameters over the Cu-ZSM-5 SCR catalyst were estimated following a sequential approach of fitting the transient NH_3 TPD, steady-state NH_3 oxidation, NO oxidation, standard SCR, fast and NO₂SCR. The estimated SCR parameters combined with NH₃ oxidation kinetic parameters were combined to finally simulate the steady-state NH₃ oxidation over Pt/Al₂O₃@Cu-ZSM-5 with great degree of accuracy. Using the model, we were able to further optimize the core-shell catalyst by reduction of Pt loading in the core by more than 50 % and for an optimal shell thickness, we were able to improve the NH₃ oxidation light-off without effecting the N₂ selectivity.

5.2 Future work

Based on the insights gained in this study, some recommendations are made for the future work in the area of exhaust after-treatment system.

The core-shell Pt/Al₂O₃@Cu-ZSM-5 (CS) showed enhanced NH₃ oxidation activity and N₂ selectivity for the entire operating temperature ranges. The CS catalysts outperformed a physical mixture of Pt/Al₂O₃ and Cu-ZSM-5 in terms of both NH₃ oxidation and N₂ selectivity. The enhanced NH₃ activity was from the Silicalite - 1seeding of the Pt/Al₂O₃ core. The CS catalyst also showed good resilience after 10 h of hydrothermal aging. All these results indicate towards CS being a promising ammonia slip catalyst. However further work still needs to be done in the following areas:

- Aging of the CS catalyst: A more robust aging study needs to be conducted to check the resilience of the CS catalysts. This is important as the close interactions between the Cu-ZSM-5 shell and the Pt/Al₂O₃ core gives the CS catalyst its good performance characteristic. A systematic performance evaluation of the CS catalyst must be performed at different aging conditions with incremental rise in the aging time (>10 h)
- 2. Optimization of core-shell catalyst: The optimization study performed in the Section 4.4.9 showed a core-shell catalyst with much lower Pt loading of 0.02 wt % and much thinner 0.83 μ m Cu-ZSM-5 shell. The simulation predicted an enhancement in NH₃ oxidation activity improved to 80% from 50% without

affecting the N_2 selectivity. However this still needs to be validated with experimental data.

3. Pt/Al₂O₃@Cu-ZSM-5 washcoated monoliths: The next step would be to coat the synthesized Pt/Al₂O₃@Cu-ZSM-5 (CS) particles onto a monolith and compare the performance with that of conventual dual-layer ASC of similar Pt and Cu loading. The core of Pt/Al₂O₃ is of 40 – 50 microns in size along with a 2 micron thick Cu-ZSM-5 shell, hence effort must be made to further reduce the particle size of the catalyst for effective washcoating.

The second major study in this dissertation was related to the NH₃ oxidation kinetic study over Pt. The detailed kinetic along with modeling study showed the non-monotonic rate trend with respect to NH₃ concentration. In our study we considered the weighted average contribution from different Pt crystallite planes simplified into adsorption sties 'a' and 'b'. Accordingly a microkinetic scheme was developed with NH₃ adsorption on both the sites, was able to capture the non-monotonic trend along with the enhancement in NH₃ oxidation activity after milling. The enhanced activity from milling stemmed from Pt crystallite transformation and destabilization of Pt oxides. However further work still needs to be done in the following areas:

Characterization of Pt crystallites: The XRD data revealed the changed in Pt crystalline transformations. We observed a decrease in Pt<111> with increase in PtO₂<211> crystal plane. It would be interesting to expand this study by

characterizing the Pt crystal planes using TEM analysis. This would be an interesting extension to the kinetic study.

2. Kinetic study over specific Pt crystallites: As discussed earlier NH₃ oxidation rate kinetic is highly structure sensitive. In the study of NH₃ oxidation kinetics over Pt/Al₂O₃ we did not consider individual crystallite planes while measuring the kinetics, instead weighed average contribution from all Pt crystallites was considered. We need to extend this study by measuring the rate-kinetics over specific Pt crystallites at atmospheric conditions. The rate contribution from individual Pt crystallites could be incorporated into modeling which would give the microkinetic modeling a more physical meaning. This analysis can help in determining the optimal Pt loading along with ideal Pt facets that would further enhance the kinetics.

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Appendix

A1. Activation energy for Un-milled Pt(0.07)-Al₂O₃ & milled Pt(0.07)-Al₂O₃

This section provides the apparent activation energy (E_a) calculated from the kinetic experiments conducted over powder Pt-Al₂O₃ samples in fixed bed reactor. For each experiment 0.22 g of Pt(0.07)-Al₂O₃ or Pt(0.07)-Al₂O₃-20h-BM (20 h milled) was used in fixed bed reactor. Feed conditions: NH₃, 10 % O₂, Balance Ar to give 1000 sccm flow-rate.

Figure A1.1 shows the E_a at measured at different ammonia concentrations, 100, 500 and 700 ppm for Un-milled Pt(0.07)-Al₂O₃ powder sample under steady state conditions. Here in all the three regimes of ammonia concentration, the $E_a \sim 153$ kJ/moles for the un-milled Pt-Al2O3.

Figure A1.2 shows the E_a at measured at different ammonia concentrations, 100, 10000 and 25000 ppm for Pt(0.07)-Al₂O₃-20h-BM (20 h milled) powder sample under steady state conditions. The E_a at 100 and 10000 ppm is 121 kJ/moles and 107 kJ/moles at 25000 ppm of ammonia. Figures A1.1 and A1.2 collectively show the drop in E_a as we move from un-milled to milled Pt/Alumina.



Figure 38. Apparent activation energy (Ea) estimated at 100, 500 and 700 ppm of NH₃ for un-milled Pt(0.07)-Al₂O₃ catalyst tested in fixed bed reactor at 1000 sccm flowrate + 10 % O₂, balance Argon



Figure 39. Apparent activation energy (Ea) estimated at 100 ppm, 500 ppm and 700 ppm of ammonia for un-milled Pt(0.07)-Al₂O₃ catalyst tested in fixed bed reactor at 1000 sccm flow-rate + 10 % O₂, balance Argon.

A2. Microkinetic Analysis: Locating rate maximum

The following microkinetic steps are considered for NH_3 oxidation happening at lower T region [Conversion < 10 %, sole product N_2]. The reactions steps RS1 - RS6 are *taken from Table 2, with corresponding reaction step indicated.*

$NH_3 + b \leftarrow \rightarrow NH_3 - b$	$RS1 \rightarrow R1$
$NH_3 + a \leftarrow \rightarrow NH_3 - a$	RS2 → R10
$O_2 + 2a \leftarrow \rightarrow 2O - a$	<i>RS3</i> → <i>R3</i>
NH_3 - b + 1.5 O - $a \rightarrow N$ - a + 1.5 H_2O + 0.5 a + b	RS4 → R2
NH_3 - a + 1.5 O - $a \rightarrow N$ - a + 1.5 H_2O + 1.5 a	RS5 → R11
$2N-a \rightarrow N_2$	RS6 → R6

Applying sum of species coverages equal to unity:

$$\Theta_b + \Theta_{NH3-b} = 1$$

$$\Theta_a + \Theta_{NH3-a} + \Theta_{o-a} = 1$$

Assuming surface reaction steps RS4 and RS5 are rate determining, and step RS6 is fast:

 $R_d = RS4 + RS5 = k_2 \Theta_{NH3-b} \Theta_{O-a} + k_{11} \Theta_{NH3-b} \Theta_{O-a}$

Along with the adsorption of NH3 and O2 are at equilibrium, the following rate expression is derived:

$$R_d = \frac{k_{11}A.P_{NH3}}{(B + K_{10}P_{NH3})^2} + \frac{k_{2.}C.P_{NH3}}{(1 + K_1P_{NH3})(B + K_{10}P_{NH3})}$$

where,

$$A = K_{10}\sqrt{K_3P_{02}}$$
$$B = 1 + \sqrt{K_3P_{02}}$$

$$C = K_1 \sqrt{K_3 P_{02}}$$

 R_d contains the contribution of reaction rate from two pathways for the Reaction scheme 'aa + ba', Reaction scheme AA and Reaction scheme BA. Scheme AA is represented in the reaction rate as the term with reaction rate constant k_{11} while scheme BA is represented in reaction rate with the term containing reaction rate constant k_2 .

To determine the C_{NH3,m} (concentration of NH₃ at maximum rate),

$$\frac{dR_d}{dC_{NH3}} = 0$$

$$\frac{dR_d}{dC_{NH3}} = \frac{(k_{11}A.B - k_{11}K_{10}A.C_{NH3})(1 + K_1C_{NH3}) + k_2C(B + K_{10}C_{NH3})(B - K_{10}K_1C_{NH3}^2)}{(1 + K_1C_{NH3})^2(B + K_{10}C_{NH3})^3}$$

Solving the above cubic equation in C_{NH3} , gives us $C_{NH3,m}$
$C_{NH3,m} = f(Rate constants(k_{11}, k_2), Equilibrium constants(K_1, K_3, K_{10}))$

This functional dependence on both for $C_{NH3,m}$ provides further evidence on the importance of combined dual site kinetics (BA +AA) scheme. As we move from unmilled to milled, the reaction rate constants increases due to the significant drop in E_a (activation energy, for $k_{11} \rightarrow 152.7$ to 110 kJ/mol, for $k_2 \rightarrow 151$ to 132 kJ/mol).

Plotting R_d as a function of ammonia concentration, with kinetic parameters taken from the Table 2. We can predict both the increase in reactivity of milled Pt/Alumina but also the shift in concentration at which maximum rate takes place, from $C_{NH3,m} = 360$ ppm to 14000 ppm which is quite close to the model and experimental data.



Figure 40. Analytical reaction rate (Rd) versus ammonia concentration (C_{NH3}) for unmilled and milled Pt/Alumina

A3. Model Validation using microkinetic scheme AA + BA

This section provides model validation at different Pt weight percentages as show in figures, or at different feed concentrations, such a different NH₃ concentration. The aim of this section is to check the model fit using the parameters given in Table 2 with respect to NH₃ oxidation light-off and product distributions. Figure S5 shows model validation with un-milled Pt-Al₂O₃, but at higher Pt concentration of 0.15 wt % and at two different NH₃ concentrations, 500 ppm and 1000 ppm of NH₃. Figure S6 shows the model validation for milled Pt-Al₂O₃ at Pt concentration of 0.07 wt % but at two different NH₃ concentrations, 1000 ppm and 25000 ppm of NH₃. These catalysts were powder samples and tested in a fixed bed reactor. Figure S7 shows the model validation for single layer washcoated Pt layer over a monolith, with Pt concentration of 3.2 g/ft³ of monolith at two different NH₃ concentrations, 1000 ppm and 10000 ppm NH₃.



Figure 41. Steady state ammonia oxidation over fixed bed samples with un-milled Pt(0.15)-Al₂O₃ (a) 500 ppm NH₃ (b) 1000 ppm NH₃ Feed: NH₃, 10% O₂, balance Argon for a total flow rate of 1000 sccm. [symbols – experiments, lines – model]



Figure 42. Steady state ammonia oxidation over fixed bed samples with milled Pt(0.07)-Al₂O₃ (a) 1000 ppm NH₃ (b) 25000 ppm NH₃ Feed: NH₃, 10% O₂, balance Argon for a total flow rate of 1000 sccm. [symbols – experiments, lines – model]



Figure 43. Steady state ammonia oxidation over fixed bed samples with Pt -3.2 monolith sample (a) 1000 ppm NH₃ (b) 10000 ppm NH₃ Feed : NH₃, 10% O₂, Balance Argon for a total flow rate of 1000 sccm. [symbols – experiments, lines – model]

A4. Adiabatic temperature rise for NH₃ oxidation

In this section, we are providing with the maximum adiabatic temperature rise for the NH₃ oxidation taking place during reaction rate-measurements at specified ammonia conversion. Considering the following reaction of NH3 oxidation in presence of oxygen over Pt.

$$4 \text{ NH}_3 + 3 \text{ O}_2 \rightarrow 2 \text{ N}_2 + 6 \text{ H}_2\text{O}$$
 $\Delta \text{H} = -2.26 \text{ x } 10^5 \text{ J/mole NH}_3 (\text{SR } 1)$

The adiabatic temperature rise is calculated as shown below:

 $\Delta \mathbf{T} = \frac{(-\Delta \mathbf{H}) C_{0,NH3}}{\rho_g C_{pg}} \Delta \mathbf{X}$

Where,

 ΔH = enthalpy of reaction (kJ/mole NH₃)

 $C_{0.NH3}$ = Molar concentration of NH₃ (mole/m³)

 ρ_g = Density of reacting gas (kg/m³)

 C_{pg} = Specific heat of the reacting gas (kJ/kg/K)

 $\Delta X = NH_3$ conversion = 10 %

Case 1: 500 ppm NH₃, 10 vol % O₂, balance Argon @ 5 % ammonia conversion for unmilled Pt(0.05)-Al₂O₃ in fixed bed reactor.

$$\Delta T = \frac{(-\Delta H)C_{0,NH3}}{\rho_g C_{pg}} \Delta X = \frac{(-226)*0.02}{1.7414*0.56} * 0.05 = 0.23 K$$

Case 2: 10000 ppm NH₃, 10 vol % O₂, balance Argon @ 10 % ammonia conversion for milled and washcoated monolith.

$$\Delta T = \frac{(-\Delta H)C_{0,NH3}}{\rho_g C_{pg}} \Delta X = \frac{(-226)*0.25}{1.7307*0.61} * 0.1 = 8.5 K$$

Case 3: 25000 ppm NH₃, 10 vol % O₂, balance Argon @ 4 % ammonia conversion for milled and washcoated monolith.

$$\Delta T = \frac{(-\Delta H)C_{0,NH3}}{\rho_g C_{pg}} \Delta X = \frac{(-226)*1}{1.70*0.63} * 0.04 = 8.56 K$$

The ΔX values are taken from experimental measurements at specified conditions. The adiabatic temperature rise is in all the cases is < 10 K. Case 2 and 3 represents the maximum adiabatic temperature rise that can take place during the kinetic measurements.

A5. Site coverages: NH₃-a, NH₃-b, O-a, NO-a, N-a, NO₂-a

Based on the microkinetic scheme, we have following adsorbed species: NH_3 -b, NH_3 -a, O-a, NO-a, NO₂-a. Figure 6 in the paper, showed the species coverages for NH_3 -a, NH_3 -b and O-a species.Figure S7 shows the model predicted species site coverages as a function of NH_3 concentration at 190°C for the Pt-3.2 g/ft³ monolith catalyst. The the model predicted species coverages, NH_3 -a, NH_3 -b and O-a species are the major adsorbed species as shown in Figure S7(a). Figure S7(b) shows the site coverages for N-a, NO_2 -a, NO-a, vacant sites: a and b whose fractional coverage is ~ 0.025.



Figure 44. Model predicted reactant species site coverage as a function of Ammonia concentration (TOF) for (a) all species (b) N-a, NO₂-a, NO-a, a, b on Pt-3.2, monolith sample. [Feed: 500 ppm NH₃, 10 vol % O₂, balance Ar at 1000 sccm]

Figure S8, shows the model predicted site coverages for the unmilled $Pt(0.07)-Al_2O_3$ catalyst sample over a fixed bed reactor at 240°C. Here we can see that NO₂-a is a major adsorbed species along with NH₃-a, O-a and NH₃-b. The NO₂-a and O-a site coverages are comparable with each other. Here we can clearly see that site coverages on site 'a' can also be affected by other species.



Figure 45. Model predicted reactant species site coverage as a function of Ammonia concentration (TOF) for all species on un-milled Pt/Al₂O₃. [Feed: 500 ppm NH₃, 10 vol % O₂, balance Argon at 1000 sccm]

A6. Microkinetic including NHx, OH species [from Ma and Schneider]

In this section, we use the microkinetic scheme and parameters from Ma et al., [13] to compare the kinetics and product distributions for steady state NH3 oxidation with that of the experimental data. For our paper, we wanted to incorporate a much simpler microkinetic scheme that showed the presence of site competition from NH₃ concentration which had been shown in different studies [7-11, 23, 24, 25]. Another important aspect to be considered is that NHx+OH pathway considers single site for adsorption/desorption and reaction steps to take place and does not consider the different adsorption sites 'a' and 'b' over Pt shown in different studies [7-11].

However we did consider a case where we incorporated the kinetics of Ma and Schneider which included the presence of NHx, OH species. This analysis was done over monolith sample. Figure S9(a) shows the model predicted steady state NH₃ oxidation conversion and product distribution as a function of temperature based on the microkinetic step shown in Figures S10. The microkinetic scheme and kinetic parameters have taken from the study by Ma et al., [13] which included the NHx + OH pathways. On applying the kinetic parameters, Figure S9(a) shows that light-off happens at 455°C, much higher than measured for Pt-3.2 monolith and un-milled Pt-Al₂O₃ sample. Figure S9(b) shows the model predicted rate kinetics (TOF, 1/s) as a function of varying NH₃ concentration. The NHx+OH pathway with kinetics taken from Ma et al., [13] also shows the non-monotonic trend, however it is not able to predict the concentration at which maximum TOF takes place ie. 10000 ppm of NH3, also the maximum TOF of 12.5 1/s.



Figure 46. Model predicted (a) steady state NH₃ oxidation (b) TOF of NH₃ oxidation as a function of NH₃ concentration over Pt-3.2 g/ft³ using (c) microkinetic scheme developed by Ma et al. [13]. Feed: NH₃ ppm, 10 % O, balance Ar at 1000 sccm.

A7. NH₃ adsorption/desorption studies over un-milled and milled Pt-Al₂O₃

The NH₃ adsorption/desorption profiles was done for both milled and un-milled Pt/Alumina samples. The NH₃ TPD was done over 360ppm NH₃ + rest Argon, 520 sccm flowrate with 0.2 g of catalyst in fixed bed. The NH₃ adsorption was done at 100°C for 100 mins, with temperature ramp of 10°C/min starting from 110 mins to measure the desorption profile with just Argon flowing. Both the milled and unmilled catalyst samples show similar NH₃ adsorption profile.



Figure 47. NH₃ adsorption and desorption profiles for Pt(0.07)-Al₂O₃ and Pt(0.07)-Al₂O₃-20h-BM.

A8. XPS study over milled Al₂O₃ and BET analysis

The Pt loading in the Al₂O₃ for all the samples was 0.07 wt % of Pt in Alumina. In our kinetic measurements, the Pt was added via "Incipient wetness impregnation" method. The γ -Al₂O₃ powder was dispersed in a quartz glass boat and an aqueous solution of the Pt complex was added dropwise uniformly over the particles. The volume of the aqueous solution was calculated based on the pore volume of alumina powder (0.5 cm³/g). This method gives a good control over the loading of Pt. We also did XPS measurements to look out for any sample impurities from milling. The results from our previous work [39], seeding of Pt/Alumina with Silicalite-1 leads to enhancement in activity. Hence, we wanted to check if there is any Si detected as the glass beads used for ball-milling are SiO₂ beads. For this case XPS analysis was done over milled γ -Al₂O₃. However we can clearly see there is no impurity detected. It must be noted we use commercial γ -Al₂O₃ provided by SASOL. The commercial γ -Al₂O₃ support contains 3 wt% La₂O₃ to improve thermostability. Hence Lanthanum is also detected in the XPS measurement.

Table S4. XPS composition of milled Al₂O₃

Elements	0	Al	La
atomic			
%	62.3	37.3	0.4

BET surface area: The BET results will be provided in the updated paper. The BET surface area analysis showed an increase in the surface area from is $165m^2/(g \text{ of catalyst})$ for the Un-milled Pt/Al₂O₃ to 209 m²/(g of catalyst) for the case of 20 h milled Pt/Al₂O₃ catalyst. BET surface area has increased by 30 % upon milling. This is expected out of ball-milling of Alumina particles, as it exposes more surface area on reduction of particle size. However as shown in Section 4.5, the increase in surface area from milling does not impact the activity. Comparing Al₂O₃-20h-BM + Pt(0.07) with Pt(0.07)-Al₂O₃-20h-BM (20 h ball milled), we can see when Pt is added after milling of Alumina does not result in any change in the activity of the catalyst as seen in the figure below.

A9. Catalyst characterization

This section provides details of the various methods used to characterize the coreshell catalyst. Figure S2 shows the SEM micrographs of P(0.05)-AS-S1 and CS catalysts. After seeding the Pt/Al_2O_3 core, the seeded core is treated to the first hydrothermal step for the formation of shell around the seeded core. However from the SEM images we can see, the shell is not fully developed. As discussed earlier this led us to another hydrothermal growth step. After which, we can see a thick dense ZSM-5 shell formed around it.



Figure 49. SEM micrographs of seeded core after (a) first secondary growth stage, (b) second secondary growth stage resulting in formation of CS catalyst



Figure 48. SEM micrographs of core-shell catalyst to determine the shell thickness (a) original image with clear distinctive shell (b) Shell thickness indicated by arrow (thickness $\approx 1.2 \ \mu m$), to distinguish shell & core, shell has been artificially colored.

In order to determine the thickness of the shell, the CS catalyst was crushed, and SEM imaging was done thereafter. Figure S3 shows the thickness of the core-shell catalyst with shell thickness of 1.2 microns. In order to confirm the crystalline structure of shell, XRD was done over each individual synthesis steps. Figure S4 confirms the presence of ZSM-5 shell around the core.



Figure 50. Powder XRD patterns for the core-shell, seeded core (P(0.05)-AS), and core (Pt(0.05)-A). The MFI framework structure of ZSM-5 was indexed according to a reference pattern for H-ZSM-5 provided by the IZA structure database.

Elemental analysis of the core-shell catalyst was performed using a combination of X-ray photoelectron spectroscopy (XPS) and Energy dispersive X-ray (EDX) to determine the Si-to-Al ratio (SAR). EDX probes a greater depth into the catalyst particle (ca. 1 μ m), thereby assessing the bulk Si/Al ratio, whereas XPS is a surface sensitive technique with shorter penetration depth of ca. 10 nm that assesses the outer rim of the particle. Using both of these techniques, the Si/Al ratio was found to be ca. 30 for the core-shell (CS) particles.

As described later, EDX detected no Pt, which indicates that EDX probing is confined to the shell. The similar Si/Al ratio measurements using XPS and EDX also suggests an absence of Al zoning in the shell. Furthermore, EDX was also employed to determine the fraction of Cu introduced into the ZSM-5 shell via Cu ion-exchange (ca. 3%) and to confirm that there is no detectable Pt in the shell. Finally, as describe earlier, CS particles were crushed to enable measurement of the determining the shell thickness using SEM. We used EDX to analyze the exposed core. The EDX characterization indicated no Cu in the core. This is evidence that the Cu does not migrate to the core.

A10. Comparing the light-offs for: P(0.05)-A, P(0.05)-AS, CS

Figure S5 compares the steady state ammonia conversion versus bed temperature for the following catalyst samples: P(0.05)-A, P(0.05)-AS and CS. The light off temperatures, defined as temperature at 50 % conversion (T50) was observed at 305, 210 and 250°C for the three catalysts respectively. The catalysts, P(0.05)-AS and CS have lower light offs compared to the P(0.05)-A. The enhancement in activity has already been reported and studied extensively in the previous work by Ghosh et al. [9]. The reason behind the enhanced activity was due to the destabilization of Pt oxides, which led to the exposing of more metallic Pt(0) for ammonia oxidation to take place making it more active catalyst. This was done by altering the metal support interactions between Pt and support (Alumina) by the process of in-situ Silicalite- 1 seeding which was a necessary step in growth of ZSM-5 shell around the core of P(0.05)-AS. The T₅₀ for CS sample is 40°C higher than that of P(0.05)-AS sample. This is due to the presence of 1.2 micron dense ZSM-5 shell in CS sample which introduces diffusion limitations leading to the detrimental impact in light off.

The effect of diffusional resistance from dense ZSM-5 shell will be used later in the section to determine the intra-crystalline diffusivity for gases.



Figure 51. Steady state ammonia oxidation carried out over P(0.05)-A, P(0.05)-AS and CS-1.2. In each experiment, 0.18 g of powder catalyst was used in fixed bed reactor. Feed: 500 ppm NH₃, 10 vol % O₂, balance Argon at 1000 sccm.

A11. Comparing the light-off and kinetics between milled P(0.07)-A and P(0.05)-AS

Figure S6, show the similarity in enhancement of NH₃ oxidation activity for milled Pt(0.07)-Al₂O₃ and seeded core, P(0.05)-AS. However as seen in Figure S6(a), the seeded core is more active which is indicated by a lower light-off. Comparing Figure S6(a) and S5, shows that Both milled and seeded catalysts are more active than the starting catalysts, of Pt/Al₂O₃. Looking into the kinetics from Figure S6(b), both the catalysts follow similar non-monotonic trend of rate (TOF) with variation in NH3 concentration. Both the catalysts have rate maximum ~ 10000 ppm. Both the figures indicate towards a slightly more active

seeded core, P(0.05)-AS. The reason behind their enhanced activities have already been discussed in Chapter 2 and 3 of this thesis.



Figure 52. Steady state ammonia oxidation and kinetics measured for milled Pt(0.07)-Al₂O₃ and P(0.05)-AS (a) NH₃ conversion vs temperature (b)Turn over frequency (TOF) of NH₃ oxidation as a function of NH₃ concentration at 1000 sccm flow-rate at 180°C.

A12. Controlling regimes & varying diffusivity from intra-crystalline to Knudsen diffusivity

In this section we determined the true intrinsic SCR kinetic parameters by incorporating the intra-crystalline diffusivity of reaction species in the ZSM-5 crystallite. This gives us a unique opportunity to understand the extent to which diffusion transport within the pores of zeolite limits the SCR reaction rates. This can be quantified using Thiele modulus (ϕ^2). Thiele modulus is the ratio of the characteristic diffusion time to reaction time. For this purpose we have considered the standard SCR and fast SCR reactions. The characteristic times are defined as:

$$\tau_{\rm D}(\text{intracrystalline NH}_3 \text{ diffusion time}) = \frac{(\frac{R}{3})^2}{D_{NH3}},$$
 (13)

$$\tau_{R5} \text{ (standard SCR reaction time)} = \frac{C_{NH3,f}}{R5(C_{NH3,f})} \text{ and}$$
(14)

$$\tau_{\rm R6} (\text{fast SCR reaction time}) = \frac{c_{NH3,f}}{R6(c_{NH3,f})}$$
(15)

are estimated as a function of temperature as shown in Figure 9 along with Thiele modulus. 'R' radius of catalyst, D_{NH3} is the intracrystalline of NH₃ in the ZSM-5 taken from Table S3, $C_{NH3,f}$ is the molar concentration of NH₃ in the fluid phase, $R_{5/6}(C_{NH3,f})$ is the reaction rate for standard SCR (R5) or Fast SCR (R6) reactions.



Figure 53. Characteristic time scales for diffusion, standard SCR(R5), fast SCR (R6) and Thiele modulus as a function of temperature.

In another analysis, we compared the model predicted steady state NH₃ conversion and N₂ selectivity of two catalysts, CS-1.2 (described in the paper) and CS-1.2:Knudsen



Figure 54. Model predicted steady state NH₃ oxidation light off curves (Left) and N₂ selectivity (right) for CS-1.2 and CS:1.2: Knudsen diffusivity in fixed bed reactor. Feed: 500 ppm NH₃, 10 vol % O₂, balance Argon at 1000 sccm.

Diffusivity. The second catalyst is a hypothetical comparison in which the pore size of zeolite are larger and diffusivity in the shell is now based on Knudsen Diffusivity. As can be seen from Figure S8, due to the shift of diffusion regime from intra-crystalline to Knudsen, the light-off for CS-1.2:Knudsen Diffusivity behaves like a P(0.05)-AS catalyst (if light-off curve compared to Figure S5). This shows us that presence of zeolite around the core now has no diffusional impact. As a result of this lower diffusion resistance, even though it is core-shell geometry of 1.2 micron thick shell, the N₂ selectivity drops drastically. The N₂ selectivity at T = 500°C drops from 90% to ~30% for the new diffusion modified catalyst. It does not drop to 0% like the P(0.05)-AS due to the presence of Cu around the core. This another way of showing the importance of diffusivity on activity and selectivity of the core-shell catalyst.