2013

The Effects of Ceria Addition on Aging and Sulfation of Lean NOx Traps for Stand Alone and LNT-SCR Applications

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THE EFFECTS OF CERIA ADDITION ON AGING AND SULFATION OF LEAN NO\textsubscript{X} TRAPS FOR STAND ALONE AND LNT-SCR APPLICATIONS

DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

By
Vencon Glenn Easterling

Lexington, Kentucky

Co-Directors: Dr. Mark Crocker, Professor of Chemistry and Dr. Stephen Rankin, Professor of Chemical and Materials Engineering

Lexington, Kentucky

2013

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Model powder and fully formulated monolithic lean NO\textsubscript{x} trap (LNT) catalysts were used to investigate the effect of ceria on desulfation behavior. Temperature-programmed reduction (TPR) experiments (model catalysts) showed each of the oxide phases present is able to store sulfur and possesses distinct behavior (temperature at which desulfation occurs). La-CeO\textsubscript{2} or CeO\textsubscript{2}-ZrO\textsubscript{2}-containing samples (monoliths) showed a greater resistance to deactivation during sulfation and required lower temperatures to restore the NO\textsubscript{x} storage efficiency to its pre-sulfation value.

Fully formulated monolithic LNT catalysts containing varying amounts of Pt, Rh and BaO were subjected to accelerated aging to elucidate the effect of washcoat composition on LNT aging. Elemental analysis revealed that residual sulfur, associated with the Ba phase, decreased catalyst NO\textsubscript{x} storage capacity and that sintering of the precious metals resulted in decreased contact between the Pt and Ba phases.

Spatially-resolved inlet capillary mass spectrometry (SpaciMS) was employed to understand the factors influencing the selectivity of NO\textsubscript{x} reduction in LNT catalysts (degreened and thermally aged) containing Pt, Rh, BaO and Al\textsubscript{2}O\textsubscript{3}, and in one case contained La-stabilized CeO\textsubscript{2}. Stretching of the NO\textsubscript{x} storage and reduction zone (NSR) zone resulted in increased selectivity to NH\textsubscript{3} due to the fact that less catalyst was available to consume NH\textsubscript{3} by either the NH\textsubscript{3}-NO\textsubscript{x} SCR reaction or the NH\textsubscript{3}-O\textsubscript{2} reaction. Additionally, the loss of oxygen storage capacity (OSC) and NO\textsubscript{x} storage sites, along with the decreased rate of NO\textsubscript{x} diffusion to Pt/Rh sites, led to an increase in the rate of propagation of the reductant front after aging, in turn, resulting in increased H\textsubscript{2}:NO\textsubscript{x} ratios at the Pt/Rh sites and consequently increased selectivity to NH\textsubscript{3}.

Finally, a crystallite scale model was used to predict selectivity to NH\textsubscript{3} from the LNT catalysts during rich conditions after a fixed amount of NO\textsubscript{x} was stored during lean conditions. Both the experimental and model predicted data showed that the production
of NH$_3$ is limited by the rate of diffusion from the Ba storage sites to the Pt particles at 200°C. At 300°C, the process is limited by the rate at which H$_2$ is fed to the reactor.

KEYWORDS: Lean NO$_x$ Trap, Desulfation, Ceria, SpaciMS, Ammonia
THE EFFECTS OF CERIA ADDITION ON AGING AND SULFATION OF LEAN NO\textsubscript{x} TRAPS FOR STAND ALONE AND LNT-SCR APPLICATIONS

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December 12, 2012

Date
To My Family
First and foremost I would like to thank Prof. Mark Crocker for his support and direction during the pursuit of my doctorate. I would also like to state my appreciation to him for encouraging me to change from master’s to doctoral degree during my graduate studies.

I would also like to express my gratitude to Prof. Dibakar Bhattacharyya, Prof. Richard Kermode, Prof. Barbara Knutson, Prof. Stephen Rankin, and Mr. Bruce Cole for their help while I was considering returning to school after working in industry.

I would also like to recognize and credit the other members of my advisory committee: Prof. Yang-Tse Cheng and Prof. John Selegue both for their time and their helpful insight.

Thanks to Dr. Robert McCabe, Dr. Mark Dearth, Dr. Joseph Theis, Mr. Justin Ura, and others in the Research and Innovation Center (RIC) at the Ford Motor Company and Dr. Todd Toops, Dr. Jae-Soon Choi, and Dr. William Partridge, and others at the Fuels, Engines and Emissions Research Center (FEERC) at Oak Ridge National Laboratory. I was extremely fortunate to have the opportunity to conduct the majority of my research at these facilities. The experience I gained at both of these centers is immeasurable.

I would like to thank Prof. Michael Harold at the University of Houston for his support during my work on the modeling portion of my research and for allowing me to visit Houston’s campus.

I would like to recognize Dr. Robert McCabe and his wife for opening their house to me for some of my visits to Ford. I cannot say how much I appreciated a nice bed and home-cooked meal after working long hours in the laboratory.

I would like to thank the Department of Energy (DOE) and Ford Motor Company for the funding of this research.
I would like to thank my co-workers at the University of Kentucky Center for Applied Energy Research (CAER) for their support and friendship. The Biofuels and Environmental Catalysis research group has grown with me during the pursuit of this degree.

I consider myself extremely gifted to have met and made many friends over the course of my studies. Especially, I would like to thank Dr. Scott Lewis, Dr. Vinod Kanniah, and Dr. Harry Hunter for many fun experiences and keeping things light during the most demanding parts of my graduate school education.

I owe a special thanks to Miss Elizabeth Kidd for all of the emotional support she has provided me. It has been a long journey, and she was always standing beside me, ready to help me in whatever means was necessary.

Lastly and most importantly, I would like to express my appreciation to my parents, sister, and other family for their support during this educational journey. I would like to thank my sister, Mrs. Glenna Bianchin, for always setting the bar high in our sibling rivalry. I would also like to thank my cousin, Mr. Trey Hieneman, for being part of my support system when I was traveling for school and for providing at least a few opportunities to attend the UK basketball games every year. I cannot express my gratitude to my parents, Mr. Glenn Easterling and Mrs. Sharon Easterling, for their support and for the providing me a chance to make this change in my life. The lessons they have taught me have helped me get to where I am today.
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Chapter 1. General Introduction.

During the past 40 years, two interrelated changes in our society, environmental awareness and the desire for improved fuel economy, have increasingly impacted the lives of the population of the United States of America. On July 9, 1970, the Environmental Protection Agency was created as a response to growing concern over environmental protection and conservation [1]. Also during the 1970’s, two oil crises occurred in response in disruptions to global oil supply. These trends of increased environmental awareness and efforts towards decreased fuel consumption have continued into the present day. Although not necessarily obvious, the desire for increased fuel economy and reduced emissions are problems with solutions that involve a common feature: lean-burn engine operation.

1.1. Air Pollutants and Their Effect on Human Health.
To understand the need for automobile emissions control, one has to look no further than the major components present in automotive emissions and their negative effects on humans and the environment. While air pollution can be associated with natural sources such as volcanic eruptions, forest fires, or dust storms, the major sources of air pollution are from human activities [2]. A large portion from human activity corresponds to the tailpipe emissions from automobiles as shown in Figure 1.1. The major components of this pollution are carbon monoxide (CO), hydrocarbons (HC), particulate matter (PM) and oxides of nitrogen (NO\(_x\)). CO is a colorless and odorless gas that is poisonous to humans. Some HCs are linked to cancer in humans while others contribute to the greenhouse effect. PM is the term given to the fine particles that are present as aerosols during combustion processes, which have been linked to heart disease and lung cancer. Likewise, NO\(_x\) has many negative effects on our environment, including the smog that is present in many cities across the United States. Another derives from the reaction of NO\(_x\) with HCs to produce ground level ozone that can cause breathing complications. NO\(_x\) also reacts in the atmosphere to create acid rain. Acid rain is detrimental to vegetation and aquatic species. The impact exerted by these air pollutants on human health is evident in the Centers for Disease Control (CDC) estimate that exposure to air pollution
results in $40 to $50 billion dollars in health care costs per year and 50,000 to 120,000 premature deaths per year [4].

Figure 1.1. Sources of air pollution in the United States for fiscal year 2006. [3]
Source: pscleanair.org. Figure reprinted with permission.

1.2. Response to Air Pollution: Clean Air Act and its Amendments.
In response to rising concerns over the health effects attributed to these pollutants, the United States government has established legislation to determine and set limits on these different pollutants. These targets for air emissions are the result of regulations that have evolved over the past half century. The origin of air quality standards can be traced to 1955 with the passing of the Air Pollution Control Act that empowered states to control air pollution. These standards continued with the Clean Air Act in 1963, the Air Quality Act in 1967, the Clean Air Act Extension of 1970, and the Clean Air Act Amendments of 1977. Subsequent additions were made in the 1990s which are particularly important
when considering automobile exhaust. Programs for the control of acid rain were added in 1990, and the National Ambient Air Quality Standards lowered the levels of ground-level ozone that make up smog as well as the fine airborne particulate matter that makes up soot.

1.2.1. Tier 1.
The origin of today’s automotive emission standards originated with the Clean Air Act Amendments in 1990. These amendments established more stringent Tier 1 standards that were phased in between 1994 and 1997. These standards assigned emission levels to all vehicles under 8500 lbs. gross vehicle weight rating (GVWR) [5]. The standards were comprised of two milestones: 5 years/50,000 mi. and 10 years/100,000 mi. These standards divided personal vehicles such as cars, light trucks, minivans, and sport utility vehicles into categories based on the GVWR. Also the NO\textsubscript{x} standard was dependent on whether the vehicles used gasoline or diesel as fuel.

Tier 1 standards are enforced using the federal testing procedure (FTP) 75 cycle [5]. The FTP-75 cycle has been used since 1978 and is divided into three segments as shown in Figure 1.2. Emissions are measured after the engine is started; this is referred to as the cold start. Emissions continue to be measured during the transient phase and during the last phase, in which the engine is turned off and restarted. The total cycle is 11.04 miles total, lasting 1874 s, and using an average speed of 21.2 mph.

While this procedure is effective in measuring emissions, there exist some shortcomings when trying to capture real world driving conditions. In response to this issue, supplemental federal testing procedures (SFTP) were instituted. The USO6 is a representation of aggressive, high speed, and/or high acceleration driving behavior [5]. This test is comprised of an 8.01 miles loop, average speed of 42.4 mph with a maximum speed of 80.3 mph, and a duration of 596 s. The other supplement test accounts for the emissions associated with the use of air conditioning in a vehicle. This test is 3.6 miles in length with an average speed of 21.6 mph, maximum speed of 54.8 mph, and duration of 596 s.
1.2.2. Tier II.

As part of the Tier I initiative, a study on the effectiveness of reducing emissions even further and the economic impact of those more stringent standards was conducted. The study resulted in the adoption of the Tier II standards in 2007 after a phase in period beginning in 2004. The main difference between Tier I and Tier II standards is that the standards in Tier II apply to all vehicles, regardless of weight up to 8500 lbs. GVWR. Also, the standards are the same irrespective of the fuel type. The Tier II standards are structured into different emissions levels referred to as bins, as shown in Table 1.1 [6]. On account of HC and CO levels being inherently lower from diesel engines as compared to stoichiometric engines, the abatement of NO\textsubscript{x} emissions will be the focus of this dissertation. Tier II mandates that every manufacturer must average a NO\textsubscript{x} standard of 0.07 g/mi as tested on the FTP 75 cycle for the full useful life of either 10 years or 120,000 miles. As with Tier I, SFTP standards exist to correct for the aforementioned shortcomings of the FTP test.

Figure 1.2. FTP-75 Cycle [5]. Source: DieselNet.com. Figure reprinted with permission.
In addition to the emission standards, Tier II also mandates that sulfur levels in gasoline be reduced to an average of 30 ppm with a cap of 80 ppm and in diesel be reduced to 15 ppm. As will be discussed later in this dissertation, sulfur interferes with the effectiveness of emission control systems.

Table 1.1. Tier 2 emission standards, FTP 75 cycle, g/mi [6]. Source: DieselNet.com.

<table>
<thead>
<tr>
<th>Bin#</th>
<th>Intermediate life (5 years / 50,000 mi)</th>
<th>Full useful life</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMOG</td>
<td>CO</td>
</tr>
<tr>
<td>8</td>
<td>0.1</td>
<td>3.4</td>
</tr>
<tr>
<td>7</td>
<td>0.075</td>
<td>3.4</td>
</tr>
<tr>
<td>6</td>
<td>0.075</td>
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<tr>
<td>5</td>
<td>0.075</td>
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</tbody>
</table>

An interesting feature of Tier II concerns whether or not a vehicle meets, exceeds, or fails to meet the Tier II, Bin 5 standard. If the manufacturer exceeds Tier II, bin 5, a credit is earned that can be used later or traded to another manufacturer. If bin 5 is not met, the manufacturer must obtain sufficient credits no more than 3 years after the violation occurred. This is where credit trading or redemption occurs.

Figure 1.3 is effective in summarizing the preceding discussion on the degree to which tailpipe emissions have been tightened by ever increasing governmental regulations. Every drop in NOx levels as shown in the figure represents new standards coming into effect. The 0.07 g/mi. value achieves Tier II, Bin 5 levels for the full useful life of the vehicle. From 1966, beginning with the original Clean Air Act, to the enactment of Tier II, NOx limits have been reduced by slightly more than 98%. To illustrate how stringent the emissions standards have become, in order to achieve Tier II, Bin 2 status (0.02 g/mi.), a further 71% reduction in NOx tailpipe emissions would be required.

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1.3. Current State and Future of NO\textsubscript{x} Emissions.

Despite these legislative efforts, NO\textsubscript{x} emissions now are actually greater than they were in 1970. This increase is not an indictment of the failure of governmental regulation, but a result of more vehicles being driven more miles on American highways. Figure 1.4 demonstrates that these regulations have reduced NO\textsubscript{x} levels to one-fifth of the levels that would exist without emissions controls in place [10].
1.4. The Role of Fuel Economy on Emissions Regulations.

While environmental awareness and the subsequent responses were occurring, another trend was also driving the response of suppliers to consumer demand. Twice during the 1970’s, an oil crisis occurred in the United States, leading to increased gasoline prices and shortages. Since then global events (as shown in Figure 1.5), such as government volatility in oil producing countries (e.g. Iran, Venezuela), wars (both Gulf Wars) and terrorist attacks (the events of 9/11) have resulted in increased fuel prices [11]. These events, along with decreasing oil supplies, have contributed to a public desire for more fuel-efficient automobiles. In this context, the most recent Corporate Average Fuel Economy (CAFE) standards hold significant implications for vehicle emissions. The CAFE standards are applicable from 2012 to 2016, and the standards state that all vehicles with a GVWR of 10,000 lbs. or less must average 35.5 mpg. The average is subdivided into an average of 42 mpg for cars and 26 mpg for trucks, which must be met by 2016. Failure to meet this regulation will result in the manufacturer being charged $5 per vehicle for every tenth of a mile that the vehicle is short of the standard. However, as engine operation becomes more efficient, the additional changes to engine operation are
necessitated as a part of the vehicle design implemented to meet the CAFE standard might increase NO\textsubscript{x} emissions to levels above Tier II, bin 5.

Figure 1.5. Crude oil prices in 2010 dollars from 1947 to October 2011 [11]. Source: www.wtrg.com. Figure reprinted with permission.

1.5. Automobile Manufacturers’ Response to Emissions Regulations.
In response to these government standards, the automobile industry has sought solutions to decrease vehicle emissions. The first measures involved “de-tuning” engine operation in which variables such as air to fuel ratios, valve timing, etc., were modified to produce exhaust gases that meet the emission standards. Some of these methods include excess air injection and exhaust gas recirculation. In both of these methods the exhaust gas is diluted and more complete combustion is obtained. Over time, though, the standards could not be met, while at the same time they reduced fuel efficiency. The next measure taken in combating emission levels was the development of the catalytic converter. The
catalytic converter is comprised of a ceramic or metal honeycomb monolith upon which a washcoat is applied. The washcoat contains a high surface material such as alumina or titanium oxide that provides a high surface area for the platinum group metals (PGM) (i.e., platinum, rhodium and or palladium) which catalyze the reaction of the exhaust gases to more desirable products. The first catalytic converters were two-way or oxidation converters that converted CO and HC into CO₂ and water. In a response to lower NOₓ emission standards, three-way or oxidation-reduction converters were developed to also reduce NOₓ to nitrogen. The three-way converters are still in use to this day.

This desire for increased fuel efficiency helped spur the development of the catalytic converter because as mentioned previously, changing engine operation tends to decrease the efficiency of the engine. How an engine operates can be described by the ratio of air to fuel fed to the cylinder. The three possible modes of engine operation are stoichiometric, rich, and lean. Stoichiometric engine operation occurs when the weight ratio of air to fuel is equal to 14.7. This value corresponds to the point at which sufficient air is present to just consume all of the fuel (assuming that combustion of the fuel goes to completion). If the ratio is less than 14.7, the mixture is considered to be fuel-rich, while values greater than 14.7 are considered to be fuel-lean. Figure 1.6 shows how the conversion of pollutant species can vary depending on the air to fuel ratio. Under stoichiometric to rich conditions, high conversions for HC, CO, and NO are possible albeit at the cost of reduced fuel efficiency. Looking at these conversions in the lean range, CO and HC values are still very high while NO conversion plunges to levels well below 50%. This low level of conversion is due to the fact that NO and NO₂ cannot be reduced in an environment containing an excess of oxygen. As the demand from consumers for more fuel efficient vehicles increases and emission regulations concerning NOₓ tailpipe levels become more stringent, the problem of NOₓ reduction during lean burn engine operation will present a larger obstacle for manufacturers to overcome.
1.6. Viable Solutions to Obtain Improved Fuel Efficiency and Meet Emissions Regulations.

The above discussion gives one an idea of what should be expected from an automobile in terms of emissions and fuel efficiency. Currently there are many ultra-low emission vehicles available to the public. These are vehicles that meet the emission standard for Tier 2 Bin 5 for NO\textsubscript{x} levels of less than 0.07 g/mi over the full useful life of the vehicle. For the 2012 model year, there are over 250 spark injected (gasoline) vehicle available that meet or exceed the Tier 2 Bin 5 standard [13]. In addition, several hybrids, electric, and natural gas powered vehicles meet this standard. However, each of these options has drawbacks. Hybrids have the looming cost to replace the battery sets over the useful life of the vehicle. Electric vehicles are limited by driving range. Natural gas vehicles do not yet have the infrastructure to support them.
Light duty diesels (LDDs) present an interesting option due to their high fuel efficiency (up to a 30% increase compared to gasoline engines) [13], while producing significantly lower levels of HC and CO compared to stoichiometric gasoline engines. Due to the air to fuel ratios of ~ 22 (and even as high as 50) at which diesel engines operate, almost none of the NO\textsubscript{x} is converted in the oxygen-rich exhaust which is disappointing considering the advantages (i.e., greater torque and durability) of diesel engines as compared to spark-injected gasoline engines. But what if there were a way to meet NO\textsubscript{x} emission standards while retaining the benefits of diesel engines?


The development of current three way catalysts was the result of the initial efforts by manufacturers to reduce emissions as required by the adoption of the Clean Air Act in 1970 [14]. The first control systems were oxidation catalysts that converted HC and CO to CO\textsubscript{2} and H\textsubscript{2}O to levels mandated by the Clean Air Act. These catalysts consisted of a combination of Pt and Pd supported on either $\gamma$-alumina beads or a honeycomb monolith with a washcoat containing the Pt and Pd supported on $\gamma$-Al\textsubscript{2}O\textsubscript{3} applied to the channels present. This system performed well in oxidizing the desired pollutants but also suffered from sintering of the precious metals due to high operating temperatures and poisoning by Pb that was present in gasoline formulations at the time. For this reason unleaded fuels were developed in the 1970s. Stabilizers such as CeO\textsubscript{2} and La\textsubscript{2}O\textsubscript{3} were added to the washcoat to address the sintering problem.

Towards the end of the 1970s, NO\textsubscript{x} emission standards were lowered further to less than 1.0 g/mi [12]. A new control strategy was needed because NO\textsubscript{x} could not be reduced to N\textsubscript{2} in the present oxidizing system. The initial design consisted of a two stage catalyst in the exhaust manifold with the ability to inject air in between the stages. An upstream catalyst would use CO and HC present to reduce NO\textsubscript{x} to N\textsubscript{2}, and a downstream catalyst would then oxidize the remaining CO and HC remaining in the exhaust. Here additional oxygen would be supplied by air to convert the remaining CO and HC species present after the upstream catalyst.
The next step in the development of the three-way catalyst was the development of oxygen sensors that could provide feedback to the engine during operation. Designers discovered that if the air to fuel ratio was held to stoichiometric conditions (14.7 as shown in Figure 1.6) throughout the engine cycle, NO\textsubscript{x} could be reduced by CO and HC [12]. This system was made possible by the development of sophisticated oxygen sensors that could control engine operation and air input into the exhaust stream. Because the catalyst could convert all three pollutants simultaneously, the name three-way catalytic (TWC) converter was adopted. The components were similar to the first generation converter. Pt oxidized CO and HC while Rh reduced NO\textsubscript{x}. Because of the modulation of the air to fuel ratio around the stoichiometric point, an oxygen storage component was added. High surface area CeO\textsubscript{2} acted as a buffer in the three-way catalyst. CeO\textsubscript{2} provided additional oxygen when remaining reductants (e.g., CO and HC) were present after the NO\textsubscript{x} had been reduced to N\textsubscript{2} and acted as an oxygen storage material when conditions were lean. Again using γ-Al\textsubscript{2}O\textsubscript{3} as a support material, these components were applied as a washcoat to a ceramic, honeycomb material.

From the mid-1980s to the present, the third and then fourth generation catalytic converters were developed [12]. The third generation was necessitated by the desire for increased fuel economy and higher operating speeds. To address fuel economy, fuel was shut off during deceleration events. This change in operation, combined with the higher operating speeds, led to the exposure of the catalyst to highly oxidizing, high temperature conditions. Catalysts were modified by adjusting the locations of the precious metals on the CeO\textsubscript{2} and γ-Al\textsubscript{2}O\textsubscript{3} support, and by adding additional stabilizing materials such as ZrO\textsubscript{2} and La\textsubscript{2}O\textsubscript{3} to reduce the interactions that lead to deactivation at high temperatures. Pd was added to the fourth generation of catalyst in an effort to reduce the cost of using Pt and Rh. While Pd was more cost effective, Pd usage requires separation of the Pd and Rh due the risk of Pd-Rh formation at high temperature, an alloy which displays diminished activity for NO\textsubscript{x} reduction.
In summary, the development of three way converters led to the use of:

- ceramic, honeycomb supports
- precious metals such as Pt, Rh, Rd for the required oxidation and reduction reactions
- addition of stabilizers such as La$_2$O$_3$ and ZrO$_2$
- addition of CeO$_2$ to act as an oxygen buffer during engine operation
- washcoat utilizing $\gamma$-Al$_2$O$_3$ as a support

These innovations would subsequently lead to the catalysts used in current lean-burn applications.

1.6.2. Diesel Emission Control Systems.

The attractiveness of diesel engine applications is attributed to their fuel efficiency relative to gasoline spark-ignited engines. This increased efficiency is a result of the very lean engine operation at air to fuel ratios of greater than 22. While diesel exhaust contains less NO$_x$, CO, and HC species due to lean operating conditions as compared to gasoline engines, high particulate emissions exist. The particulate matter is comprised of dry soot, inorganic oxides, and liquids. If the operation of a diesel engine is changed to lower particulate emissions by increasing the combustion temperatures, more NO$_x$ is produced.

As a response to the initial adoption of the Tier II standards, diesel oxidation catalysts (DOC) and diesel particulate filters (DPF) were added to the exhaust system. The dry soot present as particulate matter is oxidized by NO$_2$ in the exhaust stream. Since NO is the predominate NO$_x$ species from the engine, the NO is oxidized upstream by a DOC such as Pt or Pd on $\gamma$-Al$_2$O$_3$. The reaction sequence is as follows [13]:
NO + ½ O₂ ↔ NO₂
2 NO₂ + C ↔ CO₂ + 2 NO
NO₂ + C ↔ CO + NO

The first reaction occurs in the DOC, and the last two reactions occur in the DPF.

1.6.3. Selective Catalytic Reduction (SCR) Catalysts.
As the Tier II standards were instituted, the more relaxed standards for NOₓ from diesel engines disappeared, as standards for gasoline and diesel had become the same. Once diesel exhaust was treated by the DOC and DPF, most of the CO and HC had been converted to CO₂ and H₂O, whereas the NOₓ had been oxidized to NO₂ and reduced back to NO as the gases passed through the tailpipe. The exhaust gas at this point was a mixture of NO and NO₂ in an oxidized atmosphere. However, the catalytic converters utilized for spark-injected applications were not capable of reducing NOₓ in the oxygen-rich environment. The first solutions to this quandary involved using the hydrocarbons that were present in diesel fuel as a reductant. After an extensive search, several candidate catalysts were proposed. For example, using propene as the HC, NO can be converted to CO₂, H₂O and N₂ over an appropriate catalyst:

C₅H₆ + 2 NO + 7/2 O₂ ↔ 3 CO₂ + 3 H₂O + N₂

Unfortunately, the reductant can be consumed by oxygen, and incomplete reduction of the NO can result in N₂O formation:

C₅H₆ + 9/2 O₂ ↔ 3 CO₂ + 3 H₂O
C₅H₆ + 2 NO + 5/2 O₂ ↔ 3 CO + 3 H₂O + N₂O

Pt and Al₂O₃ is effective in reducing the NOₓ over the Pt sites but only in a very narrow operating window of 180°C to 275°C. This limits the effectiveness of the catalyst as the exhaust temperature can vary from about 150°C to 450°C in diesel exhaust depending on the engine speed and load requirements. Another problem with using Pt/Al₂O₃ in this
application is that Pt catalyzes the reduction of NO\textsubscript{x} to N\textsubscript{2}O, which is a powerful greenhouse gas.

The other approach to NO\textsubscript{x} reduction under lean conditions involves the use of NH\textsubscript{3} as a reductant, the NH\textsubscript{3} being generated on board the vehicle via the hydrolysis of urea. Researchers at Engelhard in 1957 [15] discovered that NH\textsubscript{3} reacts with NO over Pt even in the presence of oxygen, in a reaction termed selective catalytic reduction (SCR). NH\textsubscript{3} is hydrolyzed from urea by:

\[
\text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} \rightleftharpoons 2 \text{NH}_3 + \text{CO}_2 \quad (1.7)
\]

NH\textsubscript{3} is stored on the catalyst and reacts with NO\textsubscript{x} as it is adsorbed from the exhaust stream. How NH\textsubscript{3} reacts with NO\textsubscript{x} is dependent on the exhaust temperature and the ratio of NH\textsubscript{3} and NO\textsubscript{x} on the catalyst surface. The standard SCR reaction involves a 1:1 ratio for NH\textsubscript{3} and NO:

\[
4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightleftharpoons 4 \text{N}_2 + 6 \text{H}_2\text{O} \quad (1.8)
\]

Comparatively without the presence of oxygen, this reaction is much slower and is not relevant under these conditions [16]. Another reaction involving both NO and NO\textsubscript{2} with NH\textsubscript{3} is called “fast” SCR [17,18]:

\[
4 \text{NH}_3 + 2 \text{NO} + 2 \text{NO}_2 \rightleftharpoons 4 \text{N}_2 + 6 \text{H}_2\text{O} \quad (1.9)
\]

NO\textsubscript{x} conversions resulting from these reactions are typically in the range of 80% to 90%. Some deNO\textsubscript{x} performance is lost due to the consumption of NH\textsubscript{3} by oxygen and the conversion of NO\textsubscript{x} to N\textsubscript{2}O as follows [19]:

\[
4 \text{NH}_3 + 5 \text{O}_2 \rightleftharpoons 4 \text{NO} + 6 \text{H}_2\text{O} \quad (1.10)
\]
\[
4 \text{NH}_3 + 4 \text{NO} + 3 \text{O}_2 \rightleftharpoons 4 \text{N}_2\text{O} + 6 \text{H}_2\text{O} \quad (1.11)
\]
Because diesel exhaust has a broad temperature window due to the variation in engine speed and load, it has proven difficult to find a catalyst which can span the entire operating range; as shown in Figure 1.7, different catalysts tend to operate in different temperature regions.

![Figure 1.7. Comparison of three different catalysts for NO\textsubscript{x} reduction with NH\textsubscript{3}. Reprinted from R.H. Heck, R.J. Farrauto, Catalytic Air Pollution Control: Commercial Technology, 2\textsuperscript{nd} Edition, John Wiley and Sons, Inc. New York 2002. Page 206. [13].](image)

Regarding concerns arising from the use of SCR catalysts in this application, NH\textsubscript{3} slip from the catalyst is possible if the correct NO\textsubscript{x}:NH\textsubscript{3} ratios are not maintained on the catalyst, while there is also the possibility of N\textsubscript{2}O production. NH\textsubscript{3} is a respiratory irritant and N\textsubscript{2}O is a well-known greenhouse gas. Finally, the use of a SCR catalyst requires installation of the catalyst, injection and control system, and urea storage tank. All of these add weight to the vehicle which decreases fuel efficiency numbers and adds to the purchase price and maintenance costs.
1.6.4. Lean NO$_x$ Trap (LNT) Catalysts.

An alternative to SCR catalyst is the NO$_x$ storage and reduction (NSR) or Lean NO$_x$ trap (LNT) catalyst. This type of catalyst was developed in the mid-1990s by Toyota and consists of a washcoat containing platinum group metals (PGM), storage materials (alkali or alkaline-earth metals) and a high surface area support ($\gamma$-Al$_2$O$_3$) [20,21]. The LNT is able to reduce NO$_x$ to N$_2$ by operating under two modes of engine operation: lean and periodic switches to rich. The LNT operates by storing NO$_2$ which is formed from NO oxidation on PGM sites during normal lean operating conditions. Before the storage capacity of the trap is reached, the engine operation is switched to net rich conditions upon which the stored NO$_x$ is released and reduced at the PGM sites to N$_2$. The LNT has an advantage over SCR in that an external supply of reductant is not required, since the necessary reducing agents are supplied by modifying the engine operation. This advantage does not add weight or require space on the vehicle.

Although LNTs show great promise as a technology to reduce NO$_x$ emissions from diesel engines to levels that would allow their use in all 50 states, the LNT does have some problems associated with its use. While Tier II standards reduced the amount of sulfur present in diesel fuel from 500 to 15 ppm as previously mentioned, sulfur still presents a hindrance to LNT operation. The most common storage material for LNTs is BaO. Under lean conditions, NO$_x$ is stored at the Ba sites as a mixture of barium nitrates and barium nitrites, the form depending on conditions such as temperature and gas composition at the time of storage. Herein lies the problem. While Ba is an excellent storage material for nitrates and nitrites, Ba has a greater affinity for sulfur. Upon exposure to sulfur that is created during the combustion cycle from the sulfur present in the fuel, SO$_2$ is formed. The resulting BaSO$_4$ is thermodynamically more stable than Ba(NO$_3$)$_2$ [22]. What this means to LNT operation is that high temperatures and long rich durations are required to desulfate the trap. This requirement means that the engine must operate under rich conditions for longer periods, which can negate the fuel savings associated with lean burn engine operation inherent in diesel engines. These higher temperatures can also lead to sintering of the PGMs and side reactions within the washcoat that will reduce the storage capacity of the catalyst. Finally, the cost of the
PGMs render LNT catalysts sometimes cost prohibitive as compared to other emission control technologies.

1.7. Synergy of LNT-SCR Systems.
What if these problems could be solved by modifying the composition and application of LNTs? The scope of this dissertation is to address these issues by suggesting the addition of ceria to the LNT and to use this LNT formulation in conjunction with a SCR catalyst to meet the upcoming emission standards. As will be discussed, this configuration provides a means to deal with the presence of sulfur in the exhaust stream by using ceria to preferentially store SO₂ at ceria sites instead of barium sites. The LNT-SCR system has the potential to eliminate the external supply of reductant by forming NH₃ over the LNT and to reduce the amount of PGM required for the LNT since the end result of the LNT will not be complete conversion of NOₓ to N₂, but rather to supply NH₃ for the SCR catalyst. The addition of the SCR catalyst also solves the problem of NH₃ slipping from the LNT. The most attractive attribute of this synergistic system is that for a given level of NOₓ reduction (with the addition of the SCR) the volume of the LNT catalyst, and hence the amount of PGMs and their associated cost, can be reduced.

The research reported in this dissertation has three aims: 1) to gauge the effectiveness of ceria to act as a sulfur sink and to reduce the sintering of PGM in LNT catalysts; 2) to demonstrate the effects of catalyst composition on the NH₃ selectivity of LNT catalysts during regeneration; and finally 3) to test a model designed to predict product selectivity from a LNT catalyst loaded with a fixed amount of stored NOₓ. Since HC and CO emissions are already low in lean burn applications, the focus of this dissertation will be on technologies capable of reducing NOₓ levels in lean burn engine exhaust.

The next chapter in this dissertation provides the essential background information concerning LNT composition and the chemistry involved during their operation.
Chapter 3 examines the effect of ceria incorporation on sulfation and aging of LNT catalysts. The addition of ceria to LNTs is a response to the problems that the sulfur content in fuels and engine oil presents. Ceria provides an alternative to Ba storage sites for sulfur adsorption during lean operation thereby helping to preserve NO\textsubscript{x} storage capacity. Additionally, ceria has the ability to reduce sintering of the PGM sites by limiting agglomeration of the precious metals that occurs during high temperature events, i.e., during desulfation of the catalyst.

Chapter 4 examines at the effects of washcoat composition on LNT aging characteristics. LNT catalysts with varying amounts of precious metals and storage components are exposed to sulfur and to high temperatures to see how NO\textsubscript{x} conversion and selectivity to NH\textsubscript{3} change in response to aging.

The objective of chapter 5 was to understand the factors governing NH\textsubscript{3} formation (and consumption) in LNTs, including the state of catalyst with respect to aging and the oxygen storage capacity (OSC) of the catalyst.

In chapter 6, the results of an experiment studying the reduction selectivity obtained from a fixed amount of NO\textsubscript{x} stored on a LNT are compared to a model derived to predict these results. Modeling is essential in the design of a LNT-SCR system that promotes NH\textsubscript{3} formation in the LNT while reducing PGM content.

Finally, in chapter 7, all of the significant findings from this work are summarized along with suggestions for future work on this subject. Additionally, the most common abbreviations used throughout this dissertation are included in Appendix 1. Lastly, Appendix 2 contains the derivation of the balances used by the model.

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Chapter 2. Lean NO\textsubscript{x} Trap Catalysts: Design and Operational Considerations.

Lean NO\textsubscript{x} Traps (LNTs) were developed by Toyota in the mid-1990s as a means to achieve higher fuel efficiency while reducing NO\textsubscript{x} (NO + NO\textsubscript{2}) emissions that are inherit in the use of lean burn, diesel engines [1,2]. The amount of CO\textsubscript{2} emitted from a diesel engine is less than a similar sized spark-injected gasoline engine (in terms of power output) due to the increased thermodynamic efficiency the diesel possesses [3]. The principle behind the use of these LNT catalysts is that NO\textsubscript{x} is stored during lean operation (the engine exhaust contains stoichiometrically excess oxygen). Concurrently, any hydrocarbons (HCs) and CO in the exhaust are oxidized over the platinum group metals (PGMs) to CO\textsubscript{2} and H\textsubscript{2}O. Before the maximum NO\textsubscript{x} storage capacity of the LNT catalyst is reached, the engine operating conditions are adjusted such that the engine exhaust is net rich. At this point the stored NO\textsubscript{x} is released and then reduced to nitrogen. Other N-species, such as NH\textsubscript{3} and N\textsubscript{2}O, are also potential products depending on the temperature and composition of the exhaust and duration of the rich event. The length of the lean and rich phase is dependent on the operating regime of the engine, the quality of the fuel, and the operational history of the LNT catalyst.

2.1.1. Cordierite Substrate.

The design of the LNT catalyst is comprised of four main components: substrate, support, storage material, and PGMs. The LNT may also include certain additives to improve catalyst performance. The main function of the substrate is to provide a high surface area material that possesses mechanical and thermal durability upon which a washcoat containing the other ingredients can be applied. The most common substrate used today is synthetic cordierite, 2MgO·2Al\textsubscript{2}O\textsubscript{3}·5SiO\textsubscript{2}. Cordierite mainly consists of kaolin (Al\textsubscript{2}O\textsubscript{3}·SiO\textsubscript{2}·2H\textsubscript{2}O), talc (3MgO·4SiO\textsubscript{2}·H\textsubscript{2}O) and alumina (Al\textsubscript{2}O\textsubscript{3}) that are ground, blended, and extruded into a paste. The cordierite is usually configured as a honeycomb monolith which provides a high surface area to volume ratio (e.g., 852 ft\textsuperscript{2}/ft\textsuperscript{3}) [4]. The honeycomb monolith also has a low pressure drop across the catalyst which eliminates the risk of creating a back pressure to the engine. Cordierite also possesses the
necessary mechanical and thermal properties required for operation of a catalyst located down-stream of an internal combustion engine. The low thermal expansion coefficient of cordierite (10*10^-7/°C) makes it resistant to cracking when cycled over a wide temperature range [4]. The mechanical axial strength of over 3000 psi is required for operation underneath an automobile. Moreover, the melting point of greater than 1300°C is well above the operating range of a LNT [5].

2.1.2. Catalyst Support.

A washcoat that contains PGMs, NO\textsubscript{x} storage materials, and catalyst support is applied to the cordierite monolith. Different types of supports, such as TiO\textsubscript{2}, SiO\textsubscript{2}, ZrO\textsubscript{2}, CeZrO\textsubscript{2}, TiO\textsubscript{2}-ZrO\textsubscript{2}, CeO\textsubscript{2}, and γ-Al\textsubscript{2}O\textsubscript{3}, have been studied by several groups. Each of these materials behaves differently with the other catalyst components with regards to performance under different operating regimes. Johnson et al. stated a simple goal for all catalyst supports: to provide a durable, high surface area to aid in the maintenance of the dispersion of the metallic promoters or PGMs [7]. Using this as a metric, γ-Al\textsubscript{2}O\textsubscript{3} was used as the support in all of the catalysts studied for this dissertation. Since the goal of this research effort was to look at the addition and the variation of different catalyst components, the use of γ-Al\textsubscript{2}O\textsubscript{3} as a support is ideal because γ-Al\textsubscript{2}O\textsubscript{3} is a well-known support material that has been utilized in three-way catalytic (TWC) converters, oxidation catalysts, and even in the first SCR catalysts. Additionally, the results of a study by Fekete et al. [8] studying TiO\textsubscript{2}, ZrO\textsubscript{2}, and γ-Al\textsubscript{2}O\textsubscript{3} revealed that γ-Al\textsubscript{2}O\textsubscript{3} is the most suitable support because TiO\textsubscript{2} and ZrO\textsubscript{2} have high reactivity with the Ba storage component which can lead to unwanted side reactions within the washcoat.

The properties of γ-Al\textsubscript{2}O\textsubscript{3} (surface area, pore size distribution, surface acidic properties and crystal structure) depend on its preparation, purity, and thermal history [4]. A high surface area is created by heat-treating or calcining in air, typically at about 500 °C, where a network is formed from Al\textsubscript{2}O\textsubscript{3} particles 20-50Å in diameter which bond together, forming polymer-type chains. As temperature is increased between the ranges in which a given Al\textsubscript{2}O\textsubscript{3} crystal structure is stable, there is gradual dehydration, which causes an irreversible loss in physical surface area and loss in its surface hydroxyl or Brønsted acid.
sites. Continued heating causes a complete transformation to another crystal structure with a continuing loss in physical surface area and surface OH⁻ groups. This transformation is shown by the following [3]:

Boehmite:  \( \gamma \)-monohydrate (500-850 °C), internal surface area 100-200 m²/g →
\( \delta \)-monohydrate (850-1050 °C) → \( \theta \)-monohydrate (1050-1150 °C) →
\( \alpha \)-monohydrate (>1150 °C), 1-5 m²/g

As shown, \( \gamma \)-Al₂O₃ is the structure that is most attractive for use as a support for an LNT because it exists in the operating temperature window of diesel engine operation (150 °C to 500 °C) and possesses the highest surface area. \( \gamma \)-Al₂O₃ with Pt and Ba species impregnated on the surface has a surface area of ~150 m²/g [4]. The surface of \( \gamma \)-alumina is covered in OH⁻ groups onto which storage material and precious metals are applied.

To improve certain properties such as thermal durability and bonding with the support and PGM materials, different additives have been added to \( \gamma \)-Al₂O₃. This addition is also known as doping. Schaper et al. and Pijolat et al. [9,10] pointed to two phenomena as being responsible for the loss of surface area at high temperatures (>900 °C): initial sintering due to the collapse of micropores and phase transformation from \( \gamma \)-Al₂O₃ into \( \alpha \)-Al₂O₃. Schaper et al. [11] believed the transformation from the \( \gamma \) to the \( \alpha \) phase proceeded via a surface diffusion of the oxygen ions changing the crystal lattice from a cubic to a hexagonal closed packed structure. To add additional thermal stability to the \( \gamma \)-Al₂O₃ support, lanthanum was added. Lanthanum oxide, La₂O₃, decreases the sintering of \( \gamma \)-Al₂O₃ by formation of lanthanum aluminate, LaAlO₃, on the \( \gamma \)-Al₂O₃ surface [11,12]. The addition of the La₂O₃ was found to postpone the phase transformation by 100°C by promoting the rate of nucleation of cubic LaAlO₃ on the \( \gamma \)-Al₂O₃ surface and thereby inhibiting the surface diffusion of species responsible for sintering [13].

2.1.3. NOₓ Storage Materials.
As the name suggests, the main function of the NOₓ storage material in LNTs is to store NOₓ during lean engine operation. NO₂ has been shown to be preferential to NO for
storage; this will be discussed later in this chapter in the section describing the mechanisms inherent in LNT operation. As the basicity of the storage material increases, so does its ability to store NO$_x$ [14-19]. For this reason, either alkali metals (Na, K, Cs) or alkaline earth metals (Mg, Ca, Sr, Ba) or combinations of these are used as storage materials. The criteria for determining which material is the best choice include a number of factors such as NO$_x$ storage capacity, NO$_x$ conversion, stability in the washcoat, and sulfur resistance. Many of these desired properties are determined by the basicity of the storage material. In order of increasing basicity, the metals follow the order: Mg $\leq$ Li $<$ Ca $<$ Na $\leq$ Sr $<$ Ba $<$ K $<$ Cs [19,20]. While Cs has the highest basicity of this list of metals, the HC conversion performance is the worst, which eliminates it as a suitable choice [19]. Han et al. compared Pt/Al$_2$O$_3$ catalysts that contained BaO, CaO, or SrO. Overall, BaO and SrO showed the highest NO$_x$ storage capacity, but BaO showed the best NO$_x$ conversion [21].

Although most of the literature uses BaO as the storage component, K has been the subject of increasing research. For diesel exhaust applications, the use of K has some drawbacks. Light duty diesels (passenger cars and light trucks) have exhaust temperatures between 100 and 500 °C depending on operating load and engine speed. Looking at the NO$_x$ storage capacity, Ba and K have two different temperature ranges for maximum efficiency. BaO has a higher NO$_x$ storage capacity below 400 °C, and K has a higher capacity above 400 °C [19]. Gill et al. postulated that the increased performance of K at a higher temperature was attributed to the increased stability of the nitrates formed by alkali metals [22]. Conversely, the low temperature NO$_x$ conversion was less than that of BaO due to K inhibiting the formation of NO$_2$. Another factor in determining whether K is suitable as a storage material is the water solubility of KNO$_3$. Moreover, K has the potential to react with the cordierite substrate that is common in most auto catalyst applications. The mobility of K due to its affinity for water makes maintaining K sites in the desired location on the catalyst support problematic. Additionally, as will be discussed, the formation of sulfates follows the same general mechanism as nitrates with the resulting sulfates having a greater thermodynamic stability on the LNT. On account of this, the nitrates stored at K sites are more stable than the ones stored at Ba sites;
similarly, the sulfate stored on K sites is more difficult to remove than sulfates associated with Ba. The results of the increased efforts required to remove sulfates from K are longer rich periods and/or the necessity of increased reductant concentrations. This change decreases the potential fuel savings gained by the selection of a diesel engine. The implications of sulfur for LNTs will be discussed shortly.

Lastly, it is worth mentioning that the choice of the storage component will affect the product selectivity during regeneration of the LNT. Studies by Castoldi et al [23] and Lesage et al. [24] have shown that the selectivity to N₂ is higher while the NOₓ “puff” is smaller from catalysts using K versus Ba (the NOₓ “puff” phenomenon will be discussed below).

In light of the above discussion and following the suggestions from Miyoshi et al [1], BaO seems to be the best choice for use a NOₓ storage material. As with the choice of γ-Al₂O₃ as the catalyst support, because Ba-based storage materials have been thoroughly researched, they represent a good choice when studying the addition of other components and the modification of the PGMs. Ba is present in the LNT as BaO, Ba(OH)₂, and/or BaCO₃, depending on the composition of the exhaust stream [14]. In most of the experiments discussed in this dissertation, CO₂ and H₂O were present, so all three types of Ba-compounds would be expected to be present on the catalyst surface at the end of the rich phase. During the subsequent lean phase as NOₓ is preferentially stored at the BaO and Ba(OH)₂ sites, the majority of the sites available for storage will be BaCO₃. An exception was a set of the experiments described later in this dissertation which deal with the modeling of the release of a fixed amount of NOₓ from different catalysts, in which CO₂ and H₂O were excluded. Because of that, the form of Ba could be identified as Ba(OH)₂ (due to the use of hydrogen during the rich phase). According to Lietti et al [14], NO₃ storage occurs first at the BaO sites, followed by Ba(OH)₂ and BaCO₃, in line with the higher basicity of the former compound.
2.1.4. Platinum Group Metals (PGM).

The final ingredient of LNTs consists of the PGM component: platinum, rhodium, and palladium. While there have been many different studies on PGMs in three-way catalysts and LNTs, one common finding is that these metals behave differently under varying feed gas streams and reaction conditions. The choice of which PGM to use depends on the metal’s chemistry during lean and rich operation. During the lean phase, the PGM must be able to oxidize NO to NO$_2$ that will subsequently spillover to the storage sites. Under rich conditions, the PGMs must adsorb reductants such as CO, H$_2$, and HC as well as to provide sites close to the stored nitrates and nitrites which can dissociatively adsorb NOx as part of a reverse spillover mechanism. Pt is the primary choice for oxidation of NO, but Rh and Pd are more active for NO$_x$ reduction [25-28]. Moreover, Kobayashi et al. showed that a combination of Pt/Rh had a higher trapping activity than either Pd/Rh or Pd [20]. Additionally, Theis et al. reported that a combination of Pt and Rh had the best overall NO$_x$ conversion at low temperatures (250°C) for fresh and aged catalysts as compared to Pt only samples [29]. Theis proposed the Rh increased reduction capability and also enhanced the purging of the trap by creating a concentration gradient between the catalyst surface and the exhaust that promoted the decomposition of the stored NO$_x$ and a more thorough purge [29]. The gradient was created by the ability of Rh to promote the thermodynamic instability of NO$_3^-$ stored on the catalyst at the Ba sites by more efficiently removing the NO$_x$ in the gas phase. Lastly, Amberntsson et al. showed that an alloy of Pt and Rh increased the overall efficiency of the NO$_x$ storage catalyst despite storing a lower amount of NO$_x$ than a Pt-only catalyst [27].

2.2. Mechanisms Involved LNT Catalysis.

Although a large number of experimental studies have focused on determining the mechanisms involved when using a LNT catalyst to convert NO$_x$ to N$_2$, a precise, definitive mechanism still proves elusive. Fortunately, the following series of steps are both accepted in the catalysis community and provide enough description to enable one to gain a well-informed idea of how an LNT catalyst is operated. The discussion will be focused on the type of catalysts used in the experiments that will be presented in the later chapters, rather than involving all of the different combinations of PGMs, storage
materials, supports, and reductants that have been presented in the literature. Arguments have already been made for why different catalyst components are preferred, and the effects of gases present in the exhaust during the lean and rich phases will be presented as the different steps are explained.

The steps involved in the operation of LNTs are [30,32]:

1. NO oxidation to NO$_2$ on Pt,
2. NO$_x$ (NO+NO$_2$) storage on BaO on the catalyst surface
3. Reductant evolution,
4. NO$_x$ release from the trapping site,
5. NO$_x$ reduction to N$_2$.

Although many authors agree on these five steps, the details about each step, particularly steps 1 and 2, are subject to debate.

2.2.1. Oxidation of NO to NO$_2$.

The oxidation of NO to NO$_2$ is a very important step in the operation of most aftertreatment systems. LNTs are based on NO$_x$ present in the form of NO$_2$ for efficient trapping to occur [6,33-38]. As will be discussed in section 2.2.2., most trapping metals as described previously more effectively adsorb NO$_2$ as compared to NO [6]. Therefore, the more efficiently a LNT can oxidize NO to NO$_2$, the greater the potential NO$_x$ storage capacity.

The oxidation of NO to NO$_2$ is affected by the temperature and composition of the exhaust stream and the state of the PGMs on the catalyst. The oxidation reaction is subject to limitations based on temperature. At low temperatures (below 250 °C), the reaction is kinetically limited from reaching equilibrium. As the temperature is increased (> 200 °C), the process changes from one that is limited by kinetics to one that is limited by the thermodynamic equilibrium that exists between NO, O$_2$, and NO$_2$. Where the equilibrium occurs is dependent on the temperature, oxygen concentration, and space velocity of the LNT. The space velocity can create kinetic limitations that prevent the
reaction from reaching equilibrium. The equilibrium will shift to higher temperatures as
the concentration of O2 increases. Mahzoul et al. [32] noticed that the NO\textsubscript{x} storage
capacity of a Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst increased as O2 concentration was increased from 0
to 3%, but above 3% no additional effect was observed. As the space velocity or
residence time of the system increases, not only does the temperature required to reach
equilibrium increase (the increase in temperature is required to overcome limited
kinetics), but the equilibrium conversion at that temperature decreases. Above this
temperature, the oxidation of NO is under thermodynamic control, and below it, the
process is kinetically controlled. The integral nature of LNTs presents an additional
factor influencing when or if equilibrium can be reached, since as NO\textsubscript{2} is produced and
stored on the catalyst, the equilibrium is shifted towards additional NO\textsubscript{2} production [39].

As previously discussed, Pt has unparalleled NO oxidation capacity [25-27,35]. In the
literature, NO oxidation is studied using Pt and a support (γ-Al\textsubscript{2}O\textsubscript{3}) or with a model or
fully formulated LNT containing Pt and a storage material such as Ba on a support (γ-
Al\textsubscript{2}O\textsubscript{3}). The amount and dispersion of Pt and the interaction between Pt and γ-Al\textsubscript{2}O\textsubscript{3}
impacts the kinetics of NO oxidation. Lee et al. [40] noted that higher dispersions (i.e.,
smaller particles) did not always lead to higher NO oxidation rates. Indeed, Pt particles
with lower exposed surface areas generally exhibit increased catalytic activity for NO
oxidation. Olsson et al. [41] similarly noted that after aging while the onset of oxidation
was unaffected, the rate of NO oxidation increased. This is consistent with Lee, given
that thermal aging results in Pt particle sintering [42-44]. Pt oxides are present as a
surface layer on the Pt particles [41]. Smaller particles of Pt are more likely to form PtO\textsubscript{x}
relative to larger particles [45]. This occurrence is one reason why catalysts are subjected
to slightly elevated temperatures (≥500 °C) under neutral conditions before using them in
experiments and real-world applications. After the particles become larger, it is less
likely that PtO\textsubscript{x} will form, and catalyst performance is improved. Mulla et al. observed a
4-fold increase in the NO oxidation turnover rate (TOR) for a sintered catalyst as
compared to a fresh one [46]. This observation, TOR increasing with increasing Pt
particle size, is supported in the literature [40,41,47-49].
The presence of Ba has the ability to reduce the activity of the Pt particles due to the potential for increased formation of Pt oxides during lean periods of operation. Many authors have reported that the presence of Ba in a Pt/BaO/Al₂O₃ LNT decreases the rate of oxidation reactions over Pt as compared to a Pt/Al₂O₃ catalyst [30,41,50-53]. The high surface coverage by oxygen prevents the adsorption of NO on Pt. Indeed, the presence of Ba decreases the NO oxidation activity of Pt as compared to a Ba-free catalyst for the following possible reasons. First, during the preparation by impregnation of the catalyst, some of the Pt might dissolve into the Ba phase. If the Pt dispersion is decreased due to Ba masking Pt, the activity for the oxidation of NO will decrease. Second, as NO₃ is stored at the Ba sites, some of the Pt sites might become sterically hindered by the resulting Ba(NO₃)₂, since the molar volume of Ba(NO₃)₂ is 3 times larger than that of BaO [30]. The final possible reason for the decrease in activity caused by the presence of Ba is proposed by Yoshia et al. Yoshia considered the acidity or alkalinity of the support by noting that if the support was acidic, Pt oxide formation was suppressed [52]. In a Pt/Al₂O₃ catalyst, the γ-Al₂O₃ is electrophilic and electrons are donated from the outer band in the Pt atoms to the support. When Pt oxides are formed, electrons are transferred from the Pt to the oxygen. With an acidic support, there is a lower electron density in the Pt present, and the formation of the oxides is suppressed. When added, the alkalinity of BaO decreases some of the acidic nature of the support so that there are more available electrons for the formation of PtOₓ [52]. Olsson and Fridell [41] did indeed observe from XPS data that after exposure to NO₂, Pt/BaO/Al₂O₃ had a higher occurrence of PtOₓ than Pt/γ-Al₂O₃.

An additional source of chemisorbed oxygen is NO₂ itself. NO₂ is an effective source of atomic oxygen because of its high sticking coefficient. The chemisorbed oxygen prevents the adsorption of other species thereby inhibiting the NO oxidation reaction [54,55].

The different components, Pt, NO, NO₂, and O₂, have been discussed in terms of their contributions to the oxidation of NO over Pt. Turning to the mechanism involved on the catalyst surface, some debate exists in the literature as to which type of mechanism is
occurring. Olsson et al. [39] first proposed the oxidation of NO over Pt followed an Eley-Rideal (ER) mechanism that contained the following adsorption and desorption steps:

\[
\begin{align*}
O_2 (g) + 2 \text{Pt} & \leftrightarrow 2 \text{O-Pt} \quad (2.1) \\
\text{NO} (g) + \text{Pt} & \leftrightarrow \text{NO-Pt} \quad (2.2) \\
\text{NO}_2 (g) & \leftrightarrow \text{NO}_2\text{-Pt} \quad (2.3)
\end{align*}
\]

and the reversible oxidation step [56]

\[
\begin{align*}
\text{NO} (g) + \text{O-Pt} & \leftrightarrow \text{NO}_2\text{-Pt} \quad (2.4)
\end{align*}
\]

Olsson noted that ER was preferred to a Langmuir-Hinshelwood (LH) NO oxidation step:

\[
\begin{align*}
\text{NO-Pt} + \text{O-Pt} & \leftrightarrow \text{NO}_2\text{-Pt} + \text{Pt} \quad (2.5)
\end{align*}
\]

since a high oxygen coverage in (2.5) hinders a high NO\textsubscript{2} formation rate, and Olsson’s experimental results did not indicate that NO oxidation will be self-poisoned by a high coverage. Conversely, Mahzoul et al [32] suggested a LH mechanism occurring at Pt sites close to the Ba storage sites as follows:

\[
\begin{align*}
\text{NO} + \text{Pt} & \leftrightarrow \text{NO-Pt} \quad (2.6) \\
\text{NO}_2 (g) & \leftrightarrow \text{NO}_2\text{-Pt} \quad (2.7) \\
O_2 (g) + 2 \text{Pt} & \leftrightarrow 2 \text{O-Pt} \quad (2.8)
\end{align*}
\]

The actual oxidation of NO\textsubscript{x} is discussed in section 2.2.2.3.

Later, Olsson et al. [30] considered that either ER, LH, or a combination of ER and LH mechanisms might be occurring. The initial adsorption steps for NO, NO\textsubscript{2}, and O\textsubscript{2} are the same as in the previous report, but now Olsson considers the LH and ER mechanisms for adsorbed NO and NO\textsubscript{2} reacting with chemisorbed oxygen on the Pt sites:
LH: \[ \text{Pt-NO + Pt-O} \leftrightarrow \text{Pt-NO}_2 + \text{Pt} \] (2.9)

ER: \[ \text{NO (g) + Pt-O} \leftrightarrow \text{Pt-NO}_2 \] (2.10)

For the model using LH and ER mechanisms, both of the above reactions (2.9 and 2.10) would be involved. Although all 3 of these possibilities provided satisfactory fits for their data, Olsson decided that a LH mechanism would be more probable based on reasoning by Bartram [57]. Bartram stated that \( \text{NO}_2 \) should be bridge bonded to decompose to NO and oxygen on the Pt surface. This implies that \( \text{NO}_2 \) would require two Pt sites to decompose, making a LH mechanism most probable. Nova et al. [58] also favored \( \text{NO}_x \) adsorption and oxygen dissociation over Pt (LH), while Muncrief et al. [46] also used Langmuir-Hinshelwood and Eley-Rideal mechanisms for these steps.

From the literature, evidence is given in support of each of these scenarios that describe NO oxidation over Pt. The LH mechanism is probably the most likely to occur for the reasons suggested by Bartram. The most important aspect of this step is that \( \text{NO}_2 \) is formed and adsorbed at the Pt sites.

2.2.2. Storage of NO<sub>x</sub> at BaO Sites.

Mechanisms presented in the literature agree on the following:

1. \( \text{NO}_2 \) is preferred to NO for storage at the BaO sites.
2. BaO, Ba(OH)<sub>2</sub>, and BaCO<sub>3</sub> are present on the catalyst surface.
3. \( \text{NO}_x \) stored as Ba(NO<sub>3</sub>)<sub>2</sub> is more stable than Ba(NO<sub>2</sub>)<sub>2</sub>; as temperatures and storage times increase, Ba(NO<sub>2</sub>)<sub>2</sub> is eventually oxidized to Ba(NO<sub>3</sub>)<sub>2</sub> as the oxidation state of N is increased from 3<sup>+</sup> to 5<sup>+</sup>.
4. Proximity of Pt to Ba is critical for efficient storage on the LNT.

In general, there is no consensus on the following:
1. After NO is oxidized over Pt, does it travel to the Ba sites on the catalyst surface as an adsorbed species or does it desorb from Pt and readsorb onto Ba from the gas stream?
2. While chemisorbed oxygen is necessary in every mechanism, is the oxygen supplied by spillover from the Pt sites, or is it supplied by NO₂ or through BaO₂? This point will be discussed later in this chapter.

2.2.2.1. Effects of Components in the Engine Exhaust.

The components present in the engine exhaust influence the storage of NOₓ and the phase of the Ba storage component. Two potentially reactive components that are present in large quantities (5 to 10 vol%) in the exhaust gases from diesel engines are CO₂ and H₂O. Although γ-Al₂O₃ is capable of NOₓ storage [32,36,59-62], the presence of H₂O in the gas stream reduces NOₓ storage on the γ-Al₂O₃ support. Without H₂O present, researchers [32,59-63] have estimated that between 1% and 8% of the NOₓ stored on the LNT is stored on the γ-Al₂O₃ support. Toops [64] reported a decrease of 92% of NOₓ stored on γ-Al₂O₃ when H₂O was present. The reason for this decrease is due to the presence of molecular H₂O on the γ-Al₂O₃ which hinder the NOₓ sorption process by limiting the amount of storage sites available. Since H₂O is present in the experiments that will be discuss in the later chapters in this dissertation, the remaining summary on NOₓ adsorption and desorption will focus on the Ba component.

2.2.2.2. Identity of Ba Storage Component.

Although the Ba component in most mechanisms is assumed to be BaO, when H₂O and CO₂ are present, Ba(OH)₂ and BaCO₃ co-exist on the catalyst support. The impact of these three phases can be realized by comparing their basicities. Lietti [14,65] ranked the following compounds involving Ba in order of increasing basicity, which is also a ranking of the stability of the Ba component on the catalyst.

\[
\text{BaO} < \text{Ba(OH)}_2 < \text{BaCO}_3 < \text{Ba(NO)}_2 < \text{Ba(NO}_3)_2 < \text{BaSO}_4
\]
BaSO₄ is formed when sulfur is present in the gas stream and will be discussed later in this chapter. NOₓ adsorption occurs at the Ba components that are the least stable first. As such, NOₓ is stored preferentially at the BaO sites, followed by Ba(OH)₂, and finally at BaCO₃ sites. Evidence for the type of Ba compound present is provided by Lietti et al. [14] from NOₓ storage experiments. A LNT was regenerated with varying amounts of CO₂ and H₂O present in the gas feed. Whether or not CO₂ or H₂O was present during the regeneration determined the duration of the delay before NOₓ slip occurred. NOₓ slip occurred the earliest when regeneration was performed in dry air (CO₂, no H₂O). Under these conditions, the Ba storage component would be expected to be BaCO₃. This was in line with the negative effect that CO₂ has on NOₓ storage [14,64,66,67]. When the LNT was regenerated with H₂ only, NOₓ slip occurred later with less CO₂ produced as the stored NOₓ displaced the OH⁻ and CO₃²⁻ species present in the Ba compounds. During this step the BaCO₃ compounds are gradually becoming Ba(OH)₂. As this transition occurred, the increase in the amount of Ba(OH)₂ accounted for an increase in NOₓ storage. Finally (once again with H₂ only) NOₓ slip occurred even later with more H₂O and almost no CO₂ produced. At this point in the experiment, nearly all of the BaCO₃ sites had become Ba(OH)₂. In the last two cases, H₂O reduced the impact of CO₂ by converting the BaCO₃ species into Ba(OH)₂.

\[
\text{BaCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ba(OH)}_2 + \text{CO}_2 \quad (2.11)
\]

The trends seen in this set of experiments follow the reported thermodynamic predictions in the literature [2,14, 20,66,68]. Although not present during regeneration, CO has a similar effect as CO₂ is produced, according to eqn. (2.12) [31]

\[
\text{CO} + \text{NO}_2 \leftrightarrow \text{CO}_2 + \text{NO} \quad (2.12)
\]

The presence of CO results in an increase in the concentration of NO according to (2.12). This reaction reduces the trapping efficiency of the LNT. The ratio of the two depends on the duration and temperature of NOₓ storage.
The increased stability of Ba(NO$_2$)$_2$ and Ba(NO$_3$)$_2$ compared to BaO and Ba(OH)$_2$ is a desired result because NO$_x$ stored as nitrites and nitrates will remain at the Ba sites during lean conditions, rather than being replaced by other species; conversely, the stability of BaSO$_4$ means that sulfur compounds will preferentially store at the Ba sites. As discussed later, BaSO$_4$ leads to a decrease in the available Ba sites for NO$_x$ storage over time. Ultimately, the storage capacity of the LNT is compromised.

In summary, NO$_x$ is stored as nitrites and nitrates at BaO, Ba(OH)$_2$ and BaCO$_3$ sites, in that order. Individually, CO$_2$ and H$_2$O have a negative effect on NO$_x$ storage because the resulting Ba phase is more stable than BaO; this degrades NO$_x$ storage efficiency. When CO$_2$ and H$_2$O are both present in the exhaust stream, the negative effects of CO$_2$ are reduced because the BaCO$_3$ sites can be hydrolyzed to Ba(OH)$_2$.

2.2.2.3. Mechanisms of NO$_x$ Storage.
Based on the preceding discussion, only BaO storage sites will be considered hereafter in order to simplify the discussion of the mechanisms in operation during the storage of NO$_x$ on a LNT. Additionally, it should be noted that the formation of nitrates is favored over nitrites given that the range of temperatures studied in the experiments discussed in later chapters was 200 °C to 300 °C. Nitrites are reported to be present from 150 °C to 200 °C [62,68] and at the beginning of the storage process [32,69-72]. The likelihood of the presence of nitrates at higher temperatures is due either to oxidation of the nitrites being easier as temperatures increase or to nitrites being more unstable than nitrates at these temperatures with respect to decomposition [32,36,62,69-74].

The storage of NO and NO$_2$ formed from the oxidation of NO over Pt is thought to be a sequential process [5,30,75-77]. Fridell et al. [39] described the NO$_x$ adsorption process in 3 steps. NO$_2$ formed at the Pt sites is at first loosely adsorbed on BaO as a BaO-NO$_2$ species, and then BaO-NO$_2$ decomposes to BaO$_2$, a peroxide, and NO which is released to the gas phase:
\[
\begin{align*}
\text{BaO} + \text{NO}_2 & \leftrightarrow \text{BaO-NO}_2 & \text{(2.13)} \\
\text{BaO-NO}_2 & \leftrightarrow \text{BaO}_2 + \text{NO} & \text{(2.14)}
\end{align*}
\]

The BaO\textsubscript{2} would ultimately react with NO\textsubscript{2} in the gas phase to produce Ba(NO\textsubscript{3})\textsubscript{2}

\[
\text{BaO}_2 + 2 \text{NO}_2 \leftrightarrow \text{Ba(NO}_3)_2 & \text{ (2.15)}
\]

While this mechanism does explain the NO\textsubscript{x} slip that is seen during storage and has been suggested by other authors as an intermediate step [71,78-80], direct experimental evidence for the Ba-peroxide has yet to be found [81].

Mahzoul et al. proposes that two kinds of sites are present [32]. Pt particles close to BaO crystallites (sites 1) are responsible for nitrate formation (* denotes adsorbed species). Continuing from the previous discussion of Mahzoul’s study, eqn. (2.6) through (2.8):

\[
\begin{align*}
\text{O}_2 + 2 \text{Pt}_1 & \leftrightarrow 2 (\text{O}^*)_1 & \text{(2.6)} \\
\text{NO} + \text{Pt}_1 & \leftrightarrow (\text{NO}^*)_1 & \text{(2.7)} \\
\text{NO}_2 + \text{Pt}_1 & \leftrightarrow (\text{NO}_2^*)_1 & \text{(2.8)} \\
\text{BaO} + 2 (\text{NO}^*)_1 + 3 (\text{O}^*)_1 & \leftrightarrow \text{Ba(NO}_3)_2 & \text{(2.16)}
\end{align*}
\]

Or

\[
\begin{align*}
\text{BaO} + 2 (\text{NO}_2^*)_1 + (\text{O}^*)_1 & \leftrightarrow \text{Ba(NO}_3)_2 & \text{(2.17)}
\end{align*}
\]

Pt sites far from the Ba crystallites (sites 2) allow the Pt to behave as an oxidation catalyst, forming nitrites.

\[
(\text{NO}^*)_2 + (\text{O}^*)_2 \leftrightarrow (\text{NO}_2^*)_2 & \text{ (2.18)}
\]

Kabin et al. 77, Kromer et al.84, Bhatia et al.85, Cant el al. and Kwak et al 86 have also postulated proximity theories [75, 82-84].
Lietti et al. [14] also proposed two pathways for this series of reactions to occur but differed from Mahzoul by exploring whether or not NO is adsorbed or is first oxidized to NO₂. If NO is adsorbed at Pt sites close to BaO, then the following occurs with oxygen again being dissociated over Pt:

\[
\begin{align*}
\text{BaO} + \text{O}^* + 2 \text{NO} & \leftrightarrow \text{Ba(NO}_2\text{)}_2 \quad (2.19) \\
\text{Ba(NO}_2\text{)}_2 + 2 \text{O}^* & \leftrightarrow \text{Ba(NO}_3\text{)}_2 \quad (2.20)
\end{align*}
\]

If NO is oxidized to NO₂ at Pt sites close to BaO sites first, then:

\[
\begin{align*}
\text{NO} + \frac{1}{2} \text{O}_2 & \leftrightarrow \text{NO}_2 \quad (2.21) \\
\text{BaO} + 2 \text{NO}_2 + \text{O}^* & \leftrightarrow \text{Ba(NO}_3\text{)}_2 \quad (2.22)
\end{align*}
\]

If the reaction sequence provided by Olsson [30] is continued (in which NO oxidation occurs either by ER, LH, or ER-LH mechanisms), then NOₓ is stored on the Ba component by NO or NO₂ spilling over from the Pt sites as opposed to adsorbing on the surface directly from the gas phase:

\[
\text{Pt-NO}_2 + \text{BaO-(NO}_3\text{)} \leftrightarrow \text{Ba(NO}_3\text{)}_2 + \text{Pt} \quad (2.23)
\]

The other possibility of NOₓ storage would involve NO being adsorbed on the oxidized BaO sites:

\[
2 \text{NO} \text{(g)} + \text{O-BaO} \leftrightarrow \text{Ba-(NO}_2\text{)}_2 \quad (2.24)
\]

Similarly, adsorbed NO₂ can react with an adsorbed oxygen atom and nitrate formed:

\[
\text{NO}_2 \text{(g)} + \text{BaO-O} \leftrightarrow \text{BaO-(NO}_3\text{)} \quad (2.25)
\]
with the nitrate localized on the Ba part of BaO. Another NO$_2$ (g) molecule is then adsorbed on the oxide part and Ba(NO$_3$)$_2$ is formed:

$$\text{NO}_2 \,(\text{g}) + \text{BaO-(NO}_3\text{)} \leftrightarrow \text{Ba(NO}_3\text{)}_2 \quad (2.26)$$

Probably the most accepted views on NO oxidation and subsequent storage as Ba(NO$_3$)$_2$ or Ba(NO$_2$)$_2$ are provided by Nova et al. and Forzatti et al [58,73,74,85-87]. Nova et al. presented a mechanism involving NO$_x$ adsorption and oxygen dissociation over Pt [58]:

$$\text{O}_2 + 2 \text{Pt} \leftrightarrow 2 \text{Pt-O} \quad (2.27)$$
$$\text{NO} + \text{Pt-O} \leftrightarrow \text{NO}_2\text{-Pt} \quad (2.28)$$

Nitrites are stored at BaO sites in close proximity to Pt sites, whereas the nitrate is formed on the catalyst surface and NO is released. This is described by the disproportionation reaction:

$$\text{BaO} + 3 \text{NO}_2 \leftrightarrow \text{Ba(NO}_3\text{)}_2 + \text{NO} \,(\text{g}) \quad (2.29)$$

In this reaction, NO$_2$ is the source of adsorbed oxygen needed for NO$_3^-$ formation to occur. The NO released into the gas stream is available to be oxidized again over a Pt site located downstream in the catalyst. As the catalyst becomes saturated with NO$_x$, there is less opportunity for NO to be oxidized and readorsorbed and therefore would pass unreacted through the rear of the LNT. The stoichiometry for (2.29) has been proved by several research groups. Nova et al. [74] monitored the ratio of moles of NO evolved at the reactor outlet to moles of NO$_2$ consumed. Nova found as NO$_x$ storage approached saturation, this ratio approached 0.33 which corresponds to 1 mole of NO released for every 3 moles of NO$_2$ consumed.

Forzatti et al. [74,85-87] also supports the inclusion of the disproportionation reaction. Using FTIR under In Operando conditions, Forzatti also observed that 1 mol of NO was released for every 3 mol of NO$_2$ adsorbed [85]. Forzatti postulates two parallel routes for NO$_x$ storage in the presence of oxygen. In the nitrate route, NO$_2$, from NO oxidation on
Pt, spills over to Ba sites in close proximity to Pt to form Ba(NO₃)₂ with the evolution of NO into the gas phase, eqn. (2.29).

In the other route, NO is directly oxidized on Pt to form Ba(NO₂)₂ that is oxidized by oxygen that spills over from Pt to form Ba(NO₃)₂ (as shown in eqn. 2.31).

2 NO + O₂ \rightarrow Pt-Ba(NO₂)₂ \quad (2.30)
Pt-Ba(NO₂)₂ + 2 O-Pt \rightarrow Ba(NO₃)₂ + 2 Pt \quad (2.31)

The ratio of nitrites to nitrates formed is dependent on the Ba loading on the catalyst and the temperature. Forzatti found more nitrites were formed as the Ba loading increased due to enhancement of the interface existing between Pt and Ba [74,85,86]. Kumar et al. [88] demonstrated the dependence of temperature by measuring the ratio of oxygen to nitrogen stored on BaO. Using Ba(NO₃)₂ and Ba(NO₂)₂ standards, Kumar determined the theoretical ratio of O:N to be 2.5 and 1.5, respectively. Using NO pulse experiments, at 350 °C the ratio was calculated to be 2.3 corresponding to NOₓ stored as Ba(NO₃)₂. As the temperature was reduced to 250 °C, the ratio decreased to 1.8, indicating a mixture of Ba(NO₃)₂ and Ba(NO₂)₂.

2.2.2.4. Proximity of Pt and Ba Components.

The proximity of the Pt and Ba phases has been well researched in the literature [31,32,49,58,66,74,77,82,89,90-108]. The effect of their proximity was confirmed in powder experiments that revealed that NOₓ storage was decreased when Pt and BaO were not on the same nanoparticle [89]. The proximity is considered in terms of either the type of Ba or the type of Pt. At Ba sites close to Pt, a rapid uptake of NOₓ occurs, while at Ba sites far from Pt, NOₓ uptake still occurs but at much slower rate [1,6,37]. If one considers Pt sites, the following remarks can be made. Pt in contact with Ba is thought to be responsible for NOₓ storage pathways involving the dissociative adsorption of O₂ on Pt that could provide the proximal Pt and Ba sites with a source of O-atoms for the oxidation of NO₂ to NO₃ [31]. Pt far from Ba is thought to play an important role in NO oxidation [32,109,110]. At these far sites, NO₂ formed is likely to be involved as the
oxidant in the disproportion reaction, eqn. (2.32). The proximity of Pt and Ba also helps to explain the changes in the rate of NO\textsubscript{x} uptake with NO\textsubscript{x} loading [87]. At the beginning of NO\textsubscript{x} uptake, the spillover of NO\textsubscript{x} from Pt to the Ba sites is fast and complete uptake of NO\textsubscript{x} is observed in the LNT. Uptake of NO\textsubscript{x} decreases as the formation of Ba(NO\textsubscript{3})\textsubscript{2} or Ba(NO\textsubscript{2})\textsubscript{2} creates a diffusion barrier for NO\textsubscript{2}. The development of this diffusion barrier increases the likelihood of NO\textsubscript{x} slip.

2.2.2.5. Summary of NO\textsubscript{x} Adsorption.
Even though there appear to be several pathways for the oxidation and adsorption of NO\textsubscript{x}, three distinct pathways have been suggested by Epling et al. [6] which can summarize the oxidation and adsorption steps and which are based on the topology of the active sites.

1. When Pt and Ba are close to one another, a rapid uptake of NO\textsubscript{x} occurs. O\textsubscript{2} and NO\textsubscript{2} act as the oxygen source for oxidation of nitrite species to nitrate. The sites further away trap NO\textsubscript{2} from the phase exclusively via the NO\textsubscript{2} disproportion mechanism with no O\textsubscript{2} participation.

2. Pt close to Ba sites are involved in NO oxidation, trapping of NO, and further oxidation to nitrates. Pt sites far from Ba are only involved in NO oxidation.

3. A NO\textsubscript{3}\textsuperscript{-} spillover type mechanism describes the migration of NO\textsubscript{3}\textsuperscript{-} species away from the Pt sites as they become saturated from the rapid uptake of NO\textsubscript{2} and adsorbed atomic oxygen. This is similar to a two-dimensional shrinking core mechanism.

2.2.3. Reductant Evolution.
As reported by Epling [6], three means exist to change the exhaust from a diesel engine from lean to rich conditions. If fuel is injected into the exhaust, reductants are produced from hydrocarbons (HC) present reacting with PGM in the LNT. The reductants are also produced by fuel reacting over a partial oxidation catalyst or reformer located upstream of the LNT. Lastly, the engine operation is manipulated to produce rich exhaust gases that will contain reductants.
The most common reductants utilized to reduce the stored NO\textsubscript{x} on the LNT are H\textsubscript{2}, CO, and HC such as C\textsubscript{3}H\textsubscript{6} or C\textsubscript{3}H\textsubscript{8}. Studies on the effectiveness of these reductants have shown that H\textsubscript{2} is the most effective at reducing NO\textsubscript{x} and facilitating the release of SO\textsubscript{2} from Ba storage sites (to be discussed shortly) and regenerating the LNT [28,63,111-117]. CO itself or from the partial oxidation of HC is known to poison the Pt sites at low temperatures (≤ 200 °C) and limit the regeneration of the Ba sites in the LNT [28,118]. H\textsubscript{2} is supplied directly in the case of experiments or in real world scenarios. H\textsubscript{2} is produced from the other reductants by means of:

steam reforming (> 300 °C and HCs present)

\[ C_nH_m + n H_2O \leftrightarrow n CO + \left( n + \frac{m}{2} \right) H_2 \]  
(2.32)

water gas shift (WGS) reaction

\[ CO + H_2O \leftrightarrow CO_2 + H_2 \]  
(2.33)

Based on the effectiveness of H\textsubscript{2} and complications involving CO, most of the experiments discussed in this dissertation were performed using H\textsubscript{2} as the only reductant.

2.2.4. Factors Influencing NO\textsubscript{x} Release.
Any reductant used to regenerate a LNT has to fulfill three functions:

1. Create a net reducing environment by consuming any oxygen present in the exhaust gas and adsorbed on the PGM, storage components, and catalyst support.
2. Facilitate the release of NO\textsubscript{x}.
3. Reduce the NO\textsubscript{x} to either N\textsubscript{2} for LNT stand-alone applications or NH\textsubscript{3} for LNT-SCR applications.
A reductant is passed over the catalyst to begin the regeneration of the catalyst. The Pt sites become saturated with excess oxygen present in the lean phase. The reductant reduces the Pt sites by scavenging the oxygen from the Pt-O species. The reductant is one or a combination of CO, H₂, and a HC. For the conditions to be considered rich, a net reducing environment must exist in the exhaust stream. This condition is qualified by a lambda value of less than 1. The lambda value represents the ratio of the air to fuel ratio to the ratio of the stoichiometric air to fuel ratio. The air to fuel ratio is the ratio between the mass of air in the exhaust to the mass of fuel at any given moment. A stoichiometric exhaust stream would have a lambda value equal to 1. The reductants react with barium nitrites and nitrates present on the surface. The Ba sites are now returned to their original form and ready for storage. NOₓ is converted to N₂ on the platinum sites freed by the reaction of surface oxygen and reductants present in the exhaust stream [51].

Three factors, occurring independently or in combination, can cause NOₓ to be released from the surface of the catalyst: temperature increase, change in the gas composition in contact with the surface, and/or the creation of a net reducing environment. The increase in temperature is a result of exothermic reactions, such as the oxidation of the reductant by the oxygen present both in the gas stream and stored on the surface [119]. The releases of NOₓ can be particularly pronounced when the amount of NOₓ stored on the catalyst is close to the equilibrium coverage at a given temperature, and the temperature increase is large. The reducing environment is due to a lack of oxygen present in the gas stream [114,121]. The equilibrium stability of nitrate species is dramatically reduced. This instability creates a driving force for nitrate decomposition and NOₓ release from nitrites, which are substantially less stable than nitrates.

2.2.5. Rich phase product selectivity.

2.2.5.1. Mechanisms of NOₓ reduction.

Having established the reason as to why NOₓ release occurs, the focus is shifted to the reduction of NOₓ to various N-species. The principle of reduction of stored NOₓ either involves the spillover of NOₓ from the Ba storage sites to the Pt particles.
or the spillover of adsorbed hydrogen from Pt to Ba [113]. For Pt particles in close proximity to Ba sites, H\textsubscript{2} oxidation, nitrate decomposition, and formation of N-species occur during the regeneration [59]. For Pt sites located away from Ba, H\textsubscript{2} scavenges oxygen adsorbed on the Pt sites, and provides a clean surface for the decomposition of NO to N\textsubscript{2} and N hydrogenation to NH\textsubscript{3} [59].

Many authors [24,68,89,125-129] have reported the possibility of NO\textsubscript{x}, N\textsubscript{2}, N\textsubscript{2}O, and NH\textsubscript{3} as possible products formed during LNT regeneration. The “richness”, temperature, and relative coverages of NO, N, and H adspecies on the Pt particles during the rich phase dictate the product distribution [130]. The “richness” of the regeneration of the LNT determines the identity and quantity of products evolved. Shorter purges or purges with limited amount of reductants lead to partial release of NO\textsubscript{x} and product mixes with NO, NO\textsubscript{2} and N\textsubscript{2}. Longer and deeper purges lead to the presence of N\textsubscript{2}O and NH\textsubscript{3} in the product mix [131,132]. During shorter purges any NH\textsubscript{3} that is produced is consumed by NO and NO\textsubscript{2} to form N\textsubscript{2}. The effects of the length of purge should be viewed in terms of the diffusion of NO\textsubscript{x} from the storage sites back to the PGMs. If the rate of surface diffusion of NO\textsubscript{x} is less than the rate of NO\textsubscript{x} reduction, the storage sites are only partially regenerated [131,133].

Pihl et al. [123], and subsequently others, have suggested that the ratio of H\textsubscript{2} to NO, along with the reaction temperature, determine the product selectivity. Xu et al. presented a summary of these relationships [130]:

For H\textsubscript{2}:NO ratios < 0.5 (feeds containing excess NO and temperatures below 150 °C):

\[
\text{NO} + \frac{1}{2} \text{H}_2 \leftrightarrow \frac{1}{2} \text{N}_2\text{O} + \frac{1}{2} \text{H}_2\text{O} \quad (2.34)
\]

For 0.5 < H\textsubscript{2}:NO < 2 (about stoichiometric amounts of H\textsubscript{2} and NO, and temperatures above 150 °C):

\[
\text{NO} + \text{H}_2 \leftrightarrow \frac{1}{2} \text{N}_2 + \text{H}_2\text{O} \quad (2.35)
\]
For H₂:NO ratios > 2 (feeds containing excess H₂ and temperatures above 150 °C):

\[
\text{NO} + \frac{5}{2} \text{H}_2 \leftrightarrow \text{NH}_3 + \text{H}_2\text{O} \tag{2.36}
\]

At temperatures above 350 °C, NH₃ decomposes to:

\[
\text{NH}_3 \leftrightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \tag{2.37}
\]

Many pathways have been proposed in the literature to describe the reactions between CO and HC with stored NOₓ [22,45]. For H₂ as the reducing agent, Nova [135] presented the following:

Fast formation of NH₃:

\[
\text{Ba(NO}_3\text{)}_2 + 8 \text{H}_2 \leftrightarrow 2 \text{NH}_3 + \text{BaO} + 5 \text{H}_2\text{O} \tag{2.38}
\]

Slower selective formation of N₂:

\[
3 \text{Ba(NO}_3\text{)}_2 + 10 \text{NH}_3 \leftrightarrow 8 \text{N}_2 + 3 \text{BaO} + 15 \text{H}_2\text{O} \tag{2.39}
\]

NH₃ produced can also reduce NO:

\[
6 \text{NO} + 4 \text{NH}_3 \leftrightarrow 5 \text{N}_2 + 6 \text{H}_2\text{O} \tag{2.40}
\]
\[
8 \text{NO} + 2 \text{NH}_3 \leftrightarrow 5 \text{N}_2\text{O} + 3 \text{H}_2\text{O} \tag{2.41}
\]

Again, at temperatures above 350 °C, NH₃ decomposition occurs:

\[
2 \text{NH}_3 \leftrightarrow \text{N}_2 + 3\text{H}_2 \tag{2.42}
\]

Overall, adding reactions (2.38) and (2.39):

\[
\text{Ba(NO}_3\text{)}_2 + 5 \text{H}_2 \leftrightarrow \text{N}_2 + \text{BaO} + 5 \text{H}_2\text{O} \tag{2.43}
\]
Lietti [14] provides a more comprehensive picture of the chemistry involved, taking into account the presence of different components in the gas stream (where \( O^* \) represents poorly active oxygen species and \( H^* \) represents a hydrogen species associated with Pt):

Reduction of the nitrate at the Ba sites:

\[
\begin{align*}
\text{Ba(NO}_2\text{)}_2 + 3 \text{ H}_2 & \leftrightarrow \text{BaO} + \text{N}_2 + 3 \text{ H}_2\text{O} \quad (2.44) \\
\text{Ba(NO}_3\text{)}_2 + 5 \text{ H}_2 & \leftrightarrow \text{BaO} + \text{N}_2 + 5 \text{ H}_2\text{O} \quad (2.45) \\
\text{BaO} + \text{H}_2\text{O} & \leftrightarrow \text{Ba(OH)}_2 \quad (2.46) \\
\text{O}^* + \text{H}_2 & \leftrightarrow \text{H}_2\text{O} \quad (2.47) \\
\text{H}_2 & \leftrightarrow \text{2 H}^* \quad (2.48) \\
\text{H}_2 + \frac{1}{2} \text{O}_2 & \leftrightarrow \text{H}_2\text{O} \quad (2.49) \\
\text{H}_2 + \text{O}^* & \leftrightarrow \text{H}_2\text{O} \quad (2.50)
\end{align*}
\]

\( O^* \) represents oxygen species associated with Pt sites, \( H^* \) represents a hydrogen species associated with Pt, and \( O^{*'} \) represents “poorly reactive oxygen species” from the catalyst [14].

Formation of NO and \( \text{N}_2\text{O} \):

\[
\begin{align*}
\text{Ba(NO}_2\text{)}_2 + \text{H}_2 & \leftrightarrow \text{BaO} + 2 \text{NO} + \text{H}_2\text{O} \quad (2.51) \\
\text{Ba(NO}_2\text{)}_2 + 2 \text{H}_2 & \leftrightarrow \text{BaO} + \text{N}_2\text{O} + 2 \text{H}_2\text{O} \quad (2.52) \\
\text{Ba(NO}_3\text{)}_2 + 3 \text{H}_2 & \leftrightarrow \text{BaO} + 2 \text{NO} + 3 \text{H}_2\text{O} \quad (2.53) \\
\text{Ba(NO}_3\text{)}_2 + 4 \text{H}_2 & \leftrightarrow \text{BaO} + \text{N}_2\text{O} + 4 \text{H}_2\text{O} \quad (2.54)
\end{align*}
\]

In the presence of Ba, \( \text{N}_2\text{O} \) is not favored because Ba increases the rate of NO dissociation that reduces the probability of \( \text{N}_2\text{O} \) formation by [14]:

\[
\text{N}^* + \text{NO}^* \leftrightarrow \text{N}_2\text{O} \quad (2.55)
\]
Desorption of CO$_2$:

$$\text{BaCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ba(OH)}_2 + \text{CO}_2$$  \hspace{1cm} (2.56)

Again, the water gas shift (WGS) reaction:

$$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$$  \hspace{1cm} (2.33)

As previously stated, the WGS reaction is desired because the reaction enables the CO present to be converted into H$_2$ which has been shown to be a better reductant of NO$_x$ and SO$_2$ (to be discussed shortly) [112-116].

2.2.5.2. NH$_3$ as an Intermediate.

The formation of NH$_3$ as a product during LNT regeneration can be an unwanted or wanted effect. In a standalone LNT application, NH$_3$ is an undesirable product from the reduction of NO$_x$ due to the fact that the NH$_3$ is toxic, corrosive, and is capable of being oxidized back to NO$_x$ (e.g. if NH$_3$ adsorbs to the surface during rich periods and then reacts with oxygen after the switch back to lean conditions). Conversely, NH$_3$ can be a desired product in a LNT-SCR application. The balance between the amounts of NH$_3$ and N$_2$ produced from the LNT depends on the application of the system. In a situation where NO$_x$ is emitted from the LNT during lean conditions, the selectivity of NH$_3$ should be optimized based on the amount of unreacted NO$_x$ from the LNT in a LNT-SCR application. This coupling is described at the end of this chapter.

As a means to minimize or maximize NH$_3$ selectivity, it is important that the sequence of events present during rich conditions is considered using the idea of a reductant front propagating along the length of the catalyst surface [123,125,130,134-136]. The beginning of this front is created when the conditions of the engine exhaust are adjusted from net oxidizing to net reducing. At this transition, a plug-like flow of the leading edge of the reductant front encounters stored NO$_x$ and chemisorbed oxygen on the Pt sites and catalyst surface. These oxidizing species consume hydrogen upon contact with the leading edge of the front. As more reductant passes these sites in the entrance to the
LNT, the ratio of H$_2$:NO at the Pt sites gradually increases. How this ratio influences the product selectivity was explained in the previous section.

Considering the reductant front in spatial and temporal terms, different zones are present on the catalyst surface. Pihl et al. [123] envisioned three zones: upstream of the front, at the front, and downstream of the front. Clayton et al. [14,59] and Cumaranatunge et al. [126] also describe NO$_x$ reduction using this idea of a front traveling the length of the catalyst. Using Pihl’s description of the reduction front, NH$_3$ formation and consumption is readily understood.

**Upstream of the front:** The leading edge of the front has already passed this region of the LNT, and most of the Pt and Ba storage sites in close proximity are regenerated. While the hydrogen coverage of the Pt sites is increasing, NO$_x$ that is stored on Ba sites located far from the Pt sites is transported back to the sites. By the time this NO$_x$ reaches the Pt sites, the H$_2$:NO ratio is high enough to favor NH$_3$ formation. The resulting NH$_3$ is released into the gas stream where it is either oxidized by NO$_x$ to N$_2$ or emitted from the catalyst. Given that N$_2$ is formed from the reaction of NH$_3$ and NO$_x$, Cumaranatunge [127] likened NH$_3$ to a H$_2$ carrier. NH$_3$ is just effective as a reductant as H$_2$ to reduce NO$_x$ to N$_2$.

**At the leading edge of the front (located further downstream in the catalyst):** There is an intermediate level of reductant and stored oxidants. The PGM sites in this region have a mixture of adsorbed oxygen, NO, and reductant species. Initially, an unreacted NO$_x$ “puff” is seen, and thereafter, a mixture of N$_2$O and N$_2$ is released from the PGM sites. The selectivities of N$_2$O and N$_2$ are dependent on the temperature on the catalyst surface during this period and on the ratio of H$_2$:NO. At low temperatures (T <150-200 °C) and low H$_2$:NO (~ 0.5) N$_2$O selectivity is favored [59,123,126-129,136]. Cumaranatunge et al. [125] believed N$_2$O was produced from the reaction between adsorbed NO from the gas phase and reduced Pt in the absence of adsorbed hydrogen as is the case at the leading edge of the front as the hydrogen concentration is depleted. The hydrogen on the surface of Pt reduces NO and N$_2$O before spilling over and releasing more NO. As
Cumaranatunge et al. reports [125], the production of N$_2$O continues until the Pt surface is oxidized from Pt to Pt-O at which point the reaction ceases. The Pt surface is eventually reduced back to Pt as the hydrogen concentration in the gas phase increases as the reduction front continues along the catalyst. As the coverage of adsorbed hydrogen on the Pt sites increases, so selectivity to N$_2$ and then NH$_3$ is increasingly favored [125].

**Downstream of the front:** The catalyst Pt and Ba species have yet to be regenerated. Here exists an oxidized state with most of the stored oxygen and NO$_x$ still present on the surface. Any of the NH$_3$ produced upstream of the front that slips past the leading edge of the reductant front reacts with oxygen and NO$_x$ adsorbed on the catalyst sites. The products from the oxidation of NH$_3$ by oxygen adatoms and/or NO$_x$ depend on their relative coverages on the PGM and include a mixture of NO, N$_2$, and N$_2$O.

Based on this model, the temporal sequence of H$_2$ and NH$_3$ leaving the reactor is readily explained. Most authors [58,89,137] have reported that NH$_3$ is detected only after H$_2$ breakthrough from the LNT. The concentration of H$_2$ in the gas stream over the catalyst increases with time as the reductant front travels from the front to the rear of the catalyst. By the time H$_2$ reaches the catalyst outlet, all of the Pt sites are at least at a stoichiometric ratio of H$_2$:NO. The presence of H$_2$ at the outlet of the LNT implies all of the oxidizing species adsorbed on Pt are reduced or H$_2$ would have been consumed and would not have reached the end of the catalyst. For NH$_3$ to be detected at the exit of the catalyst, almost all of the NO$_x$ absorbed at the proximal Pt/Ba sites has been released and reduced. Any of the remaining NO$_x$ stored at the other Ba sites reaches the Pt sites with conditions that favor additional NH$_3$ formation. For NH$_3$ to reach the end of the catalyst, all of the oxygen adatoms and NO$_x$ at the proximal Pt/Ba sites has to be reduced, given that these species are capable of oxidizing NH$_3$ to N$_2$ and H$_2$.

The ability of NH$_3$ to reduce NO$_x$ is presented in the literature in terms of its ability to act as a hydrogen carrier or hydrogen intermediate as shown by equations (2.38) and (2.39).
2.3. Drawbacks to LNT Utilization.

2.3.1. Sulfur.

Based on the foregoing discussion, the effectiveness of the LNT to oxidize, store, release, and reduce NO\textsubscript{x} to N\textsubscript{2} is easily appreciated. However, there are some difficulties in its operation due to other components in the exhaust stream. The main concern is sulfur. Sulfur present in diesel fuel and engine oil, after conversion to sulfur dioxide (SO\textsubscript{2}) through the combustion cycle of engine operation, leads to poisoning of the NO\textsubscript{x} storage sites. In the presence of O\textsubscript{2}, the precious metals, such as Pt and Rh, are able to convert SO\textsubscript{2} to sulfur trioxide (SO\textsubscript{3}). Based on thermodynamic calculations, BaSO\textsubscript{4} is more stable than Ba(NO\textsubscript{3})\textsubscript{2}; also the sulfate is more basic than the nitrate (stability increases with basicity) [14-18]. If the sulfates are not removed periodically, eventually the NO\textsubscript{x} conversion of the LNT to N\textsubscript{2} will approach zero as all of the available sites will be filled with sulfur-species. To remove the sulfates, prolonged rich conditions at elevated temperatures are required. Breen et al. performed thermodynamic calculations to evaluate the effects of gas composition and temperature on the various reactions of BaSO\textsubscript{4} and BaCO\textsubscript{3} under oxidizing and reducing conditions [138]. Breen found that BaSO\textsubscript{4} is very stable under oxidizing conditions. For rich conditions, Breen looked at various possible reactions in which BaSO\textsubscript{4} is reduced by calculating the Gibbs reaction energy, $\Delta G_r$. The $\Delta G_r$ is used to establish the conditions under which a reaction should proceed spontaneously. For example, for the following reaction:

$$\text{BaCO}_3(s) + \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \leftrightarrow \text{BaSO}_4(s) + \text{CO}_2(g) \quad (2.57)$$

$$\Delta G_r = \Delta G^\theta + RT \left[ \ln \left( \frac{P_{CO_2}}{P_{O_2}^{\theta} P_{SO_2}} \right) \right] \quad (2.58)$$
The following partial pressures were used to calculate $\Delta G_r$ [140]:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>1 x $10^{-1}$ bar</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1 x $10^{-1}$ bar</td>
</tr>
<tr>
<td>O$_2$</td>
<td>5 x $10^{-2}$ bar</td>
</tr>
<tr>
<td>CO</td>
<td>5 x $10^{-2}$ bar</td>
</tr>
<tr>
<td>H$_2$</td>
<td>5 x $10^{-2}$ bar</td>
</tr>
<tr>
<td>SO$_2$ or H$_2$S</td>
<td>5 x $10^{-5}$ bar</td>
</tr>
</tbody>
</table>

If the temperature is greater than the temperature at which $\Delta G_r = 0$, then the forward reaction will occur spontaneously. Considering the composition of the exhaust stream with Ba as the storage material, the following reactions are possible [138]:

\[
T(\Delta G_r = 0) = 617 \, ^\circ\text{C} \\
2 \text{BaSO}_4(s) + \text{H}_2(g) + \text{CO}_2(g) + \text{CO}(g) \leftrightarrow 2 \text{BaCO}_3(s) + \text{H}_2\text{O}(g) + \text{SO}_2(g) \quad (2.59)
\]

\[
T(\Delta G_r = 0) = 984 \, ^\circ\text{C} \\
2 \text{BaSO}_4(s) + \text{H}_2(g) + \text{CO}(g) \leftrightarrow 2 \text{BaO}(s) + 2 \text{SO}_2(g) + \text{CO}_2(g) + \text{H}_2\text{O}(g) \quad (2.60)
\]

\[
T(\Delta G_r = 0) = 622 \, ^\circ\text{C} \\
\text{BaSO}_4(s) + 3 \text{H}_2(g) + \text{CO}(g) \leftrightarrow \text{BaO}(s) + \text{H}_2\text{S}(g) + \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) \quad (2.61)
\]

These results confirm that high temperatures are required to decompose BaSO$_4$.

Kim et al. [139] also described the sulfation of the Al$_2$O$_3$ sites on the support material of a LNT. As with NO oxidation, the Pt sites are oxidized by the dissociative adsorption of oxygen over Pt. The activated oxygen species then reacts with SO$_2$ to form SO$_3$ which then spills over to the Al$_2$O$_3$ support to form Al$_2$(SO$_4$)$_3$: 
\[ O_2 + 2 \text{Pt} \leftrightarrow 2 \text{Pt-O} \quad (2.62) \]
\[ \text{SO}_2 + \text{PtO} \leftrightarrow \text{Pt} + \text{SO}_3 \quad (2.63) \]
\[ 3 \text{SO}_3 + \text{Al}_2\text{O}_3 \leftrightarrow \text{Al}_2(\text{SO}_4)_3 \quad (2.64) \]

Kim went on to state that due to the greater basicity of the BaO molecule compared to Al\(_2\)O\(_3\), BaO should be more reactive with the acidic SO\(_2\) molecule [139].

The sulfates formed on the surface are classified according to their proximity to Pt sites. Sulfates located near Pt sites are typically considered to be surface sulfates, and on locations far from Pt, they are considered to be bulk sulfates. Additionally, the BaSO\(_4\) can continue to react under rich conditions to form BaS [140]. The formation of BaS begins at 550 °C and the particles continue to grow up to 800 °C. If water is present, BaS can be hydrolyzed at 550 °C to form BaO and hydrogen sulfide, H\(_2\)S. This reaction sequence is shown below:

\[ \text{BaSO}_4 + 4\text{H}_2 \leftrightarrow \text{BaS} + 4\text{H}_2\text{O} \quad (2.65) \]
\[ \text{BaS} + \text{H}_2\text{O} \leftrightarrow \text{BaO} + \text{H}_2\text{S} \quad (2.66) \]

In addition to the sulfation of the storage materials, the precious metals are also vulnerable to blockage by sulfur. Apesteguia et al. [141] stated that sulfate in close proximity to Pt sites can be reduced by H\(_2\) at 500°C, resulting in the formation of platinum sulfide:

\[ 3 \text{H}_2 + (\text{SO}_4^{2-})_{\text{support}} + \text{Pt} \leftrightarrow \text{PtS} + (\text{O}^2-)_{\text{support}} + 3 \text{H}_2\text{O} \quad (2.67) \]

Sedlmair et al. stated that this reaction begins at 350 °C and an increase of temperature to 500 °C results in an increase of PtS in the bulk phase of the catalyst [73]. In both cases, the Pt sites could be recovered by exposing them to oxidizing conditions at 450 °C. More evidence for the formation of PtS is the increased N\(_2\)O formation seen during the rich phase under increasing sulfation [140]. As discussed earlier, Ba reduces the likelihood of N\(_2\)O formation. Another consequence of the sulfation of the Pt sites is that after the Pt
sites are oxidized by exposure to lean conditions, the \( \text{SO}_2 \) released from the sites spills over to the surrounding Ba sites where BaSO\(_4\) is formed \[40,139\].

The decomposition of BaSO\(_4\) requires the LNT to be exposed to rich conditions and high temperatures (650 to 800 °C) for several minutes. This need results in a fuel penalty that reduces the gains in fuel efficiency of lean-burn engines and gives rise to sintering of the precious metals and NO\(_x\) storage components. Sintering occurs when particles such as Pt agglomerate and form less dispersed, large clusters. As discussed above, the platinum particle size affects the NO oxidation rate \[40\]. Larger particles can lead to sites becoming blocked due to steric hindrances or by the component species \[6\]. The growth of Pt particles due to sintering decreases the NO\(_x\) storage efficiency \[141-143\]. Although, under normal operating temperatures (150 °C - 400 °C), the growth of Pt particles has been shown to increase NO oxidation rates \[40,41\], at elevated temperatures the loss in the surface area of Pt results in reduced NO oxidation rates \[6\]. This decrease in efficiency is caused by the reduced spillover rate of NO\(_2\), formed from the oxidation of NO over Pt, to the storage material, i.e. Ba \[8,42,91\].

High temperatures can also result in the migration of the storage components (i.e., sintering of Pt, redistribution of the Ba phase), which is problematic based on the above discussion of the requirement of the Pt and Ba sites to be in close proximity. Another problem is the occurrence of side reactions of components in the washcoat. Barium cerate, BaCeO\(_3\), and barium aluminate, BaAl\(_2\)O\(_4\), are formed at 800 and 850 °C, respectively \[91,144-147\]. These compounds are not able to store NO\(_x\) and therefore decrease the activity of the LNT.

The aforementioned problems (sintering of the precious metals, migration of the storage components on the surface, and unwanted side reactions between the storage components and the support) can be avoided if desulfation temperatures can be reduced. A potential solution that would enable lower desulfation temperatures is the addition of ceria, CeO\(_2\), as a storage material. Recent studies have shown that ceria can store some of the sulfur in the exhaust with the consequence that fewer barium sites are poisoned \[3,17,18,146-147\].
The use of ceria as a component of three-way catalysts has been well-established because of its oxygen storage capacity that acts as a damper in maintaining stoichiometric conditions during various engine operating ranges, and also because of its ability to maintain high precious metal dispersions in the washcoat [165]. The main function of ceria in a LNT is to store and release oxygen when the LNT is functioning as a TWC. Moreover, under rich conditions, platinum-promoted ceria is known to promote the WGS reaction that produces H₂ and CO₂ from CO and water [155,166].

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (2.33)$$

The additional hydrogen produced is available to regenerate and desulfate the trap. Additionally, ceria has demonstrated NOₓ storage capacity at low to moderate temperatures (< 400 °C) which is significant since diesel exhaust temperatures are usually lower than exhaust from gasoline engines [159].

Different research groups have reported additional benefits from the addition of ceria to LNTs. Theis et al. reported that the addition of ceria improved the sulfur tolerance of the LNT [3]. Peralta et al. reported that sulfur can be stored as Ce(SO₄)₂ instead of BaSO₄, thereby freeing up the Ba component for NOₓ storage [167]. In addition to improved sulfur tolerance, Kwak et al. reported that ceria-containing catalysts provide excellent resistance against Pt sintering as compared to alumina-based catalysts [18]. Using DRIFTS, Ji et al. showed that the addition of ceria improved sulfur resistance by reducing sulfur accumulation on BaO sites due to the presence of CeO₂ sites [164]. Ji also proposed that the addition of ceria would lower the fuel penalty and precious metal sintering associated with catalyst desulfation because sulfur stored at Ce sites can be removed under rich conditions at temperatures below 500 °C, which is lower than the > 650 °C required for Ba sites. Furthermore, as stated in the previous paragraph, under rich conditions, Pt-promoted ceria is known to catalyze the water-gas shift reaction that produces hydrogen and CO₂ from CO and water [155,166]. The additional hydrogen produced is available to regenerate the trap, which is highly beneficial because H₂ has...
been shown to be a better NO\textsubscript{x} reductant than CO \cite{113,114,116}. Likewise, H\textsubscript{2} is a more efficient reductant for LNT desulfation than CO \cite{32,112,115,117}.

2.3.2. Additional Concerns of LNT Utilization.
In addition to the problems present when an LNT is exposed to an exhaust stream containing sulfur species, the costs inherent to the use of PGMs and undesired product formation have limited the penetration of LNT use into the automobile marketplace. Pt and Rh are two of the most expensive precious metals traded on the open market today. The one year averages for Pt and Rh are $1538.18/oz. and $1409.21/oz, respectively \cite{168}, thus making these metals as precious as gold. It is these high prices that are driving research efforts to reduce or replace their use in LNT catalysts. As discussed previously, depending on the NO\textsubscript{x} loading and reaction conditions present during the rich phase, products such as NO\textsubscript{x}, N\textsubscript{2}O, and NH\textsubscript{3} can be released from an automobile’s exhaust. NO\textsubscript{x} is a key component in photochemical smog and acid rain, N\textsubscript{2}O is a powerful greenhouse gas (7 times as powerful as CO\textsubscript{2}), and NH\textsubscript{3} is toxic and corrosive. What if there existed a means of not only reducing the use and therefore the costs of PGMs while eliminating the release of unwanted compounds?

2.4. LNT-SCR.
As methods of reducing NO\textsubscript{x} emissions, both LNT and SCR catalysts have drawbacks associated with their usage. The high cost of PGMs and susceptibility to sulfur deactivation limit application of LNT catalysts. Thermal durability and the need for an on-board reductant such as NH\textsubscript{3} and its required injection system limit SCR catalyst use. In the past 4 to 6 years, significant efforts have been made to investigate the effects of using LNT and SCR catalysts together \cite{169-189}. One of the first commercial applications of this technology was demonstrated on the 2007 Mercedes E320 Bluetec automobile. The catalyst system on the E320 was a LNT with a high-loading of PGM and a Fe-based zeolite SCR catalyst \cite{189}.

SCR catalysts were originally developed by Engelhard Corporation (now BASF Corporation) in 1957 for reducing NO\textsubscript{x} emissions from coal-powered installations such as
boilers and power plants. SCR catalysts are either base metal catalysts such as V_2O_5/WO_3/TiO_2 or ion-exchanged zeolites [190] These zeolites have higher thermal durability than the base metal SCR catalysts [191]. Two of the most common ion-exchanged zeolites, and the most active for the urea/NH_3-SCR process are Fe- and Cu-ZSM-5 [6,193,194]. ZSM-5 is aluminosilicate zeolite composed of five membered rings named pentasils that form its structure.

As stated before, a LNT possesses the ability to produce NH_3 during the rich phase as NO_x is released and reduced by H_2 depending on the temperature and composition of the exhaust emitted from the engine. When a SCR catalyst is positioned downstream of the LNT, the NH_3 that manages to “slip” from the LNT is trapped and stored on the SCR. NH_3 storage continues for the remaining duration of the rich phase until the exhaust gas is switched back to lean conditions. As mentioned during the description of NO_x storage during lean conditions, when the storage capacity of the LNT is reached, NO_x will also slip from the catalyst. The NO_x from the LNT reacts with stored NH_3 on the SCR catalyst. This reaction can occur according to several different pathways, i.e., via the standard and so-called “fast” SCR reactions.

Standard SCR reaction:

\[
4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \leftrightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}
\]  

(2.68)

Here the advantage of the SCR is realized as NO_x is now reduced to N_2 in the presence of oxygen. The efficiency of the ion-exchanged zeolite is increased as the concentration of NO_2 from the LNT increases, since this facilitates the occurrence of the so called “fast” SCR reaction [194,195].

Fast SCR reaction

\[
\text{NO} + \text{NO}_2 + 2 \text{NH}_3 \leftrightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O}
\]  

(2.69)

This is also facilitated by the fact that Fe- and Cu-ZSM-5 SCR catalysts have the capability to oxidize NO to NO_2 in the presence of oxygen. Wang et al., Xu et al., and
Corbos et al. have reported that NO\textsubscript{x} can additionally be reduced by a non-NH\textsubscript{3} mechanism if hydrocarbons are present in the exhaust [175,191,196].

Examples of the improved performance afforded by the LNT-SCR synergy are provided by Forzatti et al., Lindholm et al., and Xu et al. [176,183,193]. Forzatti reported reduced amounts of NH\textsubscript{3} from a LNT-SCR system at 150 °C as compared to a LNT-only system. As the temperature was increased to the 200 °C to 300 °C range, complete N\textsubscript{2} selectivity was seen with the fast SCR reaction more likely to occur due to more NO\textsubscript{2} being produced by the LNT at these temperatures [176]. Lindholm reported an improvement in NO\textsubscript{x} removal efficiency from 86% to 99.5% at 300 °C and a decrease in NH\textsubscript{3} yield from 34% to 21% [183]. Lastly, Xu reported that their LNT-SCR configuration (a low PGM-loaded LNT paired with a Cu-ZSM-5 catalyst) had a NO\textsubscript{x} conversion of > 90% at 175 °C after aging for the equivalent of 70,000 miles. Xu summarized the benefits of the placement of a SCR downstream of a LNT [191]:

1. Reduced levels of NH\textsubscript{3} emitted from the catalyst system with neither the fuel consumption penalty nor the need to operate the LNT as a NH\textsubscript{3} generator.
2. Enhanced NO\textsubscript{x} conversion
3. Potential PGM reduction as seen by the performance of LNTs with 30% less PGMs
4. H\textsubscript{2}S emissions mitigated.

As will be discussed in the Chapter 3 concerning LNT sulfation, the majority of the sulfur is emitted as H\textsubscript{2}S as the LNT undergoes desulfation. The placement of the SCR after the LNT enables the H\textsubscript{2}S and COS present to be converted back to SO\textsubscript{2}. This conversion allows the system to operate with quicker desulfation events without exceeding the odor threshold of H\textsubscript{2}S [197].

The arrangement of the LNT-SCR system has been studied by Theis et al. and Morita et al. [186,198]. Theis investigated the effect of the arrangement of the catalysts on system
performance as measured by NO\textsubscript{x} and NH\textsubscript{3} concentrations. In this study, 4 and 8 alternating catalysts were compared to LNT-and SCR-only systems before and after hydrothermal aging and sulfur deactivation. The LNT-SCR systems with the alternating configurations demonstrated higher conversions of NO\textsubscript{x} to N\textsubscript{2}, along with lower NH\textsubscript{3} and N\textsubscript{2}O yields. The improved NO\textsubscript{x} to N\textsubscript{2} conversion was due to an improved balance of NO\textsubscript{x} and NH\textsubscript{3} in the SCR segments. The lower amount of N\textsubscript{2}O generated was a result of more NO\textsubscript{x} conversion in the SCR segments, since SCR catalysts are less prone to produce N\textsubscript{2}O than a Pt-containing LNT [186]. The findings reported by Corbos et al. support this idea of alternating the catalysts based on similar studies with powder catalysts [175]. The selectivity to N\textsubscript{2} was increased with less NO\textsubscript{x} and NH\textsubscript{3} slip for a physical mixture than for a configuration with a bed of LNT catalyst powder followed by a SCR bed. Morita et al. deposited the SCR catalyst on top of the LNT in a dual layer application to a support. This arrangement was reported to ensure sufficient NO\textsubscript{x} and NH\textsubscript{3} adsorption even at low temperatures while offering high NO\textsubscript{x} reduction efficiency [198].
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Chapter 3. Effect of Ceria on the Desulfation Characteristics of Model Lean NO\textsubscript{x} Trap Catalysts.

Note - This chapter was published as an article in the following journal:


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3.1. Introduction.
Lean-burn engines have the potential to provide better fuel economy than current stoichiometric engines though reduced pumping losses and enhanced combustion thermodynamics [1]. Although reduced CO\textsubscript{2} and hydrocarbon emissions are seen from lean-burn engines, NO\textsubscript{x} emissions do not meet current emission standards when these engines are coupled with three-way catalytic converters. This short-coming is caused by the inability of NO\textsubscript{x} to be reduced to nitrogen in atmospheres containing excess oxygen. To date, two main solutions have been proposed and implemented. One method is selective catalytic reduction (SCR) where ammonia is used as the reductant to convert NO\textsubscript{x} to nitrogen [2]. The other method is the use of lean NO\textsubscript{x} traps (LNTs). A LNT catalyst usually consists of a platinum group metal to oxidize the NO to NO\textsubscript{2}, an alkali or alkaline earth metal oxide to store NO\textsubscript{x}, and a high surface area support material (e.g., γ-alumina) [3].

Although LNTs are starting to find commercial application, the issue of LNT durability remains problematic. Sulfur present in fuel and engine oil is converted to SO\textsubscript{2} through the combustion cycle of engine operation, and the SO\textsubscript{2} can subsequently undergo oxidation over platinum group metals (PGMs), such as Pt and Rh, to form SO\textsubscript{3}. Barium oxide has a greater affinity for SO\textsubscript{3} than NO\textsubscript{2} (the resulting BaSO\textsubscript{4} being
thermodynamically more stable than Ba(NO₃)₂ [4]), resulting in poisoning of the NOₓ storage sites. The decomposition of BaSO₄ requires the LNT to be exposed to rich conditions and high temperatures (650 to 800 °C) for several minutes. This requirement results in a fuel penalty that reduces the gains in fuel efficiency of lean-burn engines and gives rise to sintering of the precious metals and NOₓ storage components. The high temperatures also enable unwanted side reactions between the LNT washcoat components (e.g., resulting in formation of BaAl₂O₄ and BaCeO₃) [5-8]. The formation of BaAl₂O₄ and BaCeO₃ and growth of Pt particles due to sintering decreases LNT NOₓ storage efficiency [9-11]. Some researchers have attributed this decrease in efficiency to the reduced spillover rate of NO₂, formed from the oxidation of NO over Pt, to the storage material [5,12,13].

Recent studies have shown that ceria in LNTs is able to store some of the sulfur in the exhaust with the consequence that fewer barium sites should be poisoned [1,14-17]. The use of ceria as a component of three-way catalysts is well established based on its ability to reversibly store oxygen (that acts as a damper in maintaining stoichiometric conditions during various engine operating ranges) and its ability to maintain high precious metal dispersions in the washcoat [18]. The main function of ceria in lean burn gasoline LNTs is similarly to act as an oxygen storage material, thereby enabling the LNT to function as a conventional three-way catalyst when the engine is operating under stoichiometric conditions. However, different research groups have reported additional benefits from the incorporation of ceria in LNTs. Theis et al. reported that the addition of ceria improved the sulfur tolerance of the LNT [1]. In addition to improved sulfur tolerance, Kwak et al. reported that ceria containing catalysts provide excellent resistance against Pt sintering as compared to alumina-based catalysts [16]. Using DRIFTS, Ji et al. showed the addition of ceria improved sulfur resistance by reducing sulfur accumulation on BaO sites [17]. In addition, Ji proposed that the addition of ceria would lower the fuel penalty and precious metal sintering associated with catalyst desulfation because the operating period between desulfation events could be extended. The presence of ceria has also been shown to improve the NOₓ storage and reduction properties of LNTs, particularly at
low temperatures [19-21]. Furthermore, under rich conditions, Pt promoted ceria is known to catalyze the water-gas shift reaction that produces hydrogen and CO\textsubscript{2} from CO and water [22,23]. The additional hydrogen produced is available to regenerate the trap, which is very beneficial given that H\textsubscript{2} has been shown to be a better NO\textsubscript{x} reductant than CO [24-29]; likewise, H\textsubscript{2} is a more efficient reductant for LNT desulfation than CO [29,30].

Although ceria possesses these attractive characteristics when used in LNT catalysts, to date relatively few reports have dealt directly with its role in LNT sulfation and desulfation. In this study the effect of ceria on sulfation and desulfation behavior was investigated, using both model powder catalysts and fully formulated monolithic catalysts. The effect of precious metal loading and the importance of Pt location (relative to the Ba phase) on the ease of LNT desulfation were also examined.

3.2. Experimental.

3.2.1. Preparation of Powder Catalyst Samples.

Powder samples were prepared by incipient wetness impregnation. Pt/Al\textsubscript{2}O\textsubscript{3} was made by impregnating \(\gamma\)-alumina (Sasol, surface area of 132 m\textsuperscript{2}/g) with an aqueous solution of tetraamine platinum (II) nitrate. The sample was then dried under vacuum at 100 °C overnight and calcined in air at 500 °C for 3 h. Pt/CeO\textsubscript{2} was prepared by the same method using ceria (Rhodia, surface area of 119 m\textsuperscript{2}/g). A stepwise method was used to make the Pt/BaO/Al\textsubscript{2}O\textsubscript{3} sample (denoted PBA). \(\gamma\)-alumina was impregnated with aqueous Ba(NO\textsubscript{3})\textsubscript{2}, dried and calcined at 500 °C in air. The Ba-loaded Al\textsubscript{2}O\textsubscript{3} was then impregnated with aqueous tetraamine platinum (II) nitrate and again calcined at 500 °C. Finally, in order to investigate the effect of ceria addition on the Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst, a sample was prepared by physically mixing the Pt/BaO/Al\textsubscript{2}O\textsubscript{3} and Pt/CeO\textsubscript{2} powders in a 76:24 weight ratio (denoted PBAC). All of the powders were pressed into pellets using an IR pellet press and then crushed and screened to a size of ASTM 20 to 40 mesh.
3.2.2. Temperature Programmed Sulfation-Desulfation Experiments.

Each of the powder catalysts was subjected to a temperature-programmed reduction (TPR) procedure to determine the temperature required to decompose the sulfates stored on the different storage components. The microreactor used consisted of a ¼ inch o.d. quartz tube in which a section of ca. 3 inch length contained the 150 mg of powder catalyst. The tube was heated by a programmable Lindberg Blue furnace. A V&F Airsense 2000 chemical ionization mass spectrometer (CI-MS) analyzed the product gases from the reactor. A gas flow rate of 120 sccm was used, corresponding to a gas space velocity of ca. 30,000 h⁻¹. Table 3.1 shows the lean and rich feed gas compositions for the powder reactor. All of the inlet and outlet lines for the reactor were heated using heat tape to above 100 °C to prevent water condensation prior to analysis in the CI-MS. Prior to the experiments, each sample was subjected to pretreatment at 450 °C. The sample was first oxidized in a mixture of 8% O₂, 5% CO₂ and 5% H₂O (with Ar as the balance) for 15 min, after which it was purged with 5% CO₂ and 5% H₂O (with Ar as the balance) for 10 min. The sample was then reduced in 2% H₂, 5% CO₂, 5% H₂O, and balance Ar. Finally, the sample was cooled to 350 °C while it was exposed to 5% CO₂ and 5% H₂O (with Ar as the balance).

Table 3.1. Feed composition for experiments utilizing powder catalysts.

<table>
<thead>
<tr>
<th>Component</th>
<th>Pre-Oxidation</th>
<th>Pre-Reduction</th>
<th>Sulfation</th>
<th>TPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>0</td>
<td>0</td>
<td>100 ppm</td>
<td>0</td>
</tr>
<tr>
<td>O₂</td>
<td>8%</td>
<td>0</td>
<td>8%</td>
<td>0</td>
</tr>
<tr>
<td>H₂</td>
<td>0</td>
<td>2%</td>
<td>0</td>
<td>2%</td>
</tr>
<tr>
<td>CO₂</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>H₂O</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Ar</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
<tr>
<td>Total Gas Flow, sccm</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>GHSV, h⁻¹</td>
<td>30,000</td>
<td>30,000</td>
<td>30,000</td>
<td>30,000</td>
</tr>
</tbody>
</table>

The powder samples were sulfated by exposure to a feed containing 100 ppm SO₂, 8% O₂, 5% CO₂, 5% H₂O, and balance Ar (feed rate of 120 sccm) for 34 minutes at 350 °C.
Assuming complete sulfur uptake, these conditions resulted in a loading equivalent to 1 g sulfur/L for a monolithic catalyst with a washcoat loading of 260 g/L. Higher loadings were achieved by extending the duration of the sulfation. The catalysts were then subjected to desulfation under reducing conditions for the TPR. The procedure consisted of exposing the sample to 2% H₂, 5% CO₂ and 5% H₂O (with Ar as the balance) as the temperature was increased from 350 to 800 °C at a rate of 5 °C/min. The product gas stream was analyzed using the CI-MS.

3.2.3. Preparation of Monolith Catalyst Samples.
The samples, listed in Table 3.2, are categorized into three groups according to the variation in components. The preparation of the catalysts has been described in detail elsewhere [21]. In brief, the samples were prepared using the incipient wetness method. In a first step, Pt and Rh were co-impregnated in a 1:1 weight ratio (using Pt(NH₃)₄(OH)₂ and Rh(NO₃)₃ as the precursors) onto γ-alumina stabilized with 3 wt% La₂O₃, after which the powder was calcined for 2 h at 500 °C. Separately, BaO/Al₂O₃ was prepared by impregnating Ba(O₂CCH₃)₂ onto γ-alumina, followed by calcination (also at 500 °C for 2 h). To this the required amount of CeO₂ or CeO₂-ZrO₂ was added. To achieve the total Pt loading, the balance of the Pt was then impregnated onto the mixture as (as Pt(NH₃)₄(OH)₂), after which it was calcined at 500 °C for 2 h. The Pt and Rh containing powder (in an amount corresponding to 30 g/L) and the powder containing BaO/Al₂O₃ and CeO₂ was added to a balance of γ-alumina powder to achieve the overall washcoat loading of 260 g/L. A small amount of boehmite sol was used as a binder. The resulting slurry was washcoated onto a 4” x 6” cordierite 400 cps/6.5 mil monolith by DCL International Inc. (Toronto, ON) using a proprietary vacuum coating process. The monoliths were calcined at 550 °C for 2 h.
Table 3.2. Composition of monolith catalysts.

<table>
<thead>
<tr>
<th>Component</th>
<th>Catalyst Code/Component Loading&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Series 1</th>
<th>Series 2</th>
<th>Series 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt, g/L (g/cuft)</td>
<td>3.53 (100)</td>
<td>3.53 (100)</td>
<td>3.53 (100), 1.77 (50)</td>
<td></td>
</tr>
<tr>
<td>Rh, g/L (g/cuft)</td>
<td>0.71 (20)</td>
<td>0.71 (20)</td>
<td>0.35 (10)</td>
<td></td>
</tr>
<tr>
<td>BaO, g/L</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>CeO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;, g/L</td>
<td>0, 50, 100</td>
<td>0</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>CeO&lt;sub&gt;2&lt;/sub&gt;-ZrO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;, g/L</td>
<td>0</td>
<td>50, 100</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;, g/L</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Nominal loadings. Total washcoat loading = 260 g/L
<sup>b</sup> Stabilized with 5 wt.% La<sub>2</sub>O<sub>3</sub>
<sup>c</sup> Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub>
<sup>d</sup> Stabilized with 3 wt.% La<sub>2</sub>O<sub>3</sub>

In series 1, the sample codes reflect the amount of barium (held constant at 30 g/L) and the amount of CeO<sub>2</sub> present (0, 50, or 100 g/L). Series 2 is composed of two samples designated 30-50z and 30-100z. The “z” refers to amount of ceria-zirconia (Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub>) present in the sample instead of CeO<sub>2</sub>. Series 3 differs from the two other series in the amount of precious metal present in the washcoat. The Rh concentration was reduced from 0.71 to 0.35 g/L for the two samples, and the Pt concentration varied at 1.77 g/L (50 g/ft<sup>3</sup>) and 3.53 g/L (100 g/ft<sup>3</sup>). The two samples in series 3 are designated by the amount of platinum present: Pt-50 and Pt-100. The CeO<sub>2</sub> loading was held constant for both samples at 50 g/L. The total washcoat loading for all of the samples was 260 g/L and was held constant by adjusting the amount of balance Al<sub>2</sub>O<sub>3</sub> present.

3.2.4. Monolith Catalyst Sulfation and Desulfation.

1.75 cm x 2.54 cm (d x l) sample cores were drilled from the monolith samples. A small hole was drilled in the center of each core so that a K-type thermocouple could be inserted to measure the temperature of the gas stream at the front face of the sample. The catalyst cores were contained in a vertical quartz tube reactor (1” outer diameter) heated by a Lindberg Blue electric furnace. Prior to sulfation/desulfation experiments, samples
were degreened (stabilized) by heating at 800 °C for 3 h in a slightly rich gas. The composition of the feed gas is listed in Table 4.3. The overall flow rate was 3 L/min, resulting in a GHSV of 30,000 h⁻¹.

Monolith samples were sulfated at 350 °C for 16 h using the gas stream shown in Table 3.3. The gas stream alternated between one min lean periods to one min rich periods (1/1 cycles). The length of the rich period was chosen to ensure that the trap was completely purged of NOₓ before the next lean cycle. NOₓ concentrations were measured using a heated chemiluminescence detector (Beckman Industrial Model 951 NO/NOₓ analyzer). The data were used to calculate the NOₓ storage efficiency at every hour from the start of sulfation to the end of the 16 h period.

Sample desulfation was performed at one of the following temperatures: 650 °C, 675 °C, 700 °C, 725 °C, or 750 °C. To begin the desulfation, the sample was ramped to the desired desulfation temperature. During the ramp, 1 min lean /1 min rich alternating cycles were used until the temperature reached 580 °C, at which point the feed was switched to the lean gas mixture to prevent desorption of the sulfur stored on the monolith sample before the desulfation temperature was reached. Once the desulfation temperature was obtained, the conditions were switched to rich and the temperature was held constant for 5 min before cooling to 580 °C under lean conditions. At this point, the gas composition was switched from lean to alternating 5 min lean, 3 min rich cycles until the sample reached 350 °C. At 350 °C data were taken from three 5/3 cycles and then five 1/1 cycles, corresponding to “steady state” cycling conditions (i.e., reproducibly periodic). The schedule of heating to the desulfation temperature, cooling to 350 °C, and then evaluating the catalyst during the 5/3 and 1/1 cycles was repeated three times. After the third time the SO₂ was turned off and the sample was heated to 750 °C under rich conditions for 10 min using the method described above. This part of the cycle is referred to as the clean-off. After the clean-off, the sample was evaluated at 350°C as before using 5/3 and 1/1 cycles. At this point the sample was ready to be sulfated again so the catalyst could be studied at another desulfation temperature. It should be noted that the data from the 1/1 cycles are very similar to the 5/3 cycles in both the storage
efficiency values obtained and the resulting trends, and consequently, the 1/1 cycle data are not discussed in this paper.

### Table 3.3. Feed gas composition during determination of NO\textsubscript{x} storage efficiency.

<table>
<thead>
<tr>
<th>Component</th>
<th>Lean</th>
<th>Rich</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td>NO\textsubscript{x}</td>
<td>500 ppm</td>
<td>500 ppm</td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td>9 ppm</td>
<td>9 ppm</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>5%</td>
<td>0</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>1.20%</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>0</td>
<td>0.40%</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

3.2.5. Measurement of Total Sulfur Release During Desulfation.

In these experiments, the same lean and rich gas mixtures were used as for the sulfation-desulfation experiments described in section 3.2.4 with the exception that in order to expedite catalyst sulfation, the samples were sulfated with 90 ppm SO\textsubscript{2} at 350°C (for 1 h under lean conditions; see Table 3.4). After sulfation, the SO\textsubscript{2} was shut off, and the sample was heated to the desired desulfation temperature under lean conditions to avoid any loss of SO\textsubscript{2}. Once the desulfation temperature was reached, the feed was switched to the rich gas mixture containing CO and H\textsubscript{2} for 10 min. Each desulfation ended with heating the sample to 750 °C under lean conditions and then switching to rich conditions for 10 min. Again, the period at 750 °C is referred to a clean-off and was performed to remove as much sulfur as possible before the next sulfation experiment and to confirm the total amount of sulfur originally stored on the catalyst. This allowed the calculation of the fractional sulfur release as a function of temperature by comparing the amount of the total sulfur released at the desulfation temperature to the amount of sulfur released during the clean-off period. The gas composition at the catalyst outlet was continuously monitored during desulfation using a V&F Systems, Inc. chemical ionization mass spectrometer (CI-MS) equipped with three ion sources of different energies. Mercury is
the low energy source and is used to detect H₂S. Xenon is the medium source and is used to detect SO₂ and COS. Krypton is the high energy source and was not used in this study. From the concentrations of the sulfur species evolved, the data were integrated to calculate how much of each species was released during desulfation and during the clean-off. The fraction of total sulfur released was used to compare and evaluate the performance of the monolith catalysts.

Table 3.4. Feed gas composition during determination of fraction of sulfur released/stored.

<table>
<thead>
<tr>
<th>Component</th>
<th>Lean</th>
<th>Rich</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td>H₂O</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td>NOₓ</td>
<td>500 ppm</td>
<td>500 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>90 ppm</td>
<td>90 ppm</td>
</tr>
<tr>
<td>O₂</td>
<td>5%</td>
<td>0</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>1.20%</td>
</tr>
<tr>
<td>H₂</td>
<td>0</td>
<td>0.40%</td>
</tr>
<tr>
<td>N₂</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

3.3. Results and Discussion.

3.3.1. Powder Model Catalysts.

3.3.1.1. Temperature Programmed Reduction.

Four model catalysts were examined in this study, comprising Pt/Al₂O₃, Pt/CeO₂, PBA, and PBAC. The Pt/Al₂O₃ and Pt/CeO₂ samples were used as references to distinguish between release events from alumina, ceria, and barium sites. Prior to TPR, the samples were sulfated to loadings of 1, 2.5, and 7.5 g sulfur adsorbed per L equivalent of monolithic catalyst (assuming a typical monolith washcoat loading of 260 g/L). A typical release of the sulfur species observed during TPR is shown in Figure 3.1 for Pt/Al₂O₃. The first species seen is SO₂ which is then followed by H₂S. COS is also seen when SO₂ release begins, but unlike the concentration of SO₂, which decreases for the remainder of the TPR, the concentration of COS continues to increase until about 750 °C. Given that
H₂S is the main product during the TPR experiment, in the following TPR plots only the H₂S release events are shown. Table 3.5 and Figure 3.2 summarize the results of the TPR experiments performed using Pt/Al₂O₃. At a loading equivalent to 1 g S/L, the H₂S release began at 369 °C, peaked at 399 °C, and ended at 627 °C. As the sulfur loading was increased to 2.5 g S/L equivalent and then 7.5 g S/L, also shown in Figure 3.2, the release of H₂S began at temperatures slightly lower than at the 1 g S/L loading (358 and 356 °C, respectively). The reason for the lowering of the first release temperature as the sulfur loading was increased is not totally clear; however, it is probably due to the fact that at low loadings sulfur is stored at the strongest adsorption sites (e.g., the most basic).

![Figure 3.1. Sulfur species released from Pt/Al₂O₃ sulfated to 2.5 g sulfur/L of catalyst equivalent during TPR. Gas composition: 2% H₂, 5% CO₂ and 5% H₂O, balance Ar, GHSV=30,000 h⁻¹.](image)

As the loading is increased, these sites are filled and sulfur is increasingly stored at sites where it is more weakly adsorbed. The maximum for this release event occurred at 368 °C for the 2.5 g S/L loading and 381 °C for the 7.5 g S/L sample. As the sulfur loadings increased so did the amount of sulfur released during TPR. In all three samples, the majority of the sulfur released was seen as H₂S, its release peaking below 400 °C. This
result is broadly comparable with results reported in the literature. Wei et al. reported that peak H$_2$S evolution from Pt/Al$_2$O$_3$ occurred at 410 °C [31], while Elbouazzaoui et al. reported H$_2$S release from Pt/Al$_2$O$_3$ starting at 300°C and peaking at 450 °C [11].

**Table 3.5. Relative amounts of H$_2$S released from different storage components during temperature-programmed reduction**

<table>
<thead>
<tr>
<th>Equivalent S loading, g/L</th>
<th>Storage Component Type</th>
<th>1</th>
<th>2.5</th>
<th>7.5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% H$_2$S</td>
<td>Peak Temperature, °C</td>
<td>% H$_2$S</td>
<td>Peak Temperature, °C</td>
</tr>
<tr>
<td>Pt/Al$_2$O$_3$</td>
<td>Al$_2$O$_3$ Surface</td>
<td>80</td>
<td>399</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ Bulk</td>
<td>20</td>
<td>797</td>
<td>N/D</td>
</tr>
<tr>
<td></td>
<td>CeO$_2$ Surface</td>
<td>100</td>
<td>518</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>CeO$_2$ Bulk</td>
<td></td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>PBA</td>
<td>Al$_2$O$_3$ Surface</td>
<td>91</td>
<td>729</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ Bulk</td>
<td>N/D</td>
<td>--</td>
<td>N/D</td>
</tr>
<tr>
<td></td>
<td>BaO Surface</td>
<td>65</td>
<td>737</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>BaO Bulk</td>
<td>N/D</td>
<td>--</td>
<td>N/D</td>
</tr>
<tr>
<td>PBAC</td>
<td>Al$_2$O$_3$ Surface</td>
<td>35</td>
<td>465</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ Bulk</td>
<td>N/D</td>
<td>--</td>
<td>N/D</td>
</tr>
<tr>
<td></td>
<td>CeO$_2$ Surface</td>
<td></td>
<td>--</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CeO$_2$ Bulk</td>
<td></td>
<td>--</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BaO Surface</td>
<td>46</td>
<td>378</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>BaO Bulk</td>
<td>N/D</td>
<td>--</td>
<td>N/D</td>
</tr>
<tr>
<td>Pt/Al$_2$O$_3$/BaO/Al$_2$O$_3$</td>
<td>Surface</td>
<td>19</td>
<td>748</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>BaO Bulk</td>
<td>34</td>
<td>791</td>
<td>25</td>
</tr>
</tbody>
</table>

* Rich phase for TPR: 2% H$_2$, 5% CO$_2$, 5% H$_2$O, Ar balance, GHSV = 30,000 h$^{-1}$

b N/D: Not detectable by Cl-MS during the experiment
Figure 3.2. Comparison of H$_2$S released from Pt/Al$_2$O$_3$ sulfated to 1.0, 2.5, and 7.5 g sulfur/L of catalyst during TPR. Gas composition as for Figure 3.1.

TPR results for Pt/CeO$_2$ are shown in Table 3.5 and Figure 3.3. For the sulfur loadings of 1.0 g S/L, 2.5 g S/L and 7.5 g S/L, H$_2$S evolution commenced at 459, 415, and 423 °C, respectively, with the corresponding peak H$_2$S releases at 518, 463, and 451 °C. These values compare well with the temperatures reported by Ji et al. (450 °C) [17], Bazin et al. (400-500 °C) [32,33], and Waqif et al. (480-550 °C) [34] for sulfate reduction and concomitant sulfur release from sulfated ceria. Similar to the Pt/Al$_2$O$_3$ samples, the total amount of sulfur released from Pt/CeO$_2$ during TPR increased with increasing sample exposure to SO$_2$, while for all three sulfur loadings H$_2$S was the main species released by mass. In addition, there were indications of a possible minor secondary H$_2$S release event centered at approximately 750 °C (see inset, Fig. 3.3). However, the magnitude of this event was such that it is hard to distinguish it from analytical noise, and consequently we have chosen not to include it in Table 3.5.
Figure 3.3. Comparison of H$_2$S released from Pt/CeO$_2$ sulfated to 1.0, 2.5, and 7.5 g sulfur/L of catalyst during TPR. Gas composition as for Figure 3.1.

Turning to catalyst PBA, for the 1 g S/L loading (Table 3.5 and Figure 3.4), SO$_2$ release was observed at 400 °C, followed by the release of H$_2$S that peaked at 477 °C. The evolution of these sulfur species can be assigned to sulfur release from alumina as seen for the Pt/Al$_2$O$_3$ reference sample. A second release event started at about 573 °C and continued until 800 °C with the peak H$_2$S concentration occurring at 729 °C. This is second release event for both loadings took place at 550 °C and in the case of the 2.5 g S/L sample reached a maximum concentration at 706 °C, a slightly lower value than for the sample sulfated to 1 g S/L. This result is consistent with the increase in sulfur loading and shift to a lower release temperature observed for the other samples. In the case of the
7.5 g S/L sample, a double peak was observed at high temperature. The first maximum of this double peak occurred at 682 °C, and the second occurred at 773 °C. The first of the maxima can be assigned to the release of sulfur stored as surface BaSO$_4$, while the second can be attributed to sulfur stored as bulk BaSO$_4$.

Several authors have made similar observations that temperatures above 700 °C are required for the decomposition of bulk BaSO$_4$ [4,11,35]. Sedlmair et al. reported that during sulfation surface sulfates can undergo migration into the support material to become bulk sulfates [36]. Elbouazzaouï et al. concluded that peaks corresponding to surface and bulk BaSO$_4$ were present in the TPR profile of a sulfated Pt/BaO/Al$_2$O$_3$ catalyst [4,11]. These workers postulated that Pt promotes the reduction of surface BaSO$_4$ deposited in the vicinity of Pt but has no effect on BaSO$_4$ located far from the

Figure 3.4. Comparison of H$_2$S released from PBA sulfated to 1.0, 2.5, 6.0, and 7.5 g sulfur/L of catalyst during TPR. Gas composition as for Figure 3.1.
metal sites. Using Raman spectroscopy, Wei et al. concluded that BaSO₄ close to Pt particles has a small crystallite size (< 3 nm) and is reduced at moderate temperatures (~650 °C). On the other hand, bulk sulfate has a larger crystallite size (> 10 nm) and is reducible only at high temperatures (~750 °C) [31]. Stakheev et al. also proposed that the presence of two peaks is due to surface and bulk barium sulfates or to BaSO₄ located close to and far away from Pt particles [35].

Based on the results from the two reference samples and catalyst PBA, the effects of ceria addition to PBA can be demonstrated. Looking at the TPR result for the PBAC sample loaded to 1 g S/L (Figure 3.5), two desorption maxima occur at 465 and 737 °C. The first release event can be assigned to release from ceria as seen with the Pt/CeO₂ sample, while the second corresponds to the release of sulfur from BaSO₄, as seen with PBA. Comparing the PBAC and PBA samples at 1g S/L, Table 3.5, the amount of H₂S released from Ba sites reflects the presence of ceria with a difference of 26% less H₂S released from the Ba in PBAC compared to PBA. Comparing the release from the Al sites in PBA to the Ce sites in PBAC, a 26% difference is again seen in the amount of H₂S evolved. The release of sulfur species from the Ce phases in PBAC demonstrates the additional storage provided by the Ce sites. As seen in Figure 3.5, when the loadings were increased from 1 to 2.5 to 7.5 g S/L, the height of the peak from the release of CeO₂ sites increased faster than the peak from the Ba sites. This increase is also reflected in Table 3.5, where the amount of H₂S released from the Ce sites in PBAC increased from 35% of the total for 1 g S/L loading to 43% for 2.5 g S/L and 62% for 7.5 g S/L. This implies that sulfur was preferentially stored at the CeO₂ sites as opposed to the BaO sites as the loading increased.

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3.3.1.2. Effect of Platinum Location on Desulfation Efficiency.

In order to demonstrate the influence of Pt location (with respect to the Ba sites) on LNT desulfation, a sample was prepared in which the Pt and Ba phases were separated. This was done by physically mixing 1 wt% Pt/Al₂O₃ and 20 wt% BaO/Al₂O₃ powders in a 1:1 weight ratio. As shown in Table 3.5 and Figure 3.6, during TPR the physical mixture displays several H₂S release events. For the sample loaded to 1 g S/L, the first release of H₂S is seen at 356 °C and extends up to 580 °C, with a maximum at 378 °C. The second release begins at 580 °C, peaks at 748 °C and extends up to 752 °C, and the third begins at 752 °C and continues until the end of the TPR experiment at 800 °C, with a maximum at 791 °C. As the sulfur loading is increased to 2.5 g S/L, these maxima are slightly shifted towards lower temperature, as typically observed for the other catalyst samples discussed above.

Figure 3.5. Comparison of H₂S released from PBAC sulfated to 1.0, 2.5, 6.0, and 7.5 g sulfur/L of catalyst during TPR. Gas composition as for Figure 3.1.
Comparing the results for the physical mixture and sample PBA, although both samples release about the same amount of sulfur at the 1 g/L S loading (and correspondingly more at the 2.5 g/L loading), several significant differences are observed. First, sulfur release in the range 350-500 ºC is observed to occur at lower temperatures and in relatively greater amounts for the physical mixture than for PBA. The release in this temperature range is consistent with the decomposition of sulfate on alumina [11,31], while the releases seen from both samples at the higher temperatures (>580 ºC) can be assigned to the decomposition of BaSO$_4$ [4,11,35]. Second, whereas PBA shows a single H$_2$S release event corresponding to the decomposition of surface BaSO$_4$, the physical mixture shows a double peak corresponding to H$_2$S release from both surface and bulk BaSO$_4$. Third, the maxima for H$_2$S release from surface BaSO$_4$ are shifted by between ~20 and 40 ºC to higher temperature for the physical mixture as compared to PBA (the exact value being dependent on the sulfur loading). We note that a similar observation has been reported by Wei et al. during related TPR experiments [31]: for a physical mixture of Pt,Rh/Al$_2$O$_3$ and BaO/Al$_2$O$_3$, the high temperature BaSO$_4$ release maximum occurred at a temperature that was 60 ºC higher than for the corresponding peak observed for an impregnated sample containing BaO/Pt,Rh/Al$_2$O$_3$. 
Figure 3.6. Comparison of H$_2$S released from PBA and 1:1 physical mixture of Pt/Al$_2$O$_3$ and BaO/Al$_2$O$_3$ sulfated to 1.0 and 2.5 g sulfur/L of catalyst during TPR. Gas composition as for Figure 3.1. Note that for clarity the plots have been stacked.

From the foregoing it is apparent that in PBA most of the sulfur is stored on surface BaO sites, whereas in the physical mixture sulfur is stored on both Al$_2$O$_3$ and BaO sites. Sulfur storage on the Al$_2$O$_3$ sites can be attributed to spillover of SO$_3$ from Pt to the Al$_2$O$_3$ support during sulfation. More significantly, the fact that the desulfation temperature of the Ba storage component is shifted towards higher temperature for the physical mixture relative to PBA is consistent with the idea that the decomposition of surface BaSO$_4$ is facilitated by adsorbed H atoms which spill over from the Pt sites onto the sulfated Ba phase. Physical separation of the Pt and Ba phases appears to inhibit this process, with the consequence that the surface BaSO$_4$ behaves more like bulk BaSO$_4$ with respect to its desulfation properties. We note that somewhat analogous findings have
been reported for nitrate decomposition on physical mixtures of Pt/Al₂O₃ and BaO/Al₂O₃ [37]: in the absence of hydrogen spillover from Pt to the Ba phase, considerably higher temperatures are required to achieve nitrate decomposition than is usual for Pt/BaO/Al₂O₃ catalysts.

3.3.2. Monolith Catalysts.

3.3.2.1. Effects of Sulfur on NOₓ Storage Efficiency and Regeneration Temperature.

In order to shed further light on washcoat component effects in LNT sulfation and desulfation, two experiments were performed using fully formulated monolithic catalysts in which the loadings of the various components (ceria, ceria-zirconia, and precious metals) were systematically varied. In the first experiment, the effect of desulfation at different temperatures on the lean phase NOₓ storage efficiency (NSE) during lean-rich cycling was examined. In the second experiment, the ability of the monolith sample to be desulfated under rich conditions was determined by calculating the amount of sulfur released during desulfation.

Considering the results of the first experiment (Figure 3.7), sample 30-0, containing no ceria, showed the largest decrease in the NSE during the lean period, corresponding to a loss of 60% after sulfation of the sample. Furthermore, the 30-0 sample was not able to achieve its pre-sulfation NSE value at any of the desulfation temperatures from 650 to 750 °C, as shown in Figure 3.8. The highest value was seen at 750 °C, corresponding to only 95% of the original NSE. Compared to the other catalysts, the NSE of 30-0 showed the greatest dependence on desulfation temperature (difference of greater than 20% over the temperature range). This finding can be explained on the basis of the TPR results presented above for catalyst PBA. Looking at Figure 3.8, it is evident that a temperature of less than 750 °C is insufficient to completely desulfate sample 30-0.
Figure 3.7. Comparison of lean NO\textsubscript{x} storage efficiency values for fresh and sulfated monolith samples. Samples were sulfated with 9 ppm SO\textsubscript{2} for 16 h at 350 °C under 1 min lean/1 min rich conditions.

Turning to the 30-50 and 30-100 samples containing 50 and 100 g/L of ceria, respectively, the presence of ceria in the monolith results in a higher NSE after sulfation (relative to 30-0) and a clear lowering of the desulfation temperatures required to approach the pre-sulfation NSE values of the catalysts. The NSE values after sulfation for 30-50 and 30-100 are roughly twice the value for 30-0 (Figure 3.7). As shown in Figure 3.8, sample 30-50 reached 94% of its clean-off NSE value at 675 °C and 97% at 700 °C. Sample 30-100 was even better than 30-50, reaching 95% of its clean-off value at 650 °C. Indeed, in general the NO\textsubscript{x} storage efficiency of 30-100 was higher over the entire temperature range used for desulfation than 30-0 or 30-50. The reason for the
superior performance of 30-50 and 30-100 over 30-0 can be assigned to the presence of CeO$_2$ in the sample. As seen for PBAC, CeO$_2$ can store sulfur, thereby decreasing the extent of bulk BaSO$_4$ formation. Further, the CeO$_2$ phase can be desulfated at relatively low temperature. An additional factor may be the high water-gas shift (WGS) activity of Pt/CeO$_2$. Indeed, in previous work we have demonstrated the superior WGS activity of 30-50 and 30-100 relative to 30-0 and the higher intra-catalyst H$_2$ concentrations that result during rich operation [21].

Figure 3.8. Comparison of normalized lean NO$_x$ storage efficiency values (NO$_x$ storage efficiency after desulfation divided by the NO$_x$ storage efficiency after clean-off) for samples 30-0, 30-50, 30-100, 30-50z, and 30-100z. Desulfation conditions: 1.2% CO, 0.4% H$_2$, 10% CO$_2$, 10% H$_2$O, balance N$_2$, GHSV=30000 h$^{-1}$. 

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The effects of CeO$_2$ addition to the monolith catalysts are further supported by studying the fraction of sulfur released from the stored sulfur. Starting with series 1 (see Figure 3.9), the effect of CeO$_2$ is evidenced by the fact that larger fractions of the stored sulfur are released at lower temperatures (650 and 675 °C) as compared to catalyst 30-0. Indeed, sulfur release at these low temperatures increases with ceria loading. The amount of sulfur released during desulfation for the 30-0 sample is lower than 30-50 or 30-100 until 700 °C and higher. The increased fraction of sulfur released is attributed to the additional SO$_x$ storage sites provided by the ceria present in the sample, which as shown by the TPR results presented in section 3.3.1.1 above, releases H$_2$S and SO$_2$ at significantly lower temperatures than the BaO phase.

Figure 3.9. Comparison of fraction of sulfur released/stored after sulfation with 90 ppm SO$_2$ for 1 h for samples 30-0, 30-50, 30-100, 30-50z and 30-100z. Desulfation conditions as for Figure 3.8.
In addition to the ceria containing samples, two samples were examined that contained CeO₂-ZrO₂ so that the effects of CeO₂ and CeO₂-ZrO₂ could be compared. Both samples contained 30 g/L of BaO, as for the series discussed above; the full compositions are given in Table 3.2 (series 2). The results obtained for this series are also shown in Figures 3.7 and 3.8. While the fresh NOₓ storage efficiency value for 30-50z was only 7% lower than the value for 30-50 (84% vs. 91%), the measured value for 30-50z after sulfation was 20% lower: in absolute terms, the sample 30-50 lost 34% of its NOₓ storage efficiency and the 30-50z lost 47%. Comparing samples 30-100 and 30-100z, the difference in the fresh NSE values was slightly larger (91% for 30-100 versus 76% for 30-100z). However, the difference in the NSE values after sulfation for 30-100 and 30-100z was only 9%. Looking at the NSE values after desulfation for these four samples (Figure 3.8), the differences were less than 7% at 650 °C and less than 4% over the remaining temperature range.

Data pertaining to the sulfur release during desulfation supports the observation that the catalysts containing CeO₂-ZrO₂ display inferior desulfation characteristics as compared to their La-stabilized CeO₂-containing analogs (see Figure 3.9). This may be attributed to the less basic nature of the CeO₂-ZrO₂ (relative to CeO₂), which may lower the ability of CeO₂-ZrO₂ to store sulfur and hence result in comparatively more severe sulfation of the Ba phase. Indeed, Rohart et al. have reported that the basicity of Ce-mixed oxides affects their SOₓ storage capacity [38], sulfate adsorption being higher on ceria-rich oxides than on zirconia-rich oxides. Also relevant in this context are the results of a recent study by Bazin et al. [33], who found that the addition of zirconia into ceria limits sulfation in the bulk of the oxide, thereby limiting the total sulfur uptake. The same authors also report that zirconia addition raises the required desulfation temperature slightly; for example, weight loss maxima of 733 K and 753 K were observed during hydrogen reduction of sulfated CeO₂ and Ce₀.63Zr₀.37O₂, respectively. Note that the surface areas of the La-stabilized CeO₂ and CeO₂-ZrO₂ used in the monolithic catalysts in the present study were very similar (119 m²/g and 114 m²/g, respectively), hence surface area should not be a factor with respect to their differing sulfation-desulfation behavior.
Finally, we note that ease of catalyst desulfation (as reflected in the fraction of sulfur released/sulfur stored) holds implications for long term catalyst use, given that the catalyst is subjected to repeated sulfation-desulfation cycles over the course of its useful life. For additives or specific compositions which negatively affect sulfur release from the catalyst, there is a greater tendency to accumulate residual sulfur during repeated sulfur/desulfation events, eventually leading to reduced NO\(_x\) storage efficiency. In an accompanying paper [39] we describe the results of accelerated aging experiments performed on catalysts 30-0, 30-50, 30-100 and 30-100z in which repetitive sulfation/desulfation cycles were performed, and we correlate the residual sulfur contents of the catalysts with their composition. The resulting data confirm that ceria-containing catalysts exhibit superior sulfation and desulfation characteristics as compared to their non-ceria analog; more particularly, the ability of ceria to trap sulfur results in decreased sulfur accumulation on the main Ba NO\(_x\) storage component. In addition, while the results presented above suggest that catalyst 30-100z should perform less well in this respect than 30-100, the NO\(_x\) conversion of 30-100z after aging is in fact slightly better than that of 30-100 [39]. The reason for this is not entirely clear, although it may be a consequence of the superior stability of the Ce\(_{0.7}\)Zr\(_{0.3}\)O\(_2\) mixed oxide with respect to thermally induced sintering as compared to La-stabilized CeO\(_2\).

3.3.2.2. Effect of Precious Metal Loading on NO\(_x\) Storage Efficiency and Regeneration Temperature.

In the last group of catalysts (Series 3, Table 3.2), the amount of Pt was varied and the amount of Rh was halved. The two samples examined corresponded to Pt-50, containing 50 g/ft\(^3\) (1.77 g/L) Pt and 10 g/ft\(^3\) (0.35 g/L) Rh, and Pt-100, containing 100 g/ft\(^3\) (3.53 g/L) Pt and 10 g/ft\(^3\) (0.35 g/L) Rh. The BaO and CeO\(_2\) loadings were fixed at 30 g/L and 50 g/L, respectively (i.e., as for catalyst 30-50). Looking at the comparison of NO\(_x\) storage efficiency values for fresh and sulfated monolith samples (Figure 3.7), it is evident that the 30-50 sample, with double the amount of Rh, is less susceptible to poisoning than the Pt-50 or Pt-100 samples. Furthermore, as shown in Fig. 3.10, clear trends emerge when considering the NSE of the catalysts subjected to desulfation in the
specifically, the NSE of sample 30-50 is found to be slightly higher than that of Pt-100 after desulfation at temperatures of 700 °C and above, a finding which can be ascribed to the lower Rh loading in the latter sample. These results are consistent with the reports of Amberntsson et al. [40,41], who for Ba-based LNTs containing either Pt, Rh or Pt + Rh observed that the recovery of NOx storage capacity after desulfation in H2 at 750 °C was complete only for the samples containing both Pt and Rh. This was attributed to the fact that Rh is more easily sulfur-regenerated than Pt [40]. Furthermore, it was found that Rh suffered from severe deactivation with respect to its NO oxidation function under SO2 exposure but retained high NOx reduction activity under rich conditions; in contrast, the opposite behavior was observed for Pt. Consequently, it was concluded that a combination of Pt and Rh is preferable for minimizing the effects of sulfur deactivation [40,41]. In the case of Pt, it is known that under rich conditions Pt sulfides and/or elemental sulfur can form which block the Pt sites with respect to the adsorption of reductants [36,42]. From this it follows that desulfation should proceed most efficiently when a high concentration of Rh is present, since the Rh will be less susceptible to poisoning by the released sulfur and will enable the continuous adsorption and spillover of reductant molecules onto the sulfated oxides present.
Figure 3.10. Comparison of normalized lean NO\textsubscript{x} storage efficiency values (NO\textsubscript{x} storage efficiency after desulfation divided by the NO\textsubscript{x} storage efficiency after clean-off) for samples 30-50, Pt-50, Pt-100. Desulfation conditions as for Figure 3.8.

Catalyst Pt-100, in turn, displays higher NSE at each of the desulfation temperatures when compared to catalyst Pt-50, a result which can be directly attributed to the extra Pt present. As a consequence of the additional platinum in Pt-100, the average distance between the Pt sites and the storage components should be decreased as compared to Pt-50 [43]. The effect of the increased proximity of the Pt to the sulfates stored at BaO was demonstrated in the PBA and Pt/Al\textsubscript{2}O\textsubscript{3} + BaO/Al\textsubscript{2}O\textsubscript{3} powders in section 3.1.2.

Specifically, decreasing the Pt-Ba distance can be anticipated to result in more efficient spillover of reductants from the Pt sites and hence, more extensive desulfation. Figure 3.11 shows the effects of precious metal loading on the fraction of sulfur released from
the samples by comparing the results for the series 3 catalysts to those obtained for 30-50. At almost every temperature, Pt-100 released a greater amount of stored sulfur than Pt-50, consistent with this reasoning.

Overall, in comparing all three of the series of monolith catalysts, the CeO₂ loading is observed to exert a greater influence on catalyst desulfation characteristics than the Pt loading (within the range studied), particularly at temperatures below 700 °C. Correspondingly, the results from the experiments in which sulfur evolution was monitored parallel the results gained from the NOₓ storage efficiency experiments. Comparing the three series of catalysts, the catalysts with the highest amounts of CeO₂ or CeO₂-ZrO₂ have the best performance, as measured by the temperature required during desulfation to reach each individual catalyst’s clean-off NSE value. A second measure of performance is the resistance to sulfur deactivation in the first place, where again the higher CeO₂ and CeO₂-ZrO₂ containing samples have the best performance. Catalyst 30-100, the sample with the highest amount of CeO₂, showed the best performance in NOₓ storage efficiency across all of the desulfation temperatures.
Figure 3.11. Comparison of fraction of sulfur released/stored after sulfation with 90 ppm SO₂ for 1 h for samples 30-50, Pt-50 and Pt-100. Desulfation conditions as for Figure 3.8.

3.4. Conclusions.

The effects of ceria on the sulfation and desulfation characteristics of Ba-based LNT catalysts have been demonstrated using both powder and fully formulated monolithic catalysts. TPR experiments performed on the powder catalysts showed that each of the oxide phases present (BaO, CeO₂, and Al₂O₃) is able to store sulfur and that they possess distinct behavior in terms of the temperatures at which desulfation occurs. Overall, these findings confirm the idea that ceria can function as a sulfur sink in LNT catalysts, thereby helping to protect the main Ba NOₓ storage phase from sulfation.

In addition, the importance of maintaining the Pt and Ba phases in close proximity for efficient LNT desulfation has been demonstrated. It is evident that when Pt and Ba are
physically separated, the desulfation temperature of the surface BaSO₄ is shifted by 20-40 °C towards higher temperature, i.e., towards the position characteristic of bulk BaSO₄. This observation is consistent with the idea that decomposition of surface BaSO₄ is facilitated by H ad-atoms which spill over from the Pt sites onto the sulfated Ba phase. Physical separation of the Pt and Ba phases appears to inhibit this process, with the consequence that the surface BaSO₄ behaves more like bulk BaSO₄ with respect to its desulfation properties. This finding is analogous to the results of nitrate decomposition studied on physical mixtures of Pt/Al₂O₃ and BaO/Al₂O₃ [37].

From the monolith studies, it was found that relative to a sample containing no ceria, samples containing La-stabilized CeO₂ or CeO₂-ZrO₂ showed: 1) a greater resistance to deactivation during sulfation (as reflected by the NOₓ storage efficiency), and 2) required lower temperatures to restore the NOₓ storage efficiency to its pre-sulfation value. Additionally, the CeO₂ containing catalysts (series 1) released greater fractions of stored sulfur during desulfation. In addition to the ability of ceria to store sulfur and release it at relatively low temperatures under reducing conditions, these results can be attributed to the high water-gas shift activity displayed Pt/CeO₂, which result in increased intra-catalysts concentrations of H₂ under rich conditions. The results also showed that precious metal loadings can significantly impact desulfation efficiency and that both high Rh and Pt loadings are beneficial for catalyst desulfation.

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3.5. References.


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Chapter 4. Effect of Aging on the NO\textsubscript{x} Storage and Regeneration Characteristics of Fully Formulated Lean NO\textsubscript{x} Trap Catalysts.

Disclaimer: The work provided in this chapter is the result of collaboration with Dr. Yaying Ji of the Center for Applied Energy Research at the University of Kentucky. Dr. Ji was responsible the material characterization of the catalysts used in this chapter. This information is described in sections 4.2.3. through 4.3.1.

Note - This chapter was published as an article in the following journal:

Y. Ji, V. Easterling, U. Graham, C. Fisk, M. Crocker, J.-S. Choi, Effect of Aging on the NO\textsubscript{x} Storage and Regeneration Characteristics of Fully Formulated Lean NO\textsubscript{x} Trap Catalysts. Applied Catalysis B: Environmental 103 (2011) 413-427.

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4.1. Introduction.

Lean NO\textsubscript{x} traps (LNTs), also known as NO\textsubscript{x} storage-reduction (NSR) catalysts, represent a promising technology for the abatement of NO\textsubscript{x} emissions from lean burn gasoline and diesel engines. LNT catalysts typically comprise precious metals (generally Pt and Rh) and an alkali or alkaline earth metal storage component (most commonly BaO) supported on a high surface area metal oxide such as $\gamma$-Al\textsubscript{2}O\textsubscript{3} [1]. LNT catalysts require cyclic operation between lean and rich conditions. Under lean conditions, NO is first oxidized to NO\textsubscript{2} over the precious metal, which is followed by NO\textsubscript{x} storage on the storage component as nitrates and nitrites. Stored NO\textsubscript{x} species are subsequently released and reduced to N\textsubscript{2} after switching to rich (i.e., net reducing) conditions. The trapping ability of the LNT catalysts is thus restored after a lean-rich cycle [2]. Although LNTs have been commercialized for some applications, the durability of LNT catalysts still remains problematic. Sulfur poisoning and thermal aging are recognized as two major causes of deactivation. The BaO NO\textsubscript{x} storage component of a LNT catalyst has a greater affinity for SO\textsubscript{3} than for NO\textsubscript{2}, and the resulting sulfate cannot be removed under typical rich
purging conditions as for nitrates; hence sulfur accumulates on the catalyst and blocks the Ba sites with respect to further NO\textsubscript{x} storage [3-9]. Desulfation requires high temperature treatment under rich conditions [10-14], and such treatments give rise to deactivation mechanisms such as precious metal sintering, total surface area loss, and solid state reactions between the various oxides present in the washcoat.

The presence of Pt in LNT catalysts is required not only to facilitate NO\textsubscript{x} storage through spillover of NO\textsubscript{2} from Pt to the Ba phase (subsequent to NO oxidation on Pt), but also to facilitate NO\textsubscript{x} reduction during rich purging. Both functions are related to the proximity between the Pt and Ba phases, and both can be significantly deteriorated by Pt sintering which results in decreased interaction between the two phases. An early study by Mahzoul et al. [15] showed that only the Pt sites close to BaO crystallites are responsible for nitrate formation (i.e., NO\textsubscript{x} storage), although other Pt sites can act as centers for the oxidation of NO. Nova et al. [16] studied the role of the Pt-Ba interaction in the regeneration behavior of LNTs. A comparison between Pt/BaO/Al\textsubscript{2}O\textsubscript{3} and a Pt/Al\textsubscript{2}O\textsubscript{3}-BaO/Al\textsubscript{2}O\textsubscript{3} physical mixture showed that the promoting effect of Pt on the rate of nitrate reduction required Pt and Ba dispersed on the same support, this being in line with the role of the Pt-Ba interface in nitrate decomposition suggested by Coronado et al. [17] and the involvement of NO\textsubscript{x} spillover from Ba to its nearest Pt sites suggested by Olsson et al. [18]. Similarly, Cant and co-workers [19] inferred the occurrence of forward and reverse spillover of NO\textsubscript{x} during exchange between gaseous \textsuperscript{15}NO and stored NO\textsubscript{x}, these processes being five times faster when Pt and BaO were located on the same support.

In another study, Büchel et al. examined the influence of Pt location – on BaCO\textsubscript{3} or Al\textsubscript{2}O\textsubscript{3} – for Pt/Ba/Al\textsubscript{2}O\textsubscript{3} catalysts prepared by flame spray pyrolysis [20]. The benefit of a close interaction between Pt and Ba was confirmed for NO\textsubscript{x} storage, although Pt on Al\textsubscript{2}O\textsubscript{3} exhibited better NO oxidation activity which was limiting for NO\textsubscript{x} storage at low temperatures. During NO\textsubscript{x} reduction, Pt on Ba showed superior activity to Pt on Al\textsubscript{2}O\textsubscript{3}, which was attributed to the importance of reverse spillover and the promotional effect of Ba on the Pt reduction activity. A recent TAP reactor study by Kumar et al. has provided further evidence of the role of spillover processes and the importance of the Pt/Ba
interface during NO\textsubscript{x} storage and reduction [21]. Their data suggests that NO\textsubscript{x} storage proceeds radially outward from the Pt sites and that the stored NO\textsubscript{x} possesses some degree of mobility. In essence, Pt acts as a conduit for spillover to and from the Ba phase, in addition to playing a key role in catalyzing the NO oxidation and reduction reactions themselves. In another recent study [22] concerned with fast NO\textsubscript{x} storage on Pt/BaO/Al\textsubscript{2}O\textsubscript{3} (that is, the initial phase of storage when there is essentially no NO\textsubscript{x} slip from the LNT), it was concluded that the Pt-Ba interface plays a key role, associated with the spillover of dissociated oxygen atoms from Pt to Ba which participate in the adsorption of NO and NO\textsubscript{2} on the Ba sites via nitrite and nitrate formation. In summary, therefore, close proximity of Pt and Ba is required to achieve both efficient NO\textsubscript{x} storage and NO\textsubscript{x} reduction during lean-rich cycling.

Pt sintering mainly occurs under oxidizing conditions during thermal aging. Graham et al. compared the behavior of Pt under both reducing and oxidizing conditions [23], and found that the most significant Pt particle growth occurred under oxidizing conditions. A recent study by Datye and co-workers supports the notion that Pt sintering in air results from the formation of volatile Pt oxide, PtO\textsubscript{x}, leading to enhanced interparticle transport and sintering via Ostwald ripening [24]. However, sintering was significantly inhibited in reducing atmospheres, probably due to the low vapor pressure of metallic Pt; consequently, particle migration and coalescence was suggested to be the major mechanism of Pt sintering under reducing conditions. Pt sintering has a permanent impact on catalyst performance due to its irreversibility and consequently it has been recognized as a key issue associated with thermal deactivation. Indeed, a number of studies have provided evidence that Pt sintering can result in decreased interaction between the Pt and Ba phases (i.e., phase segregation) which in turn leads to degraded NO\textsubscript{x} storage and regeneration behavior [25-31]. Fekete et al. [25] attributed the observed decrease in NO\textsubscript{x} storage capacity after aging to loss of contact between the precious metals and the storage material, in addition to the formation of mixed metal oxides from unwanted side reactions between the storage material and the support. It was suggested that the diminished contact leads to a reduced spillover rate of NO\textsubscript{2} from the precious metal to the adsorbent, thereby decreasing NO\textsubscript{x} storage efficiency. Uy et al. [26]
characterized fresh and aged Pt/Ba/Al₂O₃ catalysts using in situ UV and visible Raman spectroscopy and found evidence for Ba particles “separating from” or behaving independently from the Pt/Al₂O₃ in aged Pt/Ba/Al₂O₃.

Unwanted side reactions between Ba and the support is another effect associated with thermal aging, resulting in the formation of Ba aluminate, zirconate, cerate, etc., as applicable [31-39]. From studies with Pt-Ba/Al₂O₃ catalysts, Jang et al. [31] emphasized the importance of Ba-Al mixed oxide formation as a cause of degraded NOₓ storage capacity. Upon heating Pt-Ba/Al₂O₃ from 550 to 850 °C, they observed the gradual conversion of Ba/Al₂O₃ to BaAl₂O₄. Several other authors have similarly found that BaAl₂O₄ forms at about 850 °C [33-35] and concluded that the formation of such mixed oxides is a significant factor in thermal deactivation. However, recent studies have shown that the formation of BaAl₂O₄ and BaCeO₃ is largely reversible in nature [34-39]. For example, Casapu et al. [34] studied LNT catalysts that contain CeO₂ as a support material and observed the formation of BaCeO₃ at 800 °C. Decomposition of BaCeO₃ was found to occur at 300-500 °C in the presence of NO₂/H₂O or CO₂ [34,35], resulting in an improvement in NOₓ storage capacity. Another recent report indicates that BaCeO₃ formation is inhibited in the presence of CO₂ at a concentration as low as 5% [39]. In comparison, BaAl₂O₄ is much more stable under typical operating conditions but can be converted to BaCO₃ and Al₂O₃ at room temperature in the presence of liquid water [36,37].

In a previous paper [40], we reported the results of a study into the effect of catalyst ceria content and type (La-stabilized CeO₂ or CeO₂-ZrO₂) on LNT aging characteristics. Two main causes of LNT aging were discerned, corresponding to (i) sintering of the precious metals present and (ii) the accumulation of sulfur in the washcoat as BaSO₄. In addition, spectacular improvement in LNT durability was observed for catalysts containing CeO₂ or CeO₂-ZrO₂ relative to a non-ceria containing analog. This was attributed to the ability of ceria to participate in NOₓ storage/reduction as a supplement to the main Ba NOₓ storage component, the fact that Pt and the CeO₂-ZrO₂ support remain in intimate contact, and the ability of ceria to trap sulfur, resulting in decreased sulfur accumulation.
on the Ba component. In this chapter, we report the results of a study aimed at investigating the effects of precious metal (Pt, Rh) loading and BaO loading on catalyst durability.

4.2. Experimental.

4.2.1. Catalyst Preparation.

Four fully formulated Ba-based LNT catalysts were used in this study, the compositions of which are shown in Table 4.1. Details of the catalyst preparation have been described elsewhere [41]. Briefly, the powders for washcoating were prepared using the incipient wetness method. Three different powders were required to prepare the washcoat. First, Pt-Rh/Al₂O₃ powder was prepared by co-impregnating 3 wt% La₂O₃-stabilized γ-alumina (Sasol Puralox SCFa-140 L3, BET surface area of 140 m²/g) with an aqueous solution of Pt(NH₃)₄(OH)₂ and Rh(NO₃)₃, followed by calcination at 500 °C for 2 h. Second, BaO/Al₂O₃ powder was prepared by impregnating γ-alumina (Sasol Puralox SCFa-140 L3) with aqueous Ba(O₂CCH₃)₂, followed by calcination at 500 °C for 2 h to give a powder containing either 21.5 wt% or 32 wt% BaO as appropriate (for a final BaO concentration in the catalyst of 30 or 45 g/L, respectively). Subsequently, the BaO/Al₂O₃ material was ball milled with La-stabilized CeO₂ (Advanced Material Resources, BET surface area of 119 m²/g) in a weight ratio of 140:50, after which the physical mixture was impregnated with aqueous Pt(NH₃)₄(OH)₂ to achieve the total Pt loading required in the washcoat. To prepare the washcoat, 30 g/L of the Pt-Rh/Al₂O₃ powder was slurried in deionized water with 190 g/L of the Pt/[BaO/Al₂O₃ + CeO₂] mixture to which γ-alumina powder (34 g/L) was added as balance to achieve a nominal washcoat loading of 260 g/L. Additionally, a small amount of boehmite sol (6 g/L) was added to the washcoat as a binder during preparation of the slurry. As shown in Table 4.1, these four catalysts have the same nominal loadings of CeO₂ (50 g/L) while the BaO, Pt and Rh loadings were varied as indicated. A detailed breakdown of the Pt loadings on the three different types of powder in the catalyst washcoats is given in Table 4.2, while Figure 4.1 provides a schematic representation of the composition and function of the different powders. As shown, Pt/CeO₂ functions as a supplement to the main Pt/BaO/Al₂O₃ NOₓ storage-reduction component, while the function of the Pt-Rh/Al₂O₃ component is mainly to
improve NOx reduction during rich purging. In all cases, the washcoat was applied to a 4” x 6” cordierite monolith substrate, possessing a cell density of 400 cpsi and a wall thickness of 6.5 mil.

Table 4.1. Composition of catalysts subjected to simulated road aging.

<table>
<thead>
<tr>
<th>Component</th>
<th>Catalyst code / loading(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt-50</td>
</tr>
<tr>
<td>Pt, g/L (g/cuft)</td>
<td>1.77</td>
</tr>
<tr>
<td>Rh, g/L (g/cuft)</td>
<td>0.35</td>
</tr>
<tr>
<td>BaO, g/L</td>
<td>30</td>
</tr>
<tr>
<td>CeO(_2), g/L(^b)</td>
<td>50</td>
</tr>
<tr>
<td>Al(_2)O(_3), g/L(^c)</td>
<td>Balance</td>
</tr>
</tbody>
</table>

\(^a\) Nominal loadings. Total washcoat loading = 260 g/L.

\(^b\) Stabilized with 5 wt% La\(_2\)O\(_3\).

\(^c\) Stabilized with 3 wt% La\(_2\)O\(_3\).

Table 4.2. Nominal Pt loading in the three different powders used for washcoat preparation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Nominal Pt loading in powder (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Pt-Rh/Al(_2)O(_3)(^a)</td>
</tr>
<tr>
<td>Pt-50</td>
<td>1.77</td>
</tr>
<tr>
<td>Pt-100</td>
<td>3.53</td>
</tr>
<tr>
<td>30-50</td>
<td>3.53</td>
</tr>
<tr>
<td>45-50</td>
<td>3.53</td>
</tr>
</tbody>
</table>

\(^a\) Rh loading same as for Pt loading.
4.2.2. Aging Protocol.
Catalyst aging was performed on a synthetic gas bench using cores (2.1 cm diameter x 7.4 cm long) drilled out from the LNT monoliths. The protocol used for the rapid aging has been detailed in earlier publications [40,42]. This method is designed to simulate the road aging of a LNT catalyst used in conjunction with a diesel particulate filter (DPF). Each aging cycle is composed of three modes: sulfation, desulfation, and simulated DPF regeneration, the corresponding gas compositions used being shown in Table 4.3.

Sulfation was carried out under cycling conditions (60s lean/5s rich) at 300 °C to give an equivalent sulfur loading of 1.0 g/L (assuming complete uptake of sulfur). Desulfation was performed under cycling conditions (5 s lean/15 s rich) at 700 °C for 10 min, after which the catalyst was held under lean conditions at 650 °C for 30 min (to simulate DPF regeneration). A maximum mid-bed catalyst temperature of 770 ± 10 °C was observed during desulfation due to the exotherm resulting from the fast lean-rich cycling.

Depending on actual fuel sulfur levels, one aging cycle is estimated to be equivalent to 1,000-1,500 miles of road aging. 50 cycles were used for the aging runs, requiring a total aging time of ca. 100 h per sample. At the end of each aging run a final desulfation was performed under constant rich conditions, corresponding to 2% H₂ in the presence of 5% H₂O and 5% CO₂ at 750 °C for 10 min, in order to remove as much residual sulfur as possible.

![Figure 4.1. Schematic showing the functions of the three different powders contained in the prepared catalysts. In addition, alumina powder was added to the washcoat as a balance.](image)
Table 4.3. Gas compositions used for rapid aging, oxygen storage-reduction and NOx storage-reduction cycling experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sulfation During Aging</th>
<th>Desulfation During Aging</th>
<th>Simulated DPF Regeneration During Aging</th>
<th>Oxygen Storage-Reduction Cycling</th>
<th>NOx Storage-Reduction Cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>60</td>
<td>5</td>
<td>5</td>
<td>15</td>
<td>1800</td>
</tr>
<tr>
<td>NO, ppm</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>0</td>
</tr>
<tr>
<td>SO2, ppm</td>
<td>45</td>
<td>45</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O2, %</td>
<td>8</td>
<td>0</td>
<td>8</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>H2, %</td>
<td>0</td>
<td>1.3</td>
<td>0</td>
<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td>CO, %</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>H2O, %</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>CO2, %</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>N2, %</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

*GHSV = 30,000 h⁻¹ for all conditions.

4.2.3. Catalyst Evaluation.

Catalyst evaluation was performed on a synthetic gas bench reactor. Catalyst cores were wrapped in Zetex insulation tape and inserted into a horizontal quartz reactor tube (2.2 cm inner diameter). The reactor tube was heated by an electric furnace, and simulated exhaust gas mixtures were introduced from pressurized gas bottles (ultra high purity grade, Air Liquide). The gases were metered with mass flow controllers (Unit Instruments Series 7300, Kinetics Electronics) and pre-heated before entering the quartz reactor. Water was introduced by a peristaltic cartridge pump (Cole-Parmer) to a heated zone, vaporized and added to the simulated exhaust mixture. A rapid switching 4-way valve system was used to alternate between the lean and rich gas mixtures so that the lean/rich/lean transitions in these experiments were almost instantaneous (within 0.2 s).

Three K-type thermocouples were placed just before the LNT, at the LNT mid-point and just after the LNT to monitor the temperature profiles. A multi-gas analyzer (MKS Model 2030) was used to monitor NO, NO2, N2O, NH3, CO, CO2, H2O at the reactor outlet. Determination of intra-catalyst hydrogen concentrations during oxygen storage capacity (OSC) measurements was performed using SpaciMS (Spatially Resolved
Capillary Inlet Mass Spectrometry) [43,44] with a removable capillary probe inserted into the channel of the core sample near the centerline. Activity evaluation and OSC measurements for the catalysts were performed under the conditions given in Table 4.3. During the cycling conditions described in Table 4.3, the observed catalyst breakthrough profiles stabilized to a fixed limit cycle in about 2 h, at which point it was possible to characterize the performance in terms of the ‘stationary’ concentration cycles. The selectivity to N₂ during the rich purge was determined by difference (i.e., $S_{N2} = 100% - S_{N2O} - S_{NH3}$). In the case of measurements performed on fresh catalysts, the samples were in all cases first de-greened by exposing them to lean-rich cycling conditions at 500 °C for 5 h.

4.2.4. **N₂ Physisorption.**
Surface area and pore volume measurements were performed according to the BET method by nitrogen adsorption at -196 °C using a Micromeritics Tri-Star system. Prior to the measurements catalyst samples (washcoat and monolith) were ground to a fine powder and outgassed overnight at 160 °C under vacuum.

4.2.5. **Pulsed H₂ Chemisorption.**
The dispersion of precious metal (Pt+Rh) was determined with a Micromeritics AutoChem II Analyzer by means of pulsed H₂ chemisorption at dry ice temperature (-78 °C). This temperature was chosen in an effort to minimize H spillover from the metal to the support material [45]. Unlike static volumetric methods, the total amount of chemisorbed hydrogen, as opposed to irreversibly chemisorbed hydrogen, was used to determine the metal dispersion in this study. 1 g of sample (as a fine powder), including both washcoat and substrate, was loaded into the reactor. After being oxidized at 400 °C in 10% O₂/He for 15 min, followed by reduction at 300 °C in 10% H₂/Ar for 15 min, the catalyst was heated up to 400 °C (hold time 10 min) in flowing Ar to remove adsorbed H. Pulsed H₂ chemisorption was initiated using a four-way valve after the catalyst had been cooled to -78 °C. During this measurement, 0.5 ml of 10% H₂/Ar was pulsed into the reactor every 2 min, the H₂ signal at the reactor outlet being monitored with a thermal conductivity detector (TCD). H₂ pulsing was terminated after the TCD signal had
reached a constant value, i.e., the total precious metal (Pt+Rh) sites were saturated with H\textsubscript{2}. Assuming a 1:1 ratio of atomic hydrogen to surface Pt or Rh, the metal dispersion was calculated based on the amount of H adsorbed.

4.2.6. \textit{HRTEM-EELS}.

Electron microscopy studies (EM) were performed using a JEOL 2010F STEM outfitted with a URP pole piece, GATAN 2000 GIF, GATAN DigiScan II, Fischione HAADF STEM detector, and EmiSpec EsVision software. STEM images were acquired using the high resolution probe at 2 Å. EELS spectrum imaging was performed using the 1 nm probe, an alpha of 30 mrad, and a beta of 6 mrad. Materials for the EM analysis were powdered samples and minute amounts were supported on copper grids.

4.2.7. \textit{Postmortem Sulfur Analysis}.

The amount of residual sulfur in the aged catalysts was measured by detecting the SO\textsubscript{2} evolved during heating of the ground catalyst sample to 1425 °C, using an ELTRA CS 500 Carbon Sulfur Determinator. Powder X-ray diffraction (XRD) measurements were performed on a Phillips X’Pert diffractomer using Cu K\textsubscript{α} radiation (\(\lambda = 1.5406 \) Å) and a step size of 0.02°.

4.3. \textit{Results and Discussion}.

4.3.1. \textit{Characterization}.

Physical data for the fresh and aged catalysts used in this study are listed in Table 4.4. From these data it is evident that aging resulted in a decrease in washcoat BET surface area. The decreased pore volumes and increased pore radii of the aged catalysts infer the collapse of some of the smaller pores after aging. This deterioration can be ascribed mainly to sintering of the CeO\textsubscript{2} component of the washcoat. Sintering of CeO\textsubscript{2} is unavoidable under the aging conditions used in this study, albeit that the CeO\textsubscript{2} used was stabilized by La\textsubscript{2}O\textsubscript{3}. Indeed, in our previous study [40] ceria-containing catalysts (including catalyst 30-50 used in the present study) were found to undergo a more pronounced decrease in BET surface area compared to a ceria-free analog. It is also worth noting that relative to the other three catalysts, catalyst 45-50 displayed lower BET surface area and pore volume in both the fresh and aged states relative to 30-50, which
can be ascribed to increased blockage of the pores in the alumina support at the higher BaO loading.

In principle, aggregation of the Ba phase might occur during aging as a consequence of its high mobility in the presence of water [39]. Unfortunately, the BaCO$_3$ peaks in the X-ray diffractograms of the fresh and aged catalyst were too weak (due to sample dilution by the cordierite substrate) to permit determination of the average BaCO$_3$ particle size. However, TEM data obtained for catalyst 45-50 (see below) support the idea that migration and aggregation of the Ba phase does indeed occur upon aging.

Consistent with our previous study [40], loss of platinum group metal (PGM) surface area represented the most significant impact of aging. As shown in Table 4.4, the overall PGM dispersion decreased by 62-82% (relative) after aging regardless of the Ba and PGM loading. In addition to precious metal sintering, the loss of PGM surface area after aging can be attributed to the sintering of the support materials, which can result in encapsulation of the PGM [46,47]. While sintering of the La-stabilized Al$_2$O$_3$ support is negligible at the maximum temperature experienced by the catalysts during aging (770 ºC) [48], sintering of the La-stabilized CeO$_2$ under these conditions is significant, as indicated in our earlier study [40].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Estimated Washcoat BET SA (m$^2$/g)$^a$</th>
<th>Total BET Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Average Pore Radius (nm)</th>
<th>PM Dispersion (%)</th>
<th>Oxygen Storage Capacity (mmol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>Aged</td>
<td>Fresh</td>
<td>Aged</td>
<td>Fresh</td>
<td>Aged</td>
<td>Fresh</td>
</tr>
<tr>
<td>Pt-50</td>
<td>119</td>
<td>95</td>
<td>44.8</td>
<td>35.7</td>
<td>0.146</td>
<td>0.132</td>
</tr>
<tr>
<td>Pt-100</td>
<td>126</td>
<td>96</td>
<td>51.1</td>
<td>38.9</td>
<td>0.167</td>
<td>0.143</td>
</tr>
<tr>
<td>30-50</td>
<td>126</td>
<td>88</td>
<td>47.5</td>
<td>32.7</td>
<td>0.156</td>
<td>0.12</td>
</tr>
<tr>
<td>45-50</td>
<td>120</td>
<td>82</td>
<td>43.7</td>
<td>30</td>
<td>0.134</td>
<td>0.109</td>
</tr>
</tbody>
</table>

$^a$ Estimate calculated from washcoat loading and surface area of 1 m$^2$/g for cordierite substrate.
Another effect associated with catalyst aging under simulated road conditions is the accumulation of sulfur in the washcoat. Table 4.5 summarizes the results of sulfur analyses performed on the aged catalysts. Similar sulfur contents were found in the Pt-50, Pt-100 and 30-50 washcoats after aging (0.35 wt% – 0.38 wt%), whereas a sulfur content of 0.7 wt% was measured for 45-50. This result is expected, given that residual sulfur is associated with only the Ba phase in the catalysts (see discussion of TEM results below), i.e., the higher the BaO loading, the higher the residual sulfur concentration. In the case of Pt-50, Pt-100 and 30-50, if it is assumed that all of the sulfur to which the catalysts were exposed during aging was adsorbed during sulfation, then ~95% of the adsorbed sulfur was removed during desulfation (including the final desulfation step at 750 °C). This assumption is consistent with a recent characterization study on a commercial catalyst which also contained PM, Ba, Ce, Al as major washcoat components [49]. Table 4.5 also reports the residual sulfur levels in the catalysts normalized to the Ba loading determined by elemental analysis. From the resulting S:Ba mole ratios, it can be seen that between 28% and 33% of the Ba sites in the catalysts containing 30 g BaO/L were in the sulfated state and were thus unavailable for NOx storage (assuming sulfur is located only on the Ba phase after aging), while the same figure for catalyst 45-50 was 43%. In our previous study, residual sulfur in a series of related catalysts was found to be present exclusively as sulfate according to XPS data [40]. In the present work, the presence of crystalline BaSO4 (JCPDS# 76-2013) was confirmed for aged 45-50 by powder XRD (not shown). No other sulfur species were observed, nor was BaAl2O4, the latter result being consistent with the fact that the maximum temperature experienced by the catalysts during aging did not exceed 780 °C.

Table 4.5. Summary of elemental analysis data for aged catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Measured Ba in Catalyst (wt%)</th>
<th>Residual Sulfur in Catalyst (wt%)</th>
<th>Residual Sulfur in Washcoat (wt%)</th>
<th>S:Ba Mole Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-50</td>
<td>5.79</td>
<td>0.38</td>
<td>1.02</td>
<td>0.28</td>
</tr>
<tr>
<td>Pt-100</td>
<td>4.61</td>
<td>0.35</td>
<td>0.86</td>
<td>0.33</td>
</tr>
<tr>
<td>30-50</td>
<td>4.98</td>
<td>0.38</td>
<td>1.02</td>
<td>0.33</td>
</tr>
<tr>
<td>45-50</td>
<td>7.75</td>
<td>0.78</td>
<td>2.12</td>
<td>0.43</td>
</tr>
</tbody>
</table>
It is also worth noting that the higher S:Ba ratio observed for catalyst 45-50 relative to the other catalysts is consistent with a previous report that as the BaO loading on an alumina support is increased, the BaO becomes increasingly more difficult to desulfate [50]. This is explained by the fact that as the BaO loading is increased, the amount of bulk BaO increases (as opposed to monolayer BaO) which in turn gives rise to bulk BaSO₄ upon sulfation. Several studies have shown that the decomposition of bulk BaSO₄ - corresponding to large BaSO₄ crystallites and/or Ba sulfate located far away from Pt sites - requires higher temperatures than surface BaSO₄ under typical reducing conditions [13]; indeed, we have previously found that complete decomposition of bulk BaSO₄ under conditions similar to those used in the present study requires temperatures slightly in excess of 750 °C [51]. Consequently, the high loading of BaO in catalyst 45-50 (32 wt% BaO/Al₂O₃ versus 21.5 wt% BaO/Al₂O₃ in the other catalysts) results in a higher concentration of bulk BaSO₄ relative to the other catalysts and hence a greater amount of residual sulfate after the final desulfation at 750 °C.

In addition to the foregoing analytical methods, detailed EM studies were performed on catalyst 45-50 in both the fresh and aged states in order to observe the impact of aging. The fresh catalyst is illustrated in Figure 4.2. At low magnification (Fig. 4.2a), the STEM image shows that the Al₂O₃ support has been coated with a thin BaO layer. At higher magnification in Figure 4.2b, the rod-like morphology of the Al₂O₃ support can be recognized even after addition of the thin BaO coating. It was also observed that the BaO coating is not covering all areas of the Al₂O₃ support. No large BaO agglomerates or crystallites were observed in the fresh catalyst as those would otherwise be imaged in STEM mode as bright areas next to Al₂O₃ due to the major difference in material density.
Figure 4.2(a-c). Illustration of fresh catalyst sample 45-50 using STEM imaging.

Figure 4.2c illustrates Al2O3 with ultra small Pt nanoparticles on the surface that range in size from 2-8 nm and show excellent dispersion on the support surface. The aged 45-50 catalyst material is depicted in the STEM images in Figure 4.3. The Ba-rich areas now occur in clusters over the Al2O3 support surface and in certain locations have formed coarse crystals. Note that the STEM image does not distinguish between BaO and BaSO4. From Figure 4.3a it appears that in the aged catalyst more of the Al2O3 surfaces are exposed without a BaO layer, suggesting a possible migration and aggregation of the BaO phase during thermal treatment. Additionally, Figure 4.3b highlights a magnified area showing the rod-shaped Al2O3 support with Pt nanoparticles on the surface. In comparison with the fresh material, the aged sample is characterized by a significant degree of Pt nanoparticle sintering; indeed, the image shows a Pt particle that is >20nm. Not all of the Pt nanoparticles participate in the sintering process, however, as there is evidence of residual Pt nanoparticles in the original size range of 2-8 nm. Figure 4.3b also illustrates the presence of a dense Ba phase. In the Al2O3-rich areas the EM study did not reveal any encapsulation of Pt nanoparticles by the support media. Figure 4.4
shows the presence of Al₂O₃ and CeO₂ particles side-by-side in the aged catalyst material. Figure 4.4b has a STEM insert that shows a dense CeO₂ particle with Pt nanoparticles that do not appear to have undergone such significant sintering as those on the Al₂O₃ support. The presence of a Ba-rich phase was also noticed in the vicinity of the CeO₂ grains using EELS measurements, which is illustrated in Figure 4.4b; this shows the typical M4 M5 peaks for Ba and Ce, as well as a small contribution for the La peaks which are associated with the La-stabilized CeO₂. A line-scan spectrum image was collected across the aged catalyst material to observe any special relationship of sulfur in the vicinity of Ba-rich phase that segregated over the catalyst support material. The spectrum image is a compilation of EELS measurements along a particular area or line which is depicted in Figure 4.4a as the red line that spans approximately 250 nm in length across the catalyst. Along this line EELS measurements were performed and the results are plotted in 4.4c, showing the presence and relative concentration of Al, Ba, Ce, S and Pt. It is important to note that sulfur (red line) is typically associated with the Ba-rich phase, suggesting the presence of BaSO₄, and also that the line representing Pt indicates that the Pt nanoparticles are in a size-range that suggests Pt sintering took place during aging.

Figure 4.3. Rod-shaped Al₂O₃ crystals in aged 45-50 with local agglomeration of dense Ba-rich phase. (b) Al₂O₃ support with large, sintered Pt nanoparticles.
4.3.2. Oxygen Storage Capacity.

Oxygen storage capacity (OSC) was determined under lean-rich cycling conditions at 350 °C. From Table 4.4, catalyst Pt-100 showed the highest OSC among the four catalysts in both the fresh and aged states, while catalyst Pt-50 had the lowest. This finding is evidently related to the Pt loading on the CeO₂ washcoat component. It is well known that CeO₂ is the main oxygen storage component in LNT catalysts and that dynamic oxygen storage under lean-rich cycling conditions is dependent on oxygen mobility [52]. This mobility is promoted by Pt which facilitates O₂ dissociation followed by spillover to CeO₂ during oxygen storage and H₂ dissociation followed by spillover to CeO₂ during...
One means of increasing oxygen mobility is to increase the Pt loading and hence the degree of Pt-CeO₂ contact. From this it follows that catalyst Pt-100, with the highest Pt loading on the CeO₂ washcoat component (Table 4.2), shows the greatest ability to store and reduce oxygen relative to the other catalysts (the actual CeO₂ loading of the catalysts being the same in all cases). All of the catalysts showed a significant decrease in OSC after aging, as evidenced by a drop of 35.8% for aged Pt-100 as compared to the fresh catalyst, which can be explained by the decreased surface area of the CeO₂ phase and by the decreased contact between the Pt and CeO₂ as a result of Pt sintering.

4.3.3. NOₓ Storage.
NOₓ concentration profiles for both fresh and aged catalysts under “stationary” cycling conditions are shown in Figures 4.5 and 4.6, respectively. Comparatively high lean-phase NOₓ slip was observed at 150 °C and 450 °C relative to the results obtained at 250 °C and 350 °C, regardless of the state of the catalysts. It should be noted that the observation of lean phase NO₂ slip for all of the catalysts at 150 °C implies that NOₓ storage capacity at this temperature was not limited by the kinetics of NO oxidation. While we cannot completely exclude the possibility that the kinetics of nitrate/nitrite formation may be a limiting factor at 150 °C, our previous studies [53] suggest that it is mainly the inability to remove nitrates and nitrites at low temperature during the rich phase regeneration that limits the lean phase NOₓ storage efficiency. At 250 °C and 350 °C fresh Pt-50 showed higher lean-phase NOₓ slip than the other catalysts, indicative of an inferior NOₓ storage function, while almost no lean-phase NOₓ breakthrough was observed for fresh 30-50 and 45-50. Relative to the fresh catalysts, aging in all cases resulted in increased lean-phase NOₓ slip, with earlier breakthrough times in the range 250-450 °C. Evidently, NOₓ storage efficiency (NSE) was deteriorated by aging.
Figure 4.5. NO\textsubscript{x} storage and release during lean-rich cycling for fresh catalysts.

Figure 4.6. NO\textsubscript{x} storage and release during lean-rich cycling for aged catalysts.

From Table 4.6 it is apparent that increased lean-phase NO\textsubscript{2} slip was observed for the aged catalysts relative to the fresh ones, indicating that the deteriorated NO\textsubscript{x} storage function after aging was not due to a limitation in the kinetics of NO oxidation.
Examination of the lean-phase NSE calculated from the lean-rich cycling data reveals that aging caused a decrease in NSE for all the catalysts in the range 150 to 450 °C. As shown in Table 4.6, with the exception of Pt-50, the catalysts showed only small differences in NSE in the range 250-350 °C before aging, while aging enlarged the differences between the catalysts. Pt-100 showed a less pronounced decrease in NSE than 30-50 and 45-50 after aging, as evidenced by a NSE drop of only ~5%. Consequently, Pt-100 was still able to achieve a NSE of 94% at 250 °C and 350 °C after aging.

Table 4.6. Comparison of NO\textsubscript{x} storage and release during lean-rich cycling.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>Lean-phase NO\textsubscript{2} Slip (μmol)\textsuperscript{a}</th>
<th>Lean-phase NO\textsubscript{x} Storage Efficiency (%)</th>
<th>Rich-phase NO\textsubscript{x} Release (%)\textsuperscript{b}</th>
<th>Cycle-averaged NO\textsubscript{x} Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Aged</td>
<td>Fresh</td>
<td>Aged</td>
<td>Fresh</td>
</tr>
<tr>
<td>Pt-50</td>
<td>150</td>
<td>45.3</td>
<td>48.6</td>
<td>22.6</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>9.7</td>
<td>25.1</td>
<td>91.4</td>
<td>80.9</td>
</tr>
<tr>
<td></td>
<td>350</td>
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<td>17.7</td>
<td>98.7</td>
<td>84.6</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>13.8</td>
<td>30.6</td>
<td>80</td>
<td>50.7</td>
</tr>
<tr>
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<td>69.1</td>
<td>42.8</td>
<td>17.4</td>
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<tr>
<td></td>
<td>250</td>
<td>0.5</td>
<td>7.4</td>
<td>99.6</td>
<td>94.3</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.4</td>
<td>7.2</td>
<td>99.7</td>
<td>94.3</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>5.6</td>
<td>22.9</td>
<td>88.9</td>
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<td>57.1</td>
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<td>2.3</td>
<td>40.6</td>
<td>95.8</td>
<td>39.3</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The total amount of input NO per lean-rich cycle was 171.5 μmol.

\textsuperscript{b} (NO\textsubscript{x} released in rich purge/NO\textsubscript{x} stored in lean phase) x 100%.

As discussed in our previous study [40], the NSE under “stationary” cycling conditions is different from the initial NSE measured under continuous lean conditions, the NSE under stationary cycling conditions being dependent on both the initial NSE (i.e., the NSE for a catalyst initially totally free of NO\textsubscript{x}) and the extent to which the NO\textsubscript{x} storage sites are regenerated by rich purging during lean-rich cycling. To identify the NSE-limiting step...
under lean-rich cycling, a comparison between the initial and the cycle-averaged NSE was made, as shown in Figure 4.7. Herein, the NSE obtained in the first lean cycle after complete catalyst regeneration at 500 °C is regarded as the initial (or “first-cycle”) NSE whereas the NSE obtained in the lean cycle under stationary cycling conditions is regarded as the “cycle-averaged” NSE. All of the fresh catalysts showed a very high initial NSE at the four temperatures tested, and only slight differences were observed between them. The drop in NSE under subsequent cycling was observed to be small in the range 250-450 °C, showing that the fresh catalysts were able to retain a good balance between NO\textsubscript{x} storage and regeneration under cycling conditions. After aging only small decreases in initial NSE were observed in the range 150-350 °C, which can be attributed to the contribution of ceria to NO\textsubscript{x} storage, as a supplement to the main BaO NO\textsubscript{x} storage phase. Given the inability of ceria to store NO\textsubscript{x} at 450 °C [54], a significant drop in initial NSE at 450 °C after aging indicates that the NO\textsubscript{x} storage function of the Pt/BaO/Al\textsubscript{2}O\textsubscript{3} component was severely degraded. A further drop in NSE during lean-rich cycling in the range 250-450 °C can be ascribed to the degradation of the regeneration function after aging, i.e., incomplete release of NO\textsubscript{x} from the storage sites during rich purging resulted in cycle-averaged NSE well below that of the initial NSE.
Figure 4.7. Comparison of NO\textsubscript{x} storage efficiency during the first cycle and during subsequent lean-rich cycling for fresh and aged catalysts.

Considering the data collected at 450 °C in Figure 4.7, it is interesting to note that the small difference in the first-cycle and cycle-average NSE for the fresh and aged catalysts, this being especially pronounced for catalyst Pt-50. In contrast, virtually no difference was observed at 350 °C for the fresh catalysts, indicating complete catalyst regeneration at this temperature (and by implication at higher temperatures). This discrepancy between the first-cycle and cycle-average NSE values at 450 °C is plausibly due to the creation of an exotherm from the combustion of reductants on the catalyst during the rich to lean transition, resulting in higher effective storage temperatures during the beginning of the lean phase and hence lower NSE. This effect has previously been reported by Epling et al. [55]. In this work, measured exotherms during cycling at 450 °C spanned the range 16-22 °C for the fresh catalysts and 8-12 °C after aging. Given that dispersed Ba nitrates are reported to decompose close to 450 °C [56], even a relatively modest temperature rise could be expected to exert a destabilizing effect on NO\textsubscript{x} storage. Furthermore, surface temperature swings at the precious metal sites (adjacent to the stored
NO$_x$) could be much larger, as shown in a recent paper [57]. Scrutiny of the NO$_x$ concentration profiles at 450 °C failed to show clear indications of a link between the exotherms and decreased NO$_x$ storage as reported by Epling et al. [55]; however, given the relatively small magnitude of the discrepancy between the first-cycle and cycle-average NSE values, this is unsurprising.

Turning to the role of Pt in NO$_x$ storage and reduction, in the fresh state a slight improvement in the initial NSE was observed in the range 150-250 °C with increase of the Pt loading from 1.77 g/L (Pt-50) to 3.53 g/L (Pt-100) (Figure 4.7). Aging magnified the impact of Pt loading on both the initial and cycle-averaged NSE, the decreases in both the initial and cycle-based NSE observed for Pt-50 at 250 °C and 350 °C after aging being of a greater magnitude than for Pt-100. As confirmed by our TEM analysis, Pt is highly dispersed in the fresh catalysts and consequently the Pt particles and the NO$_x$ storage components (BaO/Al$_2$O$_3$ and CeO$_2$) are in close proximity, i.e., there is a large interfacial perimeter between the Pt and NO$_x$ storage phases. As discussed above, aging resulted in significant sintering of the Pt and as a consequence the interfacial perimeter between the Pt and Ba decreased, as did that between the Pt and CeO$_2$ (although to a lesser extent). Based on the mechanism of NO$_x$ storage and reduction, as proposed in the literature [18], the limiting step during cycling is believed to be transfer of NO$_x$ between Pt and Ba, and the distance between the Pt and Ba phases can significantly impact the NO$_x$ spillover from Pt to Ba during NO$_x$ storage and reverse NO$_x$ spillover from Ba to Pt during NO$_x$ reduction. As a result, both NO$_x$ storage and reduction capability are degraded after aging due to segregation of the Pt and Ba; however, our results indicate that increasing Pt loading can, to a certain extent, alleviate the effect of aging. A further comparison between Pt-100 and 30-50 infers that a higher Pt loading on NO$_x$ storage components (BaO and CeO$_2$, see Table 4.2), as for Pt-100, can benefit the LNT performance of aged catalysts albeit the total Pt loading is the same in both of them. Consistent with these findings, Clayton et al. [58] observed that during lean-rich cycling, the amount of stored NO$_x$ increased with increasing Pt dispersion in the temperature range studied (125-340 °C) for Ba-based model catalysts; this was similarly attributed to the enhanced NO$_x$ spillover from Pt to the Ba phase that should result from the larger Pt surface area and
Pt/Ba interfacial perimeter. Likewise, a tendency for slower catalyst regeneration with increasing Pt particle size was also noted, suggesting that a kinetic process, such as reverse spillover of stored NO\textsubscript{x} or the spillover of reductant from Pt to the NO\textsubscript{x} storage phase, may limit the overall rate.

The effect of Ba loading on initial NSE also became more evident after aging. Whereas in the fresh state catalysts 30-50 and 45-50 showed little difference in initial or cycle-averaged NSE, after aging 45-50 displayed superior initial NSE at 250 °C and 350 °C. At 450 °C this trend was reversed for reasons that are not clear. However, there was little difference in the NSE values of the two catalysts under cycling conditions, implying that cycling performance was limited by catalyst regeneration rather than initial NO\textsubscript{x} storage efficiency. In other words, degradation of the NO\textsubscript{x} regeneration function is the critical issue for these catalysts with respect to their NSE after aging.

4.3.4. NO\textsubscript{x} Release and Reduction.

NO\textsubscript{x} release under rich purging is shown in Figures 4.5 and 4.6. The fresh catalysts showed much higher NO\textsubscript{x} release at 150 °C than the aged catalysts. The kinetics of NO\textsubscript{x} reduction are slow at low temperature [59], a fact which is exacerbated by the presence CO in the rich phase gas feed; at low temperatures CO coverage on the PM sites is high, thereby effectively poisoning the sites for NO\textsubscript{x} adsorption and reduction [43]. Consequently, the fresh catalysts, possessing high initial NSE, showed considerable rich phase NO\textsubscript{x} slip due to their limited NO\textsubscript{x} reduction ability. In contrast to the low temperature behavior, the rich phase slip in the range 250-350 °C increased after aging, reflecting deterioration in NO\textsubscript{x} reduction activity, and a resulting imbalance in the rates of NO\textsubscript{x} release and reduction. This is most clearly illustrated by catalyst 45-50, peak NO\textsubscript{x} concentrations of 1300 ppm being observed at 250 °C after aging, corresponding to release – without reduction – of 16% of the stored NO\textsubscript{x}. At 450 °C this effect is reversed, i.e., rich phase NO\textsubscript{x} slip is lower for the aged catalysts relative to their fresh counterparts, a finding which can be attributed to the significantly lower NSE after aging. However, even at 450 °C the amount of rich phase NO\textsubscript{x} slip expressed as a percentage of the total amount of NO\textsubscript{x} stored is generally higher for the aged catalysts compared to their fresh
analogues, e.g., 19.7% versus 11.7% for 45-50 (Table 4.6). This again reflects deterioration in the NO\textsubscript{x} reduction function of the catalysts caused by aging.

The overall impact of aging under lean-rich cycling is reflected in the cycle-averaged NO\textsubscript{x} conversions reported in Table 4.6. Overall, NO\textsubscript{x} conversion is observed to decrease after aging as a consequence of decreased NSE and increased rich phase NO\textsubscript{x} slip. Whereas cycle-averaged NO\textsubscript{x} conversion in the range 250-350 °C is similar for the four catalysts in the fresh state (being close to 100% for Pt-100, 30-50 and 45-50, and only slightly lower for Pt-50), after aging a clear ordering is observed, namely: Pt-100 > 30-50 > 45-50 > Pt-50. Given the importance of the Pt-Ba interface, it follows that high Pt loadings are beneficial for catalyst performance since they provide one means of ensuring a high degree of Pt-Ba contact. On this basis, and bearing in mind that the Pt dispersions in the aged catalysts were very similar, the inferior performance of Pt-50 is readily explained. As discussed in section 4.3.3, the superior performance of Pt-100 relative to 30-50 and 45-50 is ascribed to the higher Pt loading on the BaO and CeO\textsubscript{2} NO\textsubscript{x} storage components, albeit the total Pt loading is the same in the three catalysts.

Interestingly, after aging catalyst Pt-100 was able to outperform 30-50 and 45-50 despite the fact that the Rh loading in Pt-100 was only half that of the other two catalysts. From Table 4.6, it is apparent that Pt-100 displayed superior NSE than 30-50 in both the fresh and aged states. This is not surprising, given that Rh is not considered to contribute significantly to NO oxidation, being less active than Pt. Comparing rich phase NO\textsubscript{x} release, it is found that 30-50 generally outperformed Pt-100, particularly at low temperatures when the kinetics of NO\textsubscript{x} reduction are slow. This is consistent with the superior activity of Rh, as compared to Pt, in anaerobic NO\textsubscript{x} reduction [60]. However, in general the superior NSE of Pt-100 is seen to outweigh the lower rich phase NO\textsubscript{x} release displayed by 30-50, with the consequence that aged Pt-100 showed slightly better cycle-averaged NO\textsubscript{x} conversion than aged 30-50 in the temperature range 250-450 °C.
4.3.5. Selectivity of NO\textsubscript{x} Reduction.

The selectivity to NO\textsubscript{x} reduction products during rich purging is summarized in Figure 4.8. For the fresh catalysts, N\textsubscript{2}O was the dominant product at 150 °C, while N\textsubscript{2} was the main product in the range 250-450 °C. Compared to the other three catalysts, in the fresh state Pt-50 exhibited higher N\textsubscript{2}O and lower N\textsubscript{2} selectivity, with only small differences in product selectivity being observed among Pt-100, 30-50 and 45-50. After aging, all of the catalysts exhibited decreased selectivity to N\textsubscript{2}O at 150 °C and significantly increased NH\textsubscript{3} production in the range 250-450 °C, although N\textsubscript{2} remained the dominant product at 350 °C and 450 °C.

Due to the slow response time of the FT-IR analyzer, the inherent time resolution of the data collected in this study is significantly longer than the 5 s duration of the rich phase. Consequently, it proved impossible to establish reliably the time dependence of N\textsubscript{2}O release relative to the other N-containing species evolved (NO, NO\textsubscript{2} and NH\textsubscript{3}). However, a number of previous studies have indicated that N\textsubscript{2}O is formed immediately after the lean to rich transition, and that NH\textsubscript{3} is observed after a slight delay [61-63]. This implies that N\textsubscript{2}O is formed in the reaction front, in a reaction which must proceed in close association with removal of oxygen from the surface of the Pt particles via reaction with H\textsubscript{2}. Under these conditions, the local H\textsubscript{2}/NO stoichiometry at Pt will be low, due to the simultaneous release of NO\textsubscript{x} and consumption of H\textsubscript{2} in the reaction front by stored oxygen, including that on the oxidized Pt particles (in addition to oxygen stored on the ceria washcoat component). At low temperature (75-150 °C) low H\textsubscript{2}/NO ratios are known to favor the formation of N\textsubscript{2}O [64]. This can be understood in terms of the formation of N\textsubscript{2}O via the reactions of molecularly adsorbed NO according to equations (4.1) and/or (4.2) [65,66]:

\[
\begin{align*}
2 \text{Pt-NO} & \leftrightarrow \text{N}_2\text{O} + \text{Pt-O} + \text{Pt} \\
\text{Pt-NO} + \text{Pt-N} & \leftrightarrow \text{N}_2\text{O} + 2 \text{Pt}
\end{align*}
\] (4.1) (4.2)

Based on energy barriers determined from DFT calculations, Burch et al. [66] reasoned that equation (4.1), which proceeds via an adsorbed (NO)\textsubscript{2} intermediate, should be
favored at low temperatures (ca. 100 °C), whereas equation (4.2) is likely to be responsible for N₂O formation at higher temperatures (> 200 °C).

![Graphs showing selectivity to N₂O, NH₃, and N₂ for NOₓ reduction during lean-rich cycling.]

**Figure 4.8.** Selectivity to N₂O (top), NH₃ (middle) and N₂ (bottom) for NOₓ reduction during lean-rich cycling.

Molecular adsorption of NO on Pt, as opposed to dissociative adsorption, will be favored (i) at low temperatures, when the rate of NO bond scission is low, (ii) when Pt is partially covered by O, such that the paired surface sites required for NO dissociation are scarce, and (iii) when the concentration of adsorbed hydrogen is relatively low. The latter consideration stems from reports suggesting that the presence of adsorbed hydrogen promotes NO dissociation on metal surfaces [67-69]. Hecker and Bell [67] proposed that NO dissociation results from the abstraction of molecularly adsorbed NO by adsorbed H:

\[
\text{Pt-NO + Pt-H} \leftrightarrow \text{Pt-N + Pt-OH} \quad (4.3)
\]
Indeed, calculations show that the activation energy is lower for the assisted decomposition of NO (equation 4.3) than for simple dissociation [70]:

\[
\text{Pt-NO + Pt} \leftrightarrow \text{Pt-N + Pt-O} \quad (4.4)
\]

In addition, it has been suggested that enhanced electron donation from the metal to the NO antibonding orbital when adsorbed hydrogen is present may promote NO bond scission [68].

Temporal analysis of products (TAP) experiments by Harold and co-workers [69] support the occurrence of equation (4.3), the adsorbed N reacting with NO to form N₂O (equation 4.2). From this it follows that N₂O formation can only be avoided when NO adsorbed on the catalyst is fully dissociated, a conclusion reached by Burch and Watling in their study of the C₃H₆-NO-O₂ reaction over Pt catalysts [71].

In terms of lean-rich switching, it is evident that at low temperatures and at short rich times, as H₂ removes adsorbed O from Pt, molecularly adsorbed NO will form N₂O via equations (4.1) and/or (4.2), the latter being preceded by equation (4.3). At longer rich times, when the reaction front has passed, the local concentration of H₂ will be higher (since it is not being consumed via reduction of the initially oxidized Pt particles or other forms of stored oxygen), while the NOₓ concentration will be lower. Hence, H and N ad-atoms will dominate and N₂ and NH₃ will be the main NOₓ reduction products formed [62]. Higher temperatures should also favor N₂ and NH₃ production due to more extensive NO dissociation. Finally, it should be noted that other formation routes for N₂O are conceivable, such as the reaction of NH₃ with NOₓ or the reaction of NH₃ with stored oxygen. However, the formation of N₂O from these processes is typically observed at temperatures in excess of 150 °C [64].

Turning to the factors influencing NH₃ production, as mentioned above, recent studies have shown that the product distribution during NOₓ reduction is a function of the relative NOₓ and reductant concentrations, high H₂:NOₓ ratios favoring the formation of NH₃ [65]. Since the same amount of reductant was available during rich purging for the
fresh and aged catalysts, a higher ratio of reductant to stored NO\textsubscript{x} for the aged catalysts (due to the lowered NSE) should result in increased selectivity to NH\textsubscript{3} over N\textsubscript{2}. Indeed, several recent studies have shown that selectivity to NH\textsubscript{3} increases with decreasing amount of NO\textsubscript{x} stored [72,73]. Another important factor that can influence the NO\textsubscript{x} reduction selectivity of the aged catalysts is their OSC. Previously we have shown that selectivity to N\textsubscript{2} tends to increase with increasing OSC [41]. However, in this case there is no simple correlation between product selectivity and OSC. Although the catalysts with the lowest OSC at 350 °C showed the highest selectivity to NH\textsubscript{3} in the fresh state (Pt-50 and 45-50), after aging catalysts Pt-100, 30-50 and 45-50 showed the opposite trend. However, all of the catalysts displayed a remarkable increase in selectivity to NH\textsubscript{3} after aging. In addition to the effective increase in local H\textsubscript{2}:NO\textsubscript{x} ratio mentioned above, there are several other possible reasons for this. First, a decrease in OSC brought on by aging should result in an increased reductant concentration in the gas front during rich purging (as compared to the fresh catalyst), due to reduced consumption of the reductant by reaction with the stored oxygen, thereby favoring the formation of NH\textsubscript{3}. Second, NH\textsubscript{3} formed at the front of the catalyst can be converted to N\textsubscript{2} via reaction with the oxygen stored in the rear of the catalyst. As catalyst OSC is decreased, so less NH\textsubscript{3} tends to be converted to N\textsubscript{2} at the rear of the catalyst. From Table 4.4 it is apparent that after aging, all of the catalysts showed decreased OSC. In this context, it is instructive to examine the outlet CO profile during cycling (Figure 4.9). As shown, CO slip was observed in all cases during rich purging, indicative of complete consumption of the stored oxygen. As for the NH\textsubscript{3} measured in the effluent, the amount of CO in the effluent increased after aging. This is consistent with the role of stored oxygen in consuming reducing species present in the catalyst, although in the case of CO it is possible that decreased water-gas shift activity after aging may have contributed to the higher outlet CO concentration.
Figure 4.9. Comparison of integrated outlet CO concentration before and after aging (T = 350 °C).

In addition to OSC, other factors play a role in determining the selectivity of NO\textsubscript{x} reduction. The dispersion of precious metal has recently been shown to be important on this regard, lower Pt dispersions favoring the production of NH\textsubscript{3} [58]. This can be rationalized on the basis that as the Pt/Ba interfacial perimeter decreases (with decreasing Pt dispersion), the rate of transport of stored NO\textsubscript{x} to Pt (i.e., reverse spillover) is decreased. If this rate is slower than the H\textsubscript{2} feed rate, then H\textsubscript{2} will break through with substantially more NO\textsubscript{x} remaining on the catalyst after H\textsubscript{2} breakthrough. Consequently, the Pt surface will be predominantly covered by hydrogen, and as the stored NO\textsubscript{x} transports to the Pt particles, NH\textsubscript{3} will be preferentially formed. Indeed, a recent modeling study confirms the idea that NH\textsubscript{3} generation is favored under conditions when NO\textsubscript{x} transport to the Pt/Ba interface is the rate determining process [74].

Lengthening of the NO\textsubscript{x} storage-reduction (NSR) zone can also be expected to contribute to the observed increase in selectivity to NH\textsubscript{3} after aging. A recent study employing SpaciMS suggests that the longer the NSR zone (i.e., the axial portion of the catalyst where NO\textsubscript{x} is stored and reduced), the shorter the downstream OSC-only zone (i.e., the axial portion free of stored NO\textsubscript{x}) [75]. This leads to decreased oxidation of NH\textsubscript{3}, slipping from the upstream NSR-zone, by oxygen stored in the OSC-only zone [75,76]. This effect is particularly noticeable for sulfated catalysts, since as sulfation proceeds there are fewer active sites available per unit of catalyst volume, causing the NSR zone to be
stretched towards the rear of the catalyst. Similarly, this effect is expected to be significant for the catalysts in this work based on the observed decreases in both initial and cycle averaged NSE after aging; these findings are consistent with an effective decrease in the concentration of NO\textsubscript{x} storage sites, which in turn implies that the NSR zone in the aged catalysts must be greatly expanded relative to their fresh analogues.

Finally, it should be mentioned that since overall catalyst selectivity to NH\textsubscript{3} is governed by the relative rates of NH\textsubscript{3} generation and consumption, if catalyst aging were to result in a decrease in the rate of the NO\textsubscript{x}-NH\textsubscript{3} reaction occurring in the reductant front [77], then selectivity to NH\textsubscript{3} would also be expected to increase. However, in separate work [78], we have found that the SCR reaction rate for model catalysts similar to the ones used in this study is not greatly affected by aging (under the same conditions used in this work). Consequently, we conclude that this is not a major factor in the observed increase in catalyst selectivity to NH\textsubscript{3} after aging.

4.3.6. Effects of Aging on Specific Catalyst Functions.

It is generally accepted that the functioning of LNT catalysts involves four sequential steps [18]: (i) NO oxidation to NO\textsubscript{2}, (ii) NO\textsubscript{x} storage, (iii) NO\textsubscript{x} release (i.e., nitrate decomposition) and (iv) NO\textsubscript{x} reduction. As for our previous study [40], in this work it was found that simulated road aging resulted in significant deterioration of catalyst performance in steps (ii), (iii) and (iv). Considering step (ii), besides the effect of Pt-Ba phase segregation, the other important factor responsible for decrease of the initial and cycle-averaged NSE after aging is residual sulfur. Sulfation of the Ba phase is reflected in the initial (“first cycle”) NSE values measured at 450 °C. At this temperature ceria does not contribute to NO\textsubscript{x} storage [54], hence the significant deterioration in initial NSE at 450 °C observed after catalyst aging reflects the deterioration of the ability of the Ba phase to trap NO\textsubscript{x}. In addition, we cannot rule out the effect of the likely decreased Ba dispersion caused by aging due to its high mobility.

The effect of Pt sintering is reflected in the performance of the aged catalysts with respect to steps (ii), (iii) and (iv). In the case of step (iv), rich phase NO\textsubscript{x} slip in the range 250-
350 °C increased after aging (as shown in Table 4.6), indicative of an imbalance in the rates of NO\textsubscript{x} release and reduction arising from deterioration of the NO\textsubscript{x} reduction activity. This observation is consistent with the literature for three-way catalysts, which indicates that decreased NO\textsubscript{x} reduction activity is associated with precious metal sintering [79].

In the case of steps (ii) and (iii) it is difficult to decouple the effects of Pt sintering, since under cycling conditions NO\textsubscript{x} storage efficiency is dependent on the extent to which stored NO\textsubscript{x} is released during rich purging (as discussed in section 4.3.3). However, it is instructive to consider the NSE data measured at 150 °C (Figure 4.7). Comparison of the high initial NSE with the low cycle-averaged NSE values observed for the different catalysts suggests that during cycling a kinetic process, such as reverse spillover of stored NO\textsubscript{x} or the spillover of hydrogen from Pt to the BaO and CeO\textsubscript{2} storage components, limits the nitrate decomposition rate both for the fresh and aged catalysts. This, in turn, limits the cycled-averaged NSE. As shown, the initial NSE at 150 °C does not drop significantly after aging, indicating that NO\textsubscript{x} storage (step (ii)) on the BaO and/or CeO\textsubscript{2} phases is not markedly impacted. Given that ceria plays a significant role in NO\textsubscript{x} storage at such low temperatures, this relatively small decline in initial NSE can be attributed to the retention of a reasonably high Pt dispersion on the ceria phase, as indicated by the HRTEM measurements presented above, as well as the fact that the ceria phase is not contaminated with residual sulfur (unlike the Ba phase). A more significant impact of aging is observed on the cycle-averaged NSE at 150 °C, indicating that NO\textsubscript{x} release (step (iii)) is more deteriorated by aging than the NO\textsubscript{x} storage step. However, at higher temperatures these trends become less clear. This is because the Ba storage phase plays an increasingly greater role in NO\textsubscript{x} storage as the temperature increases, and the deterioration of the initial NSE – due to sulfation of the Ba phase – becomes a more significant contributor to the overall decrease in cycled averaged NSE. However, it is clear that after aging the kinetics of nitrate release are at least partially limiting with respect to cycle-averaged NSE since the deterioration in cycle-averaged NSE in all cases exceeds the drop in initial NSE, i.e., the degradation of cycle-averaged NSE at higher temperatures cannot be explained solely by the deterioration in initial NSE.
As shown in Table 4.6, the cycled-averaged storage efficiency for all of the catalysts dropped significantly after aging at all temperatures. Comparison of the changes in cycle-averaged NO\textsubscript{x} conversion for the fresh and aged catalysts with the corresponding changes in the lean phase (cycled-averaged) NSE and with the changes in rich phase NO\textsubscript{x} release reveals a strong correlation between NO\textsubscript{x} conversion and NSE. This shown by the correlation plot depicted in Figure 4.10. As shown, when the values for the different catalyst are plotted and grouped by temperature, strong correlations are observed for the data collected at 350 and 450 ºC. In principle, a strong correlation between cycle averaged NO\textsubscript{x} conversion and storage efficiency is to be expected if there is no limitation with respect to NO\textsubscript{x} reduction. Given that the kinetics of NO\textsubscript{x} reduction are limiting at low temperatures, as evidenced by the considerable rich phase NO\textsubscript{x} slip observed at 150 ºC and 250 ºC in Figure 4.6, the weak correlations observed at these lower temperatures are not surprising. This is particularly evident for the 250 ºC data points. As shown in Table 4.6, after aging a large increase in rich phase NO\textsubscript{x} slip is observed at 250 ºC for all of the catalysts, indicative of a deterioration in the NO\textsubscript{x} reduction function. At higher temperatures, the kinetics of NO\textsubscript{x} reduction are presumably sufficiently fast that, even allowing for the deterioration, NO\textsubscript{x} reduction is not limiting.

![Figure 4.10](image_url)

**Figure 4.10.** Correlation of the change in cycle-averaged NO\textsubscript{x} conversion after aging with the change in cycle-averaged lean phase NSE.
Overall, these results show that the deterioration in catalyst performance at 350 and 450 °C after aging is largely the result of the deterioration in cycle-averaged NSE. This in turn, can be ascribed to (i) a decrease in NO\textsubscript{x} storage capacity resulting from sulfation of the Ba phase and (ii) sintering of the Pt, resulting in less efficient NO\textsubscript{x} storage and nitrate decomposition. At the lower temperatures, the deterioration in NO\textsubscript{x} reduction activity represents a significant additional factor.

4.3.7. Interfacial Pt-Support Perimeter.  
As indicated in the Introduction, previous studies [15-21] have demonstrated the importance of the proximity of the Pt and Ba phases for efficient LNT functioning. Given that Pt is believed to act as a conduit for NO\textsubscript{x} spillover to and from the Ba phase, it follows that close proximity of Pt and Ba are required to achieve efficient NO\textsubscript{x} storage and reduction. The effect of Pt sintering on the Pt-Ba interface can be illustrated by consideration of the interfacial perimeter between Pt and its support (in this case BaO) at different levels of Pt dispersion. Assuming a hemispherical morphology for Pt particles, the relationship between the number of atoms in a Pt particle (N\textsubscript{Pt}) and the particle diameter (d) is given by:

\[
N_{Pt} = \frac{2\pi (d/2)^3 \sigma Na}{Wa}
\]  

(4.5)

where \(N_a\) is Avogadro’s number, and \(W_a\) is the atomic weight. Based on face-centered cubic (FCC) packing for Pt, the number of surface atoms (N\textsubscript{Pt\_s}) as a function of particle diameter is given by:

\[
N_{Pt\_s} = 2\pi (d/2)^2 \omega
\]  

(4.6)

where \(\omega\) is the average atom density of Pt particle surface [80]. Dispersion is defined as the percentage of surface atoms in the particle, i.e.:

\[
\text{Dispersion} = \frac{N_{Pt\_s}}{N_{Pt}}
\]

(4.7)
From eqn. (4.5), it follows that the number of particles per gram of Pt ($\Sigma p$) is given by:

$$\Sigma p = \frac{3/2}{\pi(d/2)^3\sigma} \quad (4.8)$$

Assuming that the interfacial perimeter of a Pt particle corresponds directly to its circumference, the total interfacial perimeter per gram of Pt ($\lambda_{Pt}$) is obtained as follows:

$$\lambda_{Pt} = \pi^* d^* \Sigma p \quad (4.9)$$

As shown in Table 4.7, for a Pt dispersion of 38%, which is close to the values observed prior to aging for the catalysts in this study (see Table 4.4), the total perimeter of the Pt particles amounts to $6.22 \times 10^{19}$ nm/g Pt. However, for a dispersion of 11%, which is close to the values observed after aging, the total perimeter is only $5.6 \times 10^{18}$ nm/g Pt, i.e., a factor of eleven lower. These simple calculations are illustrative of the critical role that Pt particle size plays in determining the extent of Pt-Ba contact and, by implication, in governing LNT functioning. From this it follows that future attempts to predictively model the deactivation of LNT catalysts will have to incorporate the extent of Pt sintering as a key parameter.
Table 4.7. Total Pt-support interfacial perimeter as a function of Pt particle size, assuming hemispherical particle morphology.

<table>
<thead>
<tr>
<th>Average Pt Particle Size (nm)</th>
<th>Dispersion</th>
<th>Number of Atoms in Particle</th>
<th>Number of Particles/g Pt</th>
<th>Total Interfacial Perimeter (nm/g Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>18</td>
<td>1.78E+20</td>
<td>5.6E+20</td>
</tr>
<tr>
<td>2</td>
<td>57</td>
<td>139</td>
<td>2.22E+19</td>
<td>1.40E+20</td>
</tr>
<tr>
<td>3</td>
<td>38</td>
<td>468</td>
<td>6.60E+18</td>
<td>6.22E+19</td>
</tr>
<tr>
<td>4</td>
<td>29</td>
<td>1110</td>
<td>2.78E+18</td>
<td>3.50E+19</td>
</tr>
<tr>
<td>5</td>
<td>23</td>
<td>2167</td>
<td>1.42E+18</td>
<td>2.24E+19</td>
</tr>
<tr>
<td>8</td>
<td>14</td>
<td>8876</td>
<td>3.48E+17</td>
<td>8.76E+18</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
<td>17336</td>
<td>1.78E+17</td>
<td>5.60E+18</td>
</tr>
<tr>
<td>20</td>
<td>6</td>
<td>138684</td>
<td>2.22E+16</td>
<td>1.40E+18</td>
</tr>
</tbody>
</table>

4.4. Conclusions.

According to physico-chemical data for the fresh and aged catalysts in this work, aging resulted in two main changes which can explain the accompanying degradation in catalyst activity for NO\textsubscript{x} storage and reduction. First, according to H\textsubscript{2} chemisorption and TEM data, sintering of the precious metals in the washcoat occurred, being most evident for Pt located on the BaO/Al\textsubscript{2}O\textsubscript{3} washcoat component. The resulting decrease in contact between the Pt and Ba phases contributed to decreased first cycle NSE due to less efficient NO\textsubscript{x} spillover from Pt to Ba during NO\textsubscript{x} adsorption. An even larger decrease in cycle-averaged NO\textsubscript{x} storage points to the fact that the ability to regenerate the NO\textsubscript{x} storage sites was also adversely affected, i.e., Pt-Ba phase segregation adversely affected the rate of reductant spillover from Pt to Ba and hence NO\textsubscript{x} release. In addition, at low temperatures (250 °C) an increase in rich phase NO\textsubscript{x} slip was observed after aging, consistent with a decrease in the rate of the reverse NO\textsubscript{x} spillover process and/or the intrinsic rate of PM-catalyzed NO\textsubscript{x} reduction.

Second, elemental analysis, TEM and XRD data indicate the accumulation of sulfur in the washcoat, present as BaSO\textsubscript{4}. At the measured concentrations, approximately 30% of the Ba present was typically present in the sulfated form, providing an additional
explanation for the loss in initial and cycle-averaged NSE after catalyst aging.

For the four catalysts used in this study, cycle-averaged NO\textsubscript{x} conversions in the range 250-350 ºC were similar in the fresh state, while after aging a clear ordering was observed: Pt-100 > 30-50 > 45-50 > Pt-50. Given the importance of the Pt-Ba interface, it follows that high Pt loadings are beneficial for catalyst performance since they provide one means of ensuring a high degree of Pt-Ba contact. On this basis, and bearing in mind that the Pt dispersions in the aged catalysts were very similar, the inferior performance of Pt-50 is explained. The superior performance of Pt-100 relative to 30-50 and 45-50 is ascribed to the higher Pt loading on the BaO and CeO\textsubscript{2} NO\textsubscript{x} storage components in Pt-100, albeit the total Pt loading is the same in the three catalysts. The effect of Rh loading was after aging found to be marginal within the range studied; although the higher Rh loaded catalyst 30-50 showed slightly better low temperature NO\textsubscript{x} reduction activity than Pt-100 (containing half as much Rh), the superior NSE of Pt-100 outweighed this effect. Finally, it was found that increasing the BaO loading in washcoat from 30 to 45 g/L produced no measurable benefit.
4.5. References.


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Chapter 5. Application of SpaciMS to the Study of Ammonia Formation in Lean NO\textsubscript{x} Trap Catalysts.

**Note** - This chapter was published as an article in the following journal:


The article appears in this dissertation with permission from the publisher.

5.1. Introduction.

Recent years have witnessed concerted efforts to reduce NO\textsubscript{x} emissions from mobile sources of lean exhaust gas using lean NO\textsubscript{x} trap (LNT) or selective catalytic reduction (SCR) catalysts. Although both technologies have many positive features, each approach has drawbacks which have slowed their application to the automotive marketplace. For LNT catalysts, one of the main disadvantages is the cost associated with the use of platinum group metals (PGMs), while for SCR, the cost of the injection system and refilling of the NH\textsubscript{3} source adds to the consumer’s costs. However, recent studies have shown that by combining LNT and SCR catalysts in series, these drawbacks can be lessened [1-5]. In this configuration the SCR catalyst functions in a passive or in situ mode, i.e., with the storage and utilization of NH\textsubscript{3} generated by the LNT during rich purge events. Given that the presence of the SCR catalyst relaxes the NO\textsubscript{x} conversion requirements of the LNT catalyst, the volume of the LNT in the LNT-SCR system can, in principle, be lower than for an LNT-only system, thereby reducing the precious metal costs. Furthermore, the need for a urea injection system is eliminated.

To realize a LNT-SCR system capable of achieving these aims, an understanding is required of the interplay between system operating parameters and the underlying chemistry of NO\textsubscript{x} reduction. Probably the most important aspects to be considered are the generation of NH\textsubscript{3} over the LNT, and its subsequent reaction with NO\textsubscript{x} over the SCR catalyst. A potential problem in studying these processes in a LNT-SCR system is the
integral nature of the catalysts. Reactants and products can react, adsorb, and desorb multiple times before exiting the system. This makes the study of LNT-SCR systems difficult using traditional laboratory techniques based on analysis of the reactor effluent.

To overcome these problems, spatially resolved capillary inlet mass spectrometry (SpaciMS), developed at Oak Ridge National Laboratory, has been applied to monitor the composition of simulated exhaust gas as it passes through LNT catalysts [6-14]. The key feature of a SpaciMS system is the use of a capillary connected to the sample cell of a mass spectrometer. The capillary allows the internal gas stream to be analyzed at different points along the length of the LNT or SCR catalyst under study. Consequently, the gaseous components present can be monitored on both a spatial and temporal scale. Partridge et al. employed SpaciMS to study NH₃ formation and utilization over a Pt/Ba/Al₂O₃ catalyst during regeneration with H₂ [10]. It was found that NH₃ was formed at the same time as the N₂ product inside the catalyst during regeneration, and was consumed as aggressively as the H₂ reductant along the catalyst. From this it was concluded that the intermediate NH₃ regeneration pathway plays an important role in LNT catalyst regeneration. The same research group also utilized this technique to study the effect of sulfur on the spatiotemporal distribution of NOₓ storage and reduction [11]. Prior to sulfation, NOₓ storage/reduction was found to be localized in the front portion of catalyst, whereas sulfation resulted in a shift of the NOₓ storage/reduction (NSR) zone downstream, thereby decreasing the length of the downstream zone in which only oxygen was stored. These workers also reported an increase in selectivity to NH₃ after sulfation, and ascribed it to decreased oxidation of NH₃ slipping from the NSR zone by the oxygen stored downstream [11,12]. A more recent study by this group further demonstrated that NH₃ slip at the catalyst exit increased with sulfur loading due to its formation closer to the catalyst outlet and decreased NH₃ conversion by stored oxygen downstream of the NSR zone [13]. Moreover, during catalyst regeneration the extent of NOₓ readesorption downstream of the NSR zone was found to diminish after sulfation, resulting in earlier and broader NOₓ peaks at the catalyst outlet. The SpaciMS technique was also applied in another recent LNT study by Luo et al. [14] in which catalyst desulfation was examined. For a partially sulfated commercial catalyst, the plug-like sulfur profile was redistributed
after desulfation at 600 °C as a result of re-adsorption. The extent of re-adsorption was found to be determined by the catalyst formulation and sulfation degree.

We have previously investigated the effect of regeneration conditions on NH3 formation in LNT catalysts [15]. One of the findings from these studies was that NH3 selectivity is dependent on the local H2:NOx ratio at the precious metal sites. Increasing the regeneration time or reductant concentration fed to the catalyst increases this ratio and thereby increases the amount of NH3 formed, as opposed to N2. Conversely, increasing the amount of NOx stored decreases the selectivity to NH3. It was also observed that the addition of a ceria-based oxygen storage material to a Pt/Rh/BaO/Al2O3 catalyst caused a decrease in NH3 selectivity [15-18], which was explained on the basis that consumption of reductant by stored oxygen results in decreased H2:NOx ratios during regeneration, which favors the formation of N2 over NH3. In addition, oxygen stored in the rear of the catalyst can consume NH3 formed upstream via oxidation to produce N2, NO, or N2O. After aging, increased selectivity to NH3 was observed, for both the ceria-containing and ceria-free catalyst. In principle, this increase in selectivity to NH3 can be accounted for by any one of a number of factors [15]:

(i) Aging-induced Pt sintering, resulting in Pt-Ba phase segregation. Consequently, the rate of NOx transport to the Pt sites during regeneration is decreased. As Harold and co-workers have pointed out [19], if this rate is slower than the H2 feed rate, then H2 will break through with substantially more NOx remaining on the catalyst. Consequently, the Pt surface will be predominantly covered by hydrogen, and as the stored NOx diffuses to the Pt particles, NH3 will be formed with high selectivity. Modeling studies confirm this idea, i.e., that NH3 formation is favored when solid-phase diffusion of NOx to the Pt/Ba interface is the rate determining process, which becomes increasingly likely as the Pt dispersion decreases [20].

(ii) For a fixed concentration of reductant, the decreased oxygen storage capacity (OSC) of the aged catalysts should result in higher effective H2:NOx ratios in the reduction front due to decreased reductant consumption by stored oxygen, thereby
favoring NH$_3$ formation. Furthermore, there is less oxygen available downstream of the reductant front to react with formed NH$_3$.

(iii) After aging, there are fewer NO$_x$ storage sites available per unit of catalyst length. This should result in higher effective H$_2$:NO$_x$ ratios in the reductant front, again favoring NH$_3$ formation [15].

(iv) The length of the NO$_x$ storage-reduction zone increases due to the decrease in NO$_x$ storage capacity (NSC) as the catalyst ages [11,12,15]. More NH$_3$ slips from the LNT without being oxidized because the increased length of the NSR zone decreases the length of the downstream OSC-only zone.

(v) After aging, higher NH$_3$ emissions may result from decreases in the rates of NH$_3$ consumption via reaction with NO$_x$ or O$_2$ stored downstream of the reaction front.

From the foregoing, it is evident that NH$_3$ selectivity after aging is likely to be dependent – at least in part – on the residual OSC of the catalyst, as well as the amount of NO$_x$ stored. In an effort to distinguish between the factors that can account for increased LNT selectivity to NH$_3$ after aging, in this study we adjusted the amount of reductant used to regenerate each catalyst (degreened and thermally aged) based on the OSC of the catalyst and the NO$_x$ storage capacity (NSC). In this way we attempted to correct for the change in catalyst OSC and NSC after aging, thereby eliminating these as factors. SpaciMS was used to monitor the NO$_x$ storage and reduction processes for degreened and aged catalysts in order to investigate the contribution of other factors to NO$_x$ reduction selectivity.

5.2. Experimental.
5.2.1. Catalyst Preparation.

Two fully formulated Ba-based LNT catalysts were used in this study, the compositions of which are shown in Table 5.1. For simplicity, the BaO-only formulation is denoted as B-225 (where 225 refers to the washcoat loading in g/L), while the catalyst containing both BaO and CeO$_2$ is denoted at BC-175 (containing a washcoat loading of 175 g/L). Details of the catalyst preparation have been described elsewhere [16,17]. In both cases, the washcoat was applied to a 4” x 6” cordierite monolith substrate, possessing a cell density of 400 cpsi and a wall thickness of 6.5 mil. The BaO component (21.5 wt %) was
supported on γ-alumina, while bare alumina was also used as a balance to bring the total washcoat loadings to the values indicated in Table 5.1.

Table 5.1. Composition of catalysts used in this study.

<table>
<thead>
<tr>
<th>Component</th>
<th>Catalyst code / nominal loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B-225</td>
</tr>
<tr>
<td>Pt, g/L</td>
<td>3.05</td>
</tr>
<tr>
<td>Rh, g/L</td>
<td>0.61</td>
</tr>
<tr>
<td>BaO$^a$, g/L</td>
<td>26</td>
</tr>
<tr>
<td>CeO$_2$ $^b$, g/L</td>
<td>0</td>
</tr>
<tr>
<td>γ-Al$_2$O$_3$ $^c$, g/L</td>
<td>Balance</td>
</tr>
<tr>
<td>Total washcoat, g/L</td>
<td>225</td>
</tr>
</tbody>
</table>

$^a$ 21.5 wt% supported on γ-Al$_2$O$_3$.
$^b$ Stabilized with 5 wt% La$_2$O$_3$.
$^c$ Stabilized with 3 wt% La$_2$O$_3$.

5.2.2 Catalyst Aging.

A 1.75 cm x 2.54 cm (d x l) core was drilled out from the LNT monolith and was wrapped with ceramic fiber and positioned in a quartz tube. Degreening the catalyst consisted of exposing the catalyst to neutral conditions (5% CO$_2$, 5% H$_2$O, balance N$_2$) at 800 °C for 2 h. Aging the catalyst involved subjecting the catalyst to continuous lean conditions (8% O$_2$, 5% CO$_2$, 5% H$_2$O, and balance N$_2$) at 800 °C for 24 h. In both cases, the gas flow was adjusted to give a GHSV of 30,000 h$^{-1}$. 

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5.2.3. Catalyst Characterization.

5.2.3.1. N₂ Physisorption.
Surface area and pore volume analysis was performed according to the BET method by nitrogen adsorption at -196 °C using a Micromeritics Tri-Star system. Prior to the measurements catalyst samples (washcoat and monolith) were ground to a fine powder and outgassed overnight at 160 °C under vacuum.

5.2.3.2. Pulsed H₂ Chemisorption.
The dispersion of precious metal (Pt + Rh) was determined with a Micromeritics AutoChem II Analyzer by means of pulsed H₂ chemisorption at dry ice temperature (−78 °C). This temperature was chosen in an effort to minimize H spillover from the metal to the support material [21]. 1 g of sample (as a fine powder), including both washcoat and substrate, was loaded into the reactor. After being oxidized at 400 °C in 10% O₂/He for 15 min, followed by reduction at 300 °C in 10% H₂/Ar for 15 min, the catalyst was heated to 400°C (hold time 10 min) in flowing Ar to remove adsorbed H. Pulsed H₂ chemisorption was initiated using a four-way valve after the catalyst had been cooled to −78 °C. During this measurement, 0.5 mL of 10% H₂/Ar was pulsed into the reactor every 2 min, the H₂ signal at the reactor outlet being monitored with a thermal conductivity detector (TCD). H₂ pulsing was terminated after the TCD signal had reached a constant value, i.e., the total precious metal (Pt + Rh) sites were saturated with H₂. Assuming a 1:1 ratio of atomic hydrogen to surface Pt or Rh, the metal dispersion was calculated based on the amount of H adsorbed.

5.2.4. SpaciMS Measurements.

5.2.4.1. Determination of the Amount of Reductant Required for Catalyst Regeneration.
Determination of the amount of reductant required for catalyst regeneration was based on the catalyst oxygen storage capacity (OSC) and the amount of NOₓ stored during lean-rich cycling. Hydrogen was measured using a V & F Airsense H-sense mass spectrometer. All other species, i.e., NO, NO₂, O₂, H₂O, and NH₃, were measured using a V & F Airsense 2000 mass spectrometer using the low energy source, Hg, as the ion source; this enabled these species to be tracked individually, without interference from
other species present. The mass spectrometer had been modified for SpaciMS measurements by incorporating a 0.37 mm outer diameter (0.18 mm i.d.) stainless steel capillary connected to the sample chamber. The sampling rate was 14 sccm and data were collected at 3 Hz. After the SpaciMS was calibrated, the sample was purged by heating it to 450 °C under a 4.2% H2 in N2 flow until the NH3 concentration measured by the SpaciMS fell to below 4 ppm at a position 1 mm from the rear of the catalyst. Once this level was achieved, the reactor temperature was dropped to the desired temperature (200 °C, 250 °C, or 300 °C) and the samples were exposed to 60 s lean/5 s rich cycles. The lean phase gas contained 8% O2, 5% CO2, 5% H2O, and balance N2, while the rich phase gas contained 4.2% H2, 5% CO2, 5% H2O, and balance N2. After 5 cycles the flow was switched from the outlet of the reactor to the reactor bypass so that the baseline hydrogen level could be measured. The OSC was determined by subtracting the cycle-averaged outlet H2 concentration from the inlet H2 concentration.

In separate experiments, the NOx storage capacity of the LNT was determined. The feed was switched to neutral conditions (5% CO2, 5% H2O, and balance N2), and once equilibrated, the catalyst was subjected to lean conditions for 60 s, using a feed consisting of 300 ppm NO, 8% O2, 5% CO2, 5% H2O, and balance N2. Simultaneously, the outlet NOx concentration was monitored by the SpaciMS probe at a position 1 mm from the rear catalyst face. At the end of the lean 60 s period, the SpaciMS probe was moved to a position 4 cm in front of the catalyst and the measurement was repeated. The difference between the two integrated NOx concentrations gave the amount of NOx stored. The amount of reductant required for LNT regeneration was then calculated from the sum of the measured OSC and 2.5 times the value of the NOx storage measurement. This factor of 2.5 represents the stoichiometry of NOx reduction by H2 to give N2 (assuming that NOx is stored as nitrate) as reported in the literature [22,23]:

\[
\text{Ba(NO}_3\text{)}_2 + 8 \text{H}_2 \leftrightarrow 2 \text{NH}_3 + \text{Ba(OH)}_2 + 4 \text{H}_2\text{O} \tag{5.1}
\]

\[
3 \text{Ba(NO}_3\text{)}_2 + 10 \text{NH}_3 \leftrightarrow 8 \text{N}_2 + 3 \text{Ba(OH)}_2 + 12 \text{H}_2\text{O} \tag{5.2}
\]
The sum of reactions (5.1) and (5.2) leads to the overall stoichiometry for the reduction of Ba nitrate by H₂:

\[
\text{Ba(NO}_3\text{)}_2 + 5 \text{ H}_2 \leftrightarrow \text{ N}_2 + \text{ Ba(OH)}_2 + 4 \text{ H}_2\text{O} \quad (5.3)
\]

5.2.4.2. NO\textsubscript{x} Storage and Reduction Measurements.

With the required reductant amounts having been determined for each catalyst (both degreened and aged) at 200, 250, and 300 °C, NO\textsubscript{x} storage and reduction measurements were performed at these temperatures during 60 s lean/5 s rich cycles. The lean phase gas contained 300 ppm NO, 8% O₂, 5% CO₂, 5% H₂O, and balance N₂, while the rich phase gas contained the calculated amount of H₂ for each catalyst, 5% CO₂, 5% H₂O, and balance N₂. Prior to the measurements, each sample was exposed to the cycling conditions until the component concentrations in the reactor effluent were constant from one cycle to the next. Once “stationary” cycles had been attained (~ 1 h), data pertaining to the concentrations of NO, NO\textsubscript{2}, O₂, H₂O and NH\textsubscript{3} were collected at different positions using SpaciMS. The first of these positions corresponded to the rear face of the catalyst (25.4 mm from the catalyst inlet), with successive sampling at, 16.4 mm, 8.4 mm, 4.4 mm, and the front face (0 mm from the inlet). By sampling in this manner (from rear to front), the chances of contaminating the capillary with particles from the washcoat of the catalyst were lessened. Note that the “0 mm” position actually corresponds to a position of 0.1 mm; this was done in order to ensure that the capillary was correctly aligned with the selected channel. Consequently, when feeding NO in the lean phase, some NO\textsubscript{2} (corresponding to ca. 15% NO conversion) was detected at the 0.1 mm position, arising from a combination of catalyzed NO oxidation in the first 0.1 mm of the catalyst and gas phase NO oxidation in the feed lines. For each position, the system was allowed to stabilize for two 60 s/5 s cycles before data were taken over five successive cycles. These cycles were then averaged to produce the spatio-temporal plots of species concentration versus time for each axial location.
NO$_x$ storage efficiency (NSE) is defined in this study as:

$$\frac{\text{Inlet concentration of NO}_x - \text{Concentration of NO}_x \text{ at measurement location}}{\text{Inlet concentration of NO}_x} \times 100\% \quad (5.4)$$

Rich phase NO$_x$ release is defined as:

$$\frac{\text{Concentration of rich phase NO}_x \text{ release at measurement location}}{\text{Inlet lean concentration of NO}_x - \text{Outlet lean concentration of NO}_x} \times 100\% \quad (5.5)$$

In both eqns. (5.4) and (5.5), all concentrations are cycle-averaged integrated values (ppm*s).

5.3. Results and Discussion.

5.3.1. Catalyst Characterization.

The results of N$_2$ physisorption and H$_2$ chemisorption measurements performed on the degreened and aged catalysts are collected in Table 5.2. Both catalysts displayed a small loss in surface area after aging, which for the B-225 sample was accompanied by a decrease in the pore volume. Sintering of the catalyst is evidenced by an increase in the average pore radius, which can be attributed to collapse of the smaller pores during aging. Comparing the PGM dispersions derived from H$_2$ chemisorption measurements, it is evident that exposure of the catalysts to high temperatures during aging resulted in significant PGM sintering. Indeed, for both catalysts, a decrease in PGM dispersion of ca. 75% was seen. These results are consistent with the degree of Pt sintering observed in a previous study in which model LNT catalysts were likewise subjected to continuous lean conditions at 800 °C for periods of up to 16 h [24].
### Table 5.2. Physical properties of degreened and aged catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total BET surface area (m²/g)ᵃ</th>
<th>Pore volume (cm³/g)ᵃ</th>
<th>Average pore radius (nm)ᵃ</th>
<th>PGM dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Degreened</td>
<td>Aged</td>
<td>Degreened</td>
<td>Aged</td>
</tr>
<tr>
<td>B-225</td>
<td>41.1</td>
<td>35.4</td>
<td>0.148</td>
<td>0.137</td>
</tr>
<tr>
<td>BC-175</td>
<td>26.3</td>
<td>25.4</td>
<td>0.105</td>
<td>0.109</td>
</tr>
</tbody>
</table>

ᵃ Includes cordierite monolith.

5.3.2. *Amount of Reductant Required for Complete NOₓ Reduction during Rich Purging.*

The minimum amount of reductant required to fully regenerate a LNT during lean-rich cycling can be determined from the oxygen storage capacity (OSC) and the NOₓ storage capacity (NSC). In this study, the H₂ concentration during lean-rich cycling was adjusted so that the degreened and aged catalysts would be exposed to a stoichiometric quantity of H₂ with respect to complete regeneration. This adjustment allows for a sounder basis when comparing fresh and aged catalysts in terms of the selectivity of NOₓ reduction, given that excess reductant would influence the selectivity towards NH₃ production. The results from these OSC and NSC measurements, performed on catalysts B-225 and BC-175, are shown in Fig. 5.1. The column chart is arranged such that the data for the non-ceria-containing catalyst B-225 are shown on the left half of the figure, while data for the ceria-containing catalyst are on the right. Each of the stacked columns shows the amount of H₂ required to consume the oxygen stored on the catalyst and to reduce the stored NOₓ.

The fact that H₂ concentrations required for complete regeneration of BC-175 are greater than those for B-225 can be attributed to the presence of La-stabilized CeO₂ in BC-175. Comparing the OSC and NSC with temperature, it is apparent that for both the B-225 and BC-175 catalysts the measured values increase with temperature. This trend is expected for BC-175 since CeO₂ has increased OSC at higher temperatures due to the increased concentration of oxygen defect sites [25]. In addition, the NSC of Ba-based catalysts increases with temperature for the temperature range studied here [16,17].
Figure 5.1. Required amount of H$_2$ during 60 s lean – 5 s rich cycling for catalyst regeneration. Solid colors represent values for degreened catalysts and patterned colors represent values for aged catalysts. The blue or top values in the columns represent the oxygen storage capacities, and the red or bottom values represent the NO$_x$ storage capacities.

Considering the aged catalysts, an obvious trend is that the amount of reductant required for catalyst regeneration decreases after aging due to decreases in OSC and NSC. During aging, Pt sintering occurs, leading to a decrease in the Pt-Ba interfacial perimeter [16,20], i.e., phase segregation occurs between the Pt and Ba storage sites [26-31]. Consequently, for a given length of catalyst, fewer storage sites are present and less reductant is needed. Additionally, agglomeration of the Pt during aging reduces the number of sites available for oxygen adsorption during lean conditions. Finally, in the case of BC-175, a significant portion of the decrease in OSC can be attributed to the loss of oxygen defect sites in the structure of the La-stabilized CeO$_2$ component after aging. Mamontov et al. [25] have shown that OSC correlates with defect site concentration rather than surface area, the latter being relatively unchanged after aging based on the negligible change in
total catalyst surface area (Table 5.2). Indeed, in their work Mamontov and co-workers found that significant decrease of OSC occurred upon aging a ceria sample at 800 °C. In addition, some contribution to the loss in OSC may come from the sintering of Pt supported on the CeO₂ component, given that Pt acts essentially as a conduit for oxygen storage and release.

5.3.3. Non-Ceria Containing Catalyst.
5.3.3.1. NOₓ Storage.

Once the amounts of reductant required for catalyst regeneration were determined, the catalysts were subjected to NOₓ storage-reduction experiments. The non-ceria containing sample was subjected to 60/5 s cycles and evaluated at three temperatures: 200 °C, 250 °C, and 300 °C. Data pertaining to the measured lean NOₓ storage efficiencies (NSEs) are shown in Fig. 5.2. For degreened catalyst B-225 the NSE increases along the length of the catalyst (at all temperatures), while NSE also increases with temperature in the range studied. Maximum NSE values are reached around the midpoint of the catalyst, providing an indication of the length of the NOₓ storage zone under these experimental conditions. Additional detail is provided in Figs. 5.3a and 5.3b, in which the cycle-averaged NO and NO₂ concentrations are plotted at each measurement point along the length of the catalyst. For the degreened catalyst, a rapid decrease in the NO concentration begins at 4.4 mm, the NO concentration reaching zero by the 16.4 mm position. At this juncture, an explanation is required for the slight increase in NO and NO₂ concentrations observed in moving from the 16.4 to 25.4 mm positions in Fig. 5.3. As noted by Partridge and Choi [10], the SpaciMS system is capable of great sensitivity. This, combined with possible over-sampling at the rear of the catalyst (due to the high sampling rate and sampling position) can lead to the capillary sampling gas slightly beyond the rear of the catalyst. At this location the gas is comprised of the effluent from all of the channels in the catalyst. Bearing in mind that not all of the channels in the catalyst will have exactly the same amount of washcoat, the concentration of NOₓ just outside the rear of the catalyst can be different compared to the channel in which the capillary is located. Furthermore, the outer diameter of the capillary used in these experiments (0.37 mm) was significant compared to the channel width (1.1 mm). The
resulting restriction of the gas flow in the channel may result in a slightly different residence time, and hence gas composition, compared to the surrounding channels.

Figure 5.2. Lean NO\textsubscript{x} storage efficiency as a function of position for degreened (DG) and aged (AD) catalyst B-225.
Figure 5.3. a) Lean phase NO concentration and b) lean phase NO$_2$ concentration as a function of position during NO$_x$ storage on degreened (DG) and aged (AD) catalyst B-225.

From Fig. 5.3a it is evident that the amount of NO present at each position increases with decreasing temperature. Conversely, the NO$_2$ concentrations increase with increasing temperature in the range 200-300 °C. These results are consistent with an increase in the
rate of oxidation of NO to NO\textsubscript{2} with increasing temperature. At 300 °C, the rate of NO\textsubscript{2} formation is fast relative to the linear gas velocity and NO\textsubscript{2} is stored in the front of the catalyst. At the lowest temperature, 200 °C, the slower rate of oxidation of NO results in the feed gas traveling further along the length of catalyst before NO\textsubscript{2} is generated and then stored. Consequently, more of the catalyst is used for NO\textsubscript{x} storage. This finding is consistent with a previous report that the length of the NSR zone decreases with increasing temperature [11]. In addition, at lower temperatures, a portion of the NO\textsubscript{x} can be stored as Ba(NO\textsubscript{2})\textsubscript{2}, although the literature suggests that this pathway is fairly minor. For example, under their experimental conditions Forzatti and co-workers [4] found that at 200 °C ca. 20% of NO\textsubscript{x} was stored as Ba(NO\textsubscript{2})\textsubscript{2} and 80% was stored as Ba(NO\textsubscript{3})\textsubscript{2}. Fig. 5.4 provides a schematic of the NO\textsubscript{x} storage process and depicts the relative NO and NO\textsubscript{2} concentrations measured at 200 °C along the length of the catalyst.
Fig. 5.2 also contains the NSE results for the aged B-225 catalyst. In contrast to the data for the degreened catalyst, the NSE does not reach a maximum value within the length of the catalyst, indicating that the whole of the catalyst is used for NO\textsubscript{x} storage. Indeed, the maximum NSE after aging does not exceed 60% at any measurement temperature. Hence, the OSC-only zone in the schematic shown in Fig. 5.4 (which corresponds to zone 2) is effectively eliminated after aging. NSEs at the three temperatures are very similar, although because the data point at the 8.4 mm position in Fig. 5.2 is not available, the NSE at 200 °C appears to be greater than at 250 or 300 °C. This is largely a consequence of the missing point, given that at all of the other measurement points the values at each of the temperatures are very similar.
From Fig. 5.3a, it is evident that the NO concentrations measured for the aged sample
decrease gradually compared to the degreened case, NO being present in significant
concentrations throughout the entire length of the catalyst. As shown in Fig. 5.3b, the
NO2 concentrations increase along the catalyst before reaching a maximum and then
decreasing. A comparison between the data collected for the degreened and aged catalyst
at 200 ºC is shown in Fig. 5.4. The increase in measured NO and NO2 concentrations for
the aged sample can be explained on the basis that the concentration of NOx storage sites
is decreased after aging. Due to sintering of the Pt particles, the distance between Pt and
Ba is increased, thereby necessitating that the NO2 formed on Pt has to diffuse a greater
distance to reach the Ba storage sites as compared to the degreened catalyst. This results
in an effective decrease in the number of fast NOx storage sites with the consequence that
NO2 tends to travel downstream of the NO oxidation sites before eventually being stored.
At the same time, it is evident that the NO oxidation function of the catalyst is degraded
after aging. As noted above, the NO concentration decreases quite slowly along the
length of the catalyst, whereas, a sharp drop-off in NO concentration is depicted in Fig.
5.3a for the degreened B-225 catalyst. This indicates that aging results in both a loss of
NO oxidation sites and NO2 storage sites relative to the degreened sample.

5.3.3.2. NOx Reduction.
During NOx reduction experiments, the rich phase of the 60/5 s cycles contained a
concentration of H2 determined from the OSC/NSC study shown in Fig. 5.1, along with
5% CO2, 5% H2O, and balance N2. The resulting cycle-averaged NOx conversions are
collected in Table 5.3. In general, cycle-averaged NOx conversion in lean-rich cycling
experiments show a strong correlation with NOx storage efficiencies [16]. Comparing the
cycle-averaged conversions in Table 5.3 with the lean NSE values shown in Fig. 5.2, a
larger discrepancy is seen between the two values at 200 ºC, as compared to 300 ºC (Fig.
5.5). The source of this difference can be attributed to the 1 NOx “puff” that occurs at the
beginning of the transition from lean to rich conditions. Data pertaining to the “puff” are
depicted graphically in Fig. 5.6. For the degreened B-225 catalyst, the amount of rich
NOx release decreases at 250 ºC and 300 ºC along the entire length of the catalyst,
indicating that it is re-adsorbed and subsequently reduced. In contrast, at 200 ºC the rich
NO\textsubscript{x} release increases along the length of the catalyst until 8.4 mm from the front of the catalyst and then decreases. This increased amount of NO\textsubscript{x} measured during the rich phase at 200 °C (and indeed emitted from the catalyst) can be explained on the basis that (i) NO\textsubscript{x} storage and release is moved further along the length of the catalyst at low temperatures [11,12], and (ii) the rich phase NO\textsubscript{x} release is greater at low temperatures due to the imbalance in the rates of NO\textsubscript{x} release and NO\textsubscript{x} reduction [16,17], i.e., a fraction of the NO\textsubscript{x} is rapidly released into the product stream but is not fully consumed by H\textsubscript{2}.

![Figure 5.5. Comparison of cycled-averaged NO\textsubscript{x} conversion (solid bars) and NO\textsubscript{x} storage efficiency (checkered bars) as a function of position for degreened catalysts: a) B-225 at 200 °C, b) B-225 at 300 °C, c) BC-175 at 200 °C, and d) BC-175 at 300 °C.](image-url)
Figure 5.6. Rich phase NO\textsubscript{x} release as a function of position during regeneration of degreened (DG) and aged (AD) catalyst B-225.

Selectivity to NH\textsubscript{3} as a function of the sampling position in the catalyst is shown in Table 5.3 and Fig 5.7. Note that in this work N\textsubscript{2}O, the other possible NO\textsubscript{x} reduction product along with N\textsubscript{2} and NH\textsubscript{3}, was not monitored. For the degreened B-225 catalyst the NH\textsubscript{3} selectivity first increases from the front face of the catalyst, reaches a maximum close to the end of the NO\textsubscript{x} storage zone, and then decreases. In order to explain these findings, it is necessary to consider the reductant front as it moves along the axial length of the catalyst. According to the model proposed by Ribeiro and co-workers [32,33] and others [10,23,34,35], during LNT regeneration a H\textsubscript{2}-rich reaction front propagates along the length of the catalyst in which N\textsubscript{2} and NH\textsubscript{3} are formed from the reduction of the stored NO\textsubscript{x}. The formed NH\textsubscript{3} may then react further with nitrates stored downstream of the front, resulting in the formation of N\textsubscript{2}. This explains the temporal sequence of product formation, N\textsubscript{2} breakthrough occurring before NH\textsubscript{3}. Breakthrough of the NH\textsubscript{3} corresponds to the point at which the stored NO\textsubscript{x} and O\textsubscript{2} are sufficiently depleted for the NH\textsubscript{3} consumption to be incomplete.
Table 5.3. Comparison of cycle-averaged NO\textsubscript{x} conversion and NH\textsubscript{3} selectivity during lean-rich cycling for degreened and aged catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>Position (mm)</th>
<th>Cycle-averaged NO\textsubscript{x} conversion (%)</th>
<th>NH\textsubscript{3} selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Degreened</td>
<td>Aged</td>
</tr>
<tr>
<td>B-225</td>
<td>200</td>
<td>4.4</td>
<td>43.6</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.4</td>
<td>73.4</td>
<td>--\textsuperscript{a}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.4</td>
<td>98.7</td>
<td>27.2</td>
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<td>91.6</td>
<td>49.8</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>4.4</td>
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<td>94.6</td>
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<td></td>
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<td>16.4</td>
<td>99.7</td>
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<td></td>
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<td>25.4</td>
<td>98.6</td>
<td>48.6</td>
</tr>
<tr>
<td>BC-175</td>
<td>200</td>
<td>4.4</td>
<td>9.8</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
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<td>8.4</td>
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<td>16.4</td>
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<td>8.4</td>
<td>53.3</td>
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<td></td>
<td></td>
<td>16.4</td>
<td>86.8</td>
<td>56.0</td>
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<tr>
<td></td>
<td></td>
<td>25.4</td>
<td>98.6</td>
<td>66.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Data not available for this position.
During regeneration, a number of zones effectively exist in the catalyst (see Fig. 5.8) [11-13,34-36]. Upstream of the reductant front (zone 1), hydrogen has already consumed oxygen present on the Pt sites and depending on the temperature (vide infra), may or may not have reduced all of the stored NO\textsubscript{x}. The ratio of H\textsubscript{2} to residual NO\textsubscript{x} (if present) is high (given that the reduction front has already moved downstream), and hence NH\textsubscript{3} formation is favored. In the reductant front (zones 2 and 3), NH\textsubscript{3} is both generated and consumed. Downstream of the front (zone 4), NO\textsubscript{x} and adsorbed oxygen are present. The significance of this is that NH\textsubscript{3} produced in or behind the front can be consumed in the NO\textsubscript{x}-NH\textsubscript{3} SCR or NH\textsubscript{3}-O\textsubscript{2} reactions. Zone 5 corresponds to the OSC-only zone, i.e., the region downstream of the NSR zone.

Given that at moderate to high temperatures NO\textsubscript{x} reduction displays the characteristics of a feed-limited process [33,34,36], significant NO\textsubscript{x} reduction behind the reduction front is not expected in this temperature range, i.e., stored NO\textsubscript{x} should be fully consumed in the reduction front. However, Clayton et al. [35] have observed that at lower temperatures implication being that catalyst regeneration is limited by chemical processes at the Pt/Ba interface. This explains why catalyst selectivity to NH\textsubscript{3} increases significantly with
decreasing temperature, as illustrated by the data in Table 5.3. Modeling studies by the same group [20] have confirmed that NH$_3$ generation is favored under conditions when NO$_x$ transport to the Pt/Ba interface is the rate determining process. A contributing factor to the increased NH$_3$ selectivity observed at low temperatures can be the slow kinetics of the NO$_x$-NH$_3$ SCR reaction [23]. However, several studies employing catalysts and conditions similar to those employed in the present work have shown that the SCR reaction typically lights off below 200 °C [23,35,37,38]; hence, this is not a factor in the case of degreened catalyst B-225.

Aging at 800 °C significantly affects the performance of the B-225 catalyst, as shown by the greatly decreased cycle-averaged NO$_x$ conversions reported in Table 5.3. As shown, the NO$_x$ conversions measured at 200 and 300 °C reach a maximum at the outlet of the catalyst (25.4 mm), reflecting the lengthening of the NSR zone after aging. This latter point is clearly apparent in Fig. 5.6, which shows that the rich phase NO$_x$ release increases over the length of the catalyst rather than peaking within the first 8.4 mm (as seen for the degreened catalyst). The total amount of NO$_x$ release is also greater than for the degreened sample. Higher NO$_x$ release at 0.0 mm is explained by an increase in the imbalance of NO$_x$ release and reduction rates. Aging results in sintering of the PGM sites and consequently the rate of reduction of NO$_x$ by adsorbed hydrogen at these sites is slower [40]. Furthermore, for a given length of catalyst, there are now fewer sites located downstream for the NO$_x$ in the gas phase to re-adsorb on the catalyst. This is due to the stretching of the NO$_x$ storage zone, i.e., the storage sites downstream have already been filled.

As shown in Table 5.3 and Fig. 5.7, the selectivity to NH$_3$ continues to increase to the end of the aged catalyst sample. For the degreened sample maximum NH$_3$ release is seen towards the end of the NO$_x$ storage zone; given that the NSR zone now encompasses the entire length of the sample, it follows that NH$_3$ selectivity reaches a maximum towards the rear of the sample. Indeed, as shown in Fig. 5.8, for the degreened sample both the NH$_3$ and NO concentrations reach a maximum within the first 10 mm of the catalyst, whereas these concentrations continue to increase along the length of the catalyst for the
aged sample. For the aged catalyst, two additional effects must be considered. First, stretching of the storage-reduction zone results in the elimination of the downstream OSC-only zone. Therefore, the NH₃ that is formed is less likely to be consumed by adsorbed oxygen downstream of the reduction front. Second, as discussed in the Introduction, segregation of the Pt and Ba phases during aging results in a decrease in the rate of NOₓ transport (reverse spillover) to the Pt sites. Consequently, the Pt surface will be predominantly covered by hydrogen, and as the stored NOₓ diffuses to the Pt particles, NH₃ will be preferentially formed.
Figure 5.8. Schematic showing NO\textsubscript{x} and NH\textsubscript{3} concentrations along the length of the catalyst and the mechanism of NO\textsubscript{x} reduction under rich conditions (after Pihl et al. [38]). Note that the relative concentrations depicted correspond to actual data collected at 200 °C for catalyst B-225.

Analysis of the temporal data provides additional insights. In Figs. 5.9a and 5.9b, NH\textsubscript{3} concentrations are plotted versus time at each sampling position for the degreened and aged catalysts, respectively. Note that in the plots, the feed gas was switched from lean to rich at 31 s. Examining the data for the degreened catalyst in Fig. 5.8a, the NH\textsubscript{3} concentration increases from the front of the catalyst until the midpoint of the catalyst.
(between the 8.4 mm and 16.4 mm positions). Furthermore, a delay is present in the appearance of NH₃ from one sampling position to the next over the length of the catalyst. For example, at the 4.4 mm position, a ~ 1 s delay from the onset of rich conditions to the appearance of NH₃ exists, with additional delays at each of the subsequent measurement points. This finding is consistent with previous reports [10,35] and is evidence that significant H₂ consumption precedes NH₃ formation, i.e., due to the reaction of H₂ with stored oxygen and NOₓ to generate N₂. The decrease in NH₃ concentration that begins between the 8.4 mm and 16.4 mm positions and continues until the rear of catalyst demonstrates that some of the NH₃ is being consumed before reaching the end of the catalyst.

Comparing these results with the data for the aged catalyst, a clear difference is the lack of delay between the appearance of NH₃ at each measurement point in the aged catalyst. Indeed, as shown in Fig. 5.9b, the initiation of NH₃ release at the different sampling locations occurs almost simultaneously for the aged sample. These observations clearly indicate that the reductant front propagates more rapidly along the length of the aged catalyst than the degreened sample. This increase in the velocity of the front can be attributed in part to the lower amounts of NOₓ and O₂ stored in the front of the catalyst. Similar reasoning has been used to explain the acceleration in the H₂ front typically observed along the length of LNT catalysts during regeneration, i.e., since more NOₓ is stored in the front of a given catalyst, more H₂ is needed to reduce the stored NOₓ and so the front propagates more slowly in this region than in the rear of the catalyst [36]. Additionally, if NOₓ is released more slowly from storage sites (due to Pt-Ba phase segregation), such that the kinetics of NOₓ reduction are controlled by the rate of NOₓ diffusion to the Pt sites, then an acceleration in the velocity of the front edge of the reduction zone is to be expected. Taking these factors together, the increase in selectivity to NH₃ can be readily understood.
Figure 5.9. NH₃ concentration vs. time at each sampling location at 200°C for a) degreened B-225 and b) aged B-225.

Evidence for the fact that the kinetics of NOₓ reduction in aged catalyst B-225 are not limited by the reductant supply rate is provided by the observation that NOₓ release (and hence reduction) is still on-going when NH₃ breakthrough occurs at the catalyst outlet. This is illustrated for the degreened and aged B-225 in Fig. 5.10, which displays the NOₓ concentration measured at the 16.4 mm position as a function of time for regeneration events at 200 °C and at 300 °C. The start and end of the regeneration period are indicated, as is the moment when NH₃ breakthrough occurs at the 25.4 mm position for
the different experiments (note that the data have been time aligned, such that the rich phase starts at the same time for each experiment). For degreened B-225 at 200 °C it is evident that some NO\textsubscript{x} is still being released at the 16.4 mm position when NH\textsubscript{3} breaks through, indicating that at this temperature NO\textsubscript{x} reduction is limited by the kinetics of NO\textsubscript{x} release, rather than being feed limited. This is in agreement with the report of Clayton et al. [36] cited earlier. For aged B-225 tested at 200 °C, the decrease in the NH\textsubscript{3} breakthrough time relative to the degreened catalyst is apparent (corresponding to a shift of ~0.9 s), while it is evident that considerable NO\textsubscript{x} release continues after NH\textsubscript{3} breakthrough. In contrast, at 300 °C the degreened catalyst shows essentially no NO\textsubscript{x} release at the 16.4 mm position, consistent with fast NO\textsubscript{x} release and reduction in the front of the catalyst. However, for the aged catalyst significant NO\textsubscript{x} release is observed at 300 °C, while the NH\textsubscript{3} breakthrough time is decreased by ~1.2 s. Continued NO\textsubscript{x} release after NH\textsubscript{3} breakthrough indicates that NO\textsubscript{x} reduction, unlike the degreened catalyst, is limited by the kinetics of NO\textsubscript{x} release, i.e., even at 300 °C NO\textsubscript{x} reduction is not feed limited for the aged catalyst.
5.3.4. Ceria-containing Catalyst.

5.3.4.1. NO\textsubscript{x} Storage.

As for the experiments with catalyst B-225, cycling experiments using catalyst BC-175 employed a H\textsubscript{2} concentration tailored to the OSC and NO\textsubscript{x} storage capacity of the catalyst. Fig. 5.11 reports the measured lean NO\textsubscript{x} storage efficiencies. For the degreened catalyst, the NSE increased at each point along the length of the catalyst with increasing temperature. Maximum NSE (<100% at 200 and 250 °C) was not reached until the 25.4 mm position, indicating that the whole length of the catalyst was used for storage under these experimental conditions. Additional information is provided in Figs. 5.12a and 5.12b, in which data pertaining to the cycle-averaged NO and NO\textsubscript{2} concentrations are plotted at each measurement point along the length of the catalyst. A gradual decrease in
NO concentration along the length of the degreened sample occurs at each temperature with the minimum being attained at the 25.4 mm position.

Figure 5.11. Lean NO\textsubscript{x} storage efficiency as a function of position for degreened (DG) and aged (AD) catalyst BC-175.

As with B-225, for BC-175 the NO\textsubscript{2} concentration increases along the length of the catalyst for the first third, before decreasing as the rear face of the catalyst is reached. However, it is apparent that NO\textsubscript{x} storage is less efficient on BC-175 relative to B-225, as indicated by the longer NO/NO\textsubscript{2} storage zone in the case of BC-175. This finding contrast with our previously reported results for similar catalyst compositions in which it was found that the degreened catalysts showed similar NSE at 250 °C under lean-rich cycling conditions [17]. However, in the present study the washcoat loading of BC-175 (175 g/L) was significantly lower than that of B-225 (225 g/L), in contrast to the previous study when the samples used had the same loading. Evidently, NSE under these conditions is sensitive to washcoat loading.
Figure 5.12. a) Lean phase NO concentration and  b) lean phase NO\textsubscript{2} concentration as a function of position during NO\textsubscript{x} storage on degreened (DG) and aged (AD) catalyst BC-175.

As shown in Table 5.2, aging of catalyst BC-175 results in the same effects as seen with the non-ceria catalyst, i.e., PGM sintering and hence Pt/Ba and Pt/CeO\textsubscript{2} phase segregation. However, comparison of Figs. 5.2 and 5.11 indicate that whereas before aging the NSE of B-225 at 200 °C and 250 °C was superior to that of BC-175 (at every position in the catalyst), after aging the NSE of BC-175 is superior to that of B-225. This observation is consistent with our previous studies [16,17,39] indicating the beneficial
effects of ceria addition on catalyst performance after aging. Evidently, these benefits more than compensate for the lower washcoat loading of catalyst BC-175 after aging at 800 °C.

5.3.4.2. NO\textsubscript{x} Reduction.
Cycled-averaged NO\textsubscript{x} conversion data for the degreened and aged BC-175 samples (see Table 5.3) are consistent with the NSR zone extending the whole length of the catalyst, the NO\textsubscript{x} conversion attaining its maximum value at the rear of the catalyst in each case. Considering the lean phase NSE, while aging results in a decrease in NO\textsubscript{x} conversion levels (notably at 300 °C), the deterioration is significantly less than that observed for catalyst B-225 (see Figure 5.13). Again, this serves to illustrate the importance of ceria in aiding LNT durability.

![Figure 5.13. Percent change in NO\textsubscript{x} storage efficiency (NSE) after aging as a function of position for: B-225 at 300 °C (solid bars) and BC-175 at 300 °C (checkered bars). Percent change in NSE is defined as: 100 x (degreened NSE - aged NSE)/degreened NSE.](image)

Fig. 5.14 depicts the cycle-averaged rich phase NO\textsubscript{x} release as a function of measurement position. For the degreened catalyst, the trends in rich phase NO\textsubscript{x} release are similar to catalyst B-225, i.e., at 250 and 300 °C NO\textsubscript{x} release decreases over the length of the
catalyst, indicating that readsorption and reduction of the released NO\textsubscript{x} occurs. At 200 °C the NO\textsubscript{x} release is notably higher due to the imbalance in the rates of NO\textsubscript{x} release and reduction. However, in contrast to B-225, the NO\textsubscript{x} release at 200 °C does not decrease significantly in the rear of the BC-175 sample, which can be attributed to the longer NO\textsubscript{x} storage-reduction zone in this catalyst.

![Figure 5.14. Rich phase NO\textsubscript{x} release as a function of position during regeneration of degreened (DG) and aged (AD) catalyst BC-175.](image)

As for the B-225 catalyst, NH\textsubscript{3} formation over BC-175 tracks the NO\textsubscript{x} storage zone. Consequently, as shown in Fig. 5.15, peak NH\textsubscript{3} concentrations measured for degreened BC-175 tend to occur closer to the rear of the catalyst in comparison with B-225. As for B-225, the selectivity to NH\textsubscript{3} exhibited by BC-175 increases after aging. Furthermore, the maxima in NH\textsubscript{3} selectivity are located further down the length of the catalyst after aging, consistent with stretching of the NSR zone.
Temporal data for the NH$_3$ release from catalyst BC-175 are shown in Figs. 5.16a and 5.16b. Although not as apparent as with the B-225 catalyst, a delay between the appearance of NH$_3$ for each sampling point is present for the degreened BC-175 catalyst. The fact that the delay is less pronounced than for B-225 can be attributed to the lower washcoat loading of BC-175, and hence the lower concentration of storage sites per unit catalyst length. In contrast to B-225, the NH$_3$ concentration continues to increase down the length of the catalyst. Again, this can be attributed to the lower washcoat of the BC-175 catalyst compared to B-225, which, as discussed earlier, results in utilization of a significantly larger portion of the catalyst for NO$_x$ storage. Since NH$_3$ evolution tracks the NO$_x$ storage-reduction zone, it follows that peak NH$_3$ concentrations for BC-175 are attained further along the catalyst than for B-225. In the case of the aged BC-175 catalyst (Fig. 5.16b), the delay in NH$_3$ evolution at the different measurement points is again minor, indicative of fast propagation of the reductant front. As for B-225, there is a notable increase in the amount of NH$_3$ released from the aged BC-175 sample after aging. Moreover, similar to B-225, regeneration of BC-175 at 300 °C is limited by the kinetics of NO$_x$ reduction after aging, rather than the rate of reductant supply, as indicated by the
observation that NO\textsubscript{x} release and reduction is still on-going at the 16.4 mm position when NH\textsubscript{3} breaks through the catalyst (Figure 5.17).

Figure 5.16. NH\textsubscript{3} concentration vs. time at each sampling location at 200°C for a) degreened BC-175 and b) aged BC-175.

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Figure 5.17. \(\text{NO}_x\) concentration profiles measured at the 16.4 mm position for degreened (DG) and aged (AD) BC-175 as a function of time for regeneration events at 200 °C and at 300 °C. The dashed vertical lines indicate the time at which NH\(_3\) breaks through at the 25.4 mm position.

As stated in the Introduction, there are at least five potential factors which can explain the increase in selectivity to NH\(_3\) observed for B-225 and BC-175 after aging. Factor (ii) in the list, pertaining to the decreased OSC of the aged catalysts, and factor (iii) concerning the decrease of the catalyst NSE after aging, were accounted for in this study by adjusting the \(\text{H}_2\) concentrations used. In this manner, excessively high \(\text{H}_2:\text{NO}_x\) ratios in the reductant front were avoided; instead, a stoichiometric amount of \(\text{H}_2\) (based on reaction 5.1) was used during regeneration. With these two factors largely excluded, one or all of the following explanations must be invoked to account for the increase in NH\(_3\) selectivity after aging:
(a) The imbalance in the rates of NO$_x$ release and propagation of the reductant front, resulting from the Pt-Ba phase segregation that occurs upon aging. This imbalance results in increased H$_2$:NO$_x$ ratios at the Pt sites, thereby favoring NH$_3$ formation over N$_2$.

(b) Stretching of the NSR zone, resulting from a decrease in concentration of NO$_x$ storage sites per unit length of catalyst. The stretching of this zone decreases the length of the OSC-only zone located in the rear of the catalyst, resulting in diminished NH$_3$ oxidation and decreased NH$_3$ consumption by NO$_x$ that re-adsorbs downstream of the reduction front.

(c) Higher NH$_3$ emissions may result from decreases in the rates of NH$_3$ consumption via reaction with NO$_x$ or O$_2$ stored downstream of the reaction front (due to PGM sintering).

Of these explanations, (a) and (b) are supported by the data presented in this paper. Increased NH$_3$ emissions are clearly associated with stretching of the NSR zone, a conclusion which has previously been reported by workers at Oak Ridge National Laboratory (ORNL) [10-12]. Indeed, as the data in Table 5.3 show, after aging selectivity to NH$_3$ is most clearly increased at positions towards the end of the catalyst (e.g., at the 16.4 and 25.4 mm positions). At the same time, temporal data show that after aging the rate of reductant front propagation is increased. This, combined with the fact that Pt-Ba phase segregation results in slower transport of NO$_x$ to PGM sites during catalyst regeneration [20], means that H$_2$:NO$_x$ ratios at the PGM sites will increase after aging.

Turning to point (c) above, we have previously presented steady-state, continuous flow data for a catalyst containing the same washcoat composition as B-225 (but slightly higher washcoat loading) [39]. Results showed that after aging (during which the maximum temperature was 770 ± 10 ºC) the rate of the NO$_x$-NH$_3$ SCR reaction was measurably decreased. On the other hand, for the same catalyst the kinetics of the NH$_3$-O$_2$ reaction were essentially unchanged [40]. Therefore, in the present work we cannot
exclude the possibility that a decrease in the rate of the NO$_x$-NH$_3$ SCR reaction after aging also contributes to the observed increase in catalyst selectivity to NH$_3$.

5.4. Conclusions.
SpaciMS was employed in this study to understand the factors influencing the NH$_3$ selectivity of fully formulated LNT catalysts, particularly after thermal aging. Physical characterization of the aged catalysts revealed that the surface area, pore volume and PGM dispersion decreased. This fact helps to explain the decreases in NO$_x$ storage efficiency and increases in NH$_3$ selectivity and rich phase NO$_x$ release observed during lean-rich cycling experiments. Specifically, the losses in surface area, accompanied by segregation of the Pt/Rh sites and BaO storage sites, account for the decreased NO$_x$ storage efficiency of the aged catalysts. During NO$_x$ storage during the lean phase, NO and NO$_2$ were required to travel further to reach storage sites due to the decreased storage site concentration. Consequently, after aging the NO$_x$ storage-reduction zone was elongated.

Stretching of the NSR zone has significant implications for catalyst regeneration. The first effect is the increase of the NO$_x$ “puff” that appears during the onset of the rich front as it travels along the length of the catalyst. Since NO$_x$ release from the catalyst tracks the NSR zone, for an aged catalyst the NO$_x$ concentration peaks closer to the rear of the catalyst. Hence the probability that NO$_x$ can re-adsorb downstream of the reduction front and subsequently undergo reduction by NH$_3$ is diminished, and consequently the NO$_x$ emission is higher.

Second, the “stretching” of the NSR zone causes the NH$_3$ selectivity of an aged catalyst to increase. For degreened (but not aged) catalysts, NH$_3$ is generally observed in the effluent from the catalyst after the stored NO$_x$ and adsorbed oxygen located downstream from its point of generation have been consumed; hence, a longer NSR zone for a given length of catalyst means that less catalyst (corresponding to the OSC-only zone) is available to consume NH$_3$ produced upstream by either the NH$_3$-NO$_x$ SCR or NH$_3$-O$_2$ reaction.
Third, the loss of OSC and NO\textsubscript{x} storage sites leads to an increase in the rate of propagation of the reductant front in the aged catalyst compared to the degreened catalyst. Additionally, NO\textsubscript{x} is released more slowly from storage sites (due to Pt-Ba phase segregation), such that for the aged catalysts the kinetics of NO\textsubscript{x} reduction are controlled by the rate of NO\textsubscript{x} diffusion to the Pt sites (rather than being feed limited). Taken together, these factors give rise to increased H\textsubscript{2}:NO\textsubscript{x} ratios at the Pt/Rh sites and hence selectivity to NH\textsubscript{3} increases.
5.5. References.


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Chapter 6. An Investigation into the Validity of a Crystallite-Scale Model to Predict the NH$_3$ Regeneration of a Pt/Rh/BaO/Al$_2$O$_3$ Lean NO$_x$ Trap Catalyst.

6.1. Introduction.

Over the past two decades, intensive research has been focused on reducing NO$_x$ emissions (NO + NO$_2$) from lean burn applications using Lean NO$_x$ Trap (LNT) Catalysts and Selective Catalytic Reduction (SCR) catalysts. The LNT operates by oxidizing NO$_x$ emitted during combustion over precious group metals (PGMs), such as Pt and Rh, and then storing the resulting nitrates and nitrites on a storage component such as Ba [1,2]. Before the storage capacity of the LNT is reached, engine operation is modified to rich conditions creating a net-reducing environment in which stored NO$_x$ is released and migrates back to the PGM component where it reacts with a reductant such as H$_2$ to form N-species such as N$_2$, NH$_3$, and N$_2$O. The SCR catalyst achieves NO$_x$ reduction by catalyzing the reaction of NH$_3$ with NO$_x$ emitted from the engine to form N$_2$ [3].

While either of these approaches is capable of reducing NO$_x$ concentrations in engine exhaust, neither system is without shortcomings. The application of LNTs is limited by the cost of the PGMs. In addition, undesired products are formed during the rich phase, including unreacted NO$_x$ along with NH$_3$ and N$_2$O. The SCR catalyst, on the other hand, requires an external source for the reductant. A common example of this application involves using urea as the NH$_3$ source [4-6], which requires an external storage tank and injection system for the urea to be injected into the exhaust system. Both of these requirements add additional weight and cost to the vehicle system.

In the past decade, to address the shortcomings of the LNT and SCR applications, researchers have developed LNT-SCR systems [7-34]. The aim of coupling these catalysts is to reduce the amount of LNT required thereby reducing the amount of PGM required to meet NO$_x$ emission targets. This coupling also eliminates the need for an external source of reductant by tuning the operation of the LNT such that operates as an NH$_3$ generator.
To fully implement a LNT-SCR system, operation during the lean and rich phases needs to be tuned based on the amount of NO\textsubscript{x} emitted from the engine and also based on the product selectivity that results from the LNT. Specifically, a balance must exist between the amount of NO\textsubscript{x} and NH\textsubscript{3} that is emitted from the LNT upstream of the SCR.

To achieve these aims, one must have a thorough understanding of the factors that control product selectivity during regeneration of the LNT. One factor that determines the selectivity of the products from regeneration is the ratio of hydrogen, nitrogen, and oxygen present on the PGM component [35-40]. The ratio of these species changes as the exhaust conditions are switched from lean to rich phase. If one considers the idea of a reductant front propagating along the length of the monolith, the change in the relative amount of these components is readily explained [35,36,41-47]. As the front moves along the catalyst, the adsorbed oxygen on the catalyst will be consumed by the reductants (e.g. H\textsubscript{2}, CO, HC). As the stored oxygen is consumed, a low reductant to NO\textsubscript{x} ratio exists at the PGM sites. This ratio of reductant to NO\textsubscript{x} increases after the leading edge of the front continues to travel down the length of the monolith. Eventually, a situation exists in which a large excess of reductant is present. The transition from low to equal to high ratios coincides with the shift in product selectivity from N\textsubscript{2}O to N\textsubscript{2} to NH\textsubscript{3} during the regeneration of a LNT catalyst.

The proximity of the PGM to the storage component is another factor that determines the products formed during regeneration. The proximity between these components establishes the distance that NO\textsubscript{x} must diffuse from the Ba to Pt sites. As this distances increases, the ratio of H:N species at the Pt crystallites also increases. The studies by Clayton et al. focused on this Pt/Ba proximity [45,46]. Nova et al. [48,49] stated that the Pt catalyzed reduction of stored NO\textsubscript{x} only occurs efficiently when Pt and BaO are dispersed on the same support. Cant et al. [50] discussed the importance of the Pt/Ba proximity during storage and reduction of a Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst. Cant related the observed selectivity and relative breakthrough times of H\textsubscript{2} and NH\textsubscript{3} to the transport of NO\textsubscript{x} from the storage site back to the PGM. Büchel et al. noted that the best storage and reduction performance was observed when Pt was in close proximity to Ba [51].
The preceding discussion highlights some of the experimental research that has been conducted. Equally important have been the modeling efforts that have been put forth by various research groups. Tuttlies et al. [52] proposed that a model based on the diffusion of NO\textsubscript{x} into the storage particle is strongly affected by solid volume changes. Under regeneration conditions, the dense nitrate layer formed during storage breaks up into BaCO\textsubscript{3}. Schmeißer et al. [53] described the regeneration process as one in which reductants diffuse through an increasingly thickening nitrate layer. Using experimental data from steady-state experiments focusing on the Pt-catalyzed NO/H\textsubscript{2} reaction system, Xu et al. [38] formulated a micro-kinetic model that incorporated an integral short monolith reactor model [54] using available parameters from existing literature and the remaining parameters from experiments. Their model was able to predict the NO\textsubscript{x} surface coverage during storage and the selectivities as a function of the H\textsubscript{2}:NO\textsubscript{x} ratio occurring during regeneration. Larson et al. [55] devised an elementary surface reaction model to describe the regeneration reactions occurring at the PGM sites of a LNT. Larson et al. were able to determine the parameters for their model for their extensive experimental database [35] and were able to validate some of the proposed kinetic mechanisms with data collected using DRIFTS using a commercial LNT catalyst [50]. Lindholm [57] et al. developed a model that utilized a multi-site mechanism for NO\textsubscript{x} storage. During the regeneration phase, the mechanism includes H\textsubscript{2} reacting with stored oxygen on Pt and NH\textsubscript{3} acting as intermediate in N\textsubscript{2} production from the reduction of stored NO\textsubscript{x} with H\textsubscript{2}. Kočí et al. [58] were able to compare the effect of different reductants (CO, H\textsubscript{2}, C\textsubscript{3}H\textsubscript{6}) on NH\textsubscript{3} selectivity in the presence of CO\textsubscript{2} and H\textsubscript{2}O in a heterogeneous, 1-D model. Kočí described the propagation of the reductant as well as the production and consumption of NH\textsubscript{3} as fronts travel down the axis of the monolith.

Short-comings of these modeling efforts include the lack of transparency of the parameters that constitute the model and the development of a model for a certain catalyst operating under a very specified set of conditions. In order to advance the understanding of these catalysts, models are needed that are capable of predicting the experimental data of LNTs under a wide set of conditions. Bhatia et al. proposed a crystallite-scale model to study the effect of Pt dispersion and temperature during the regeneration of a LNT.
comprising a Pt/BaO catalyst [44]. The data provided by the model was compared with
the data generated from fixed storage experiments performed by Clayton et al. [46].
Bhatia was able to achieve a good fit of the data obtained by Clayton et al. for NH₃
generation as the dispersion and temperature during storage and regeneration was varied.

Research concerning product selectivity has been conducted using both experimental and
computer simulation approaches. The goal of the present study was to validate the model
created by Bhatia et al. [44] for a catalyst slightly different than the ones used in their
study. Bhatia used Pt/BaO/Al₂O₃ LNT catalysts in which the dispersion (and hence Pt
particle size) was varied by employing different Pt loadings. For this study, the LNT
catalysts employed are also comprised of Pt/BaO/Al₂O₃ but differ due to the inclusion of
Rh. Pt is the primary choice for oxidation of NO, but Rh is more active for NOₓ
reduction [59,60]. Moreover, Kobayashi et al. showed that a combination of Pt/Rh had a
higher trapping activity than either Pd/Rh or Pd [61]. Additionally, Theis et al. reported
that a combination of Pt and Rh had the best overall NOₓ conversion at low temperatures
(250°C) for fresh and aged catalysts as compared to Pt-only samples [62]. Furthermore,
comparing the vapor pressure of both the metal and the oxide, the vapor pressure for Pt is
higher (3x for the metal, 2x for the oxide) than the vapor pressure for Rh [63]. The vapor
pressure provides an indication of the sintering behavior of the PGM, i.e., the higher the
vapor pressure, the move severe the sintering is expected to be. The dispersions of the
PGM in the catalysts used in this study were varied by sintering the catalyst. Because the
PGM will be exposed to a variety of conditions that may result in the loss of PGM
dispersion, the ability of a model to predict the behavior of an aged catalyst would be
beneficial in the design of an LNT.

6.2. Experimental.
This study incorporated two elements: first, an experimental study of the effect of Pt
dispersion and temperature on the NH₃ selectivity from a LNT regenerated with a fixed
amount of NOₓ, and second, a modeling study to predict the data gathered from the
experimental study. The experimental study used a Pt/Rh/BaO/Al₂O₃ fully formulated
catalyst whose preparation has been described elsewhere [64]. The washcoat was applied
by DCL International, Inc. (Toronto, ON) using a proprietary vacuum coating process. The washcoat was applied to a 4” x 6” cordierite monolith substrate, which had a cell density of 400 cpsi and a wall thickness of 6.5 mil. The BaO component (21.5 wt %) was supported on γ-alumina, while bare alumina was used as a balance to bring the total washcoat loading to the value indicated in Table 6.1.

Table 6.1. Composition of catalysts used in this study.

<table>
<thead>
<tr>
<th>Component</th>
<th>Catalyst code / nominal loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt, g/L</td>
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<tr>
<td>Rh, g/L</td>
<td>0.61</td>
</tr>
<tr>
<td>BaO(^a), g/L</td>
<td>26</td>
</tr>
<tr>
<td>CeO(_2)(^b), g/L</td>
<td>0</td>
</tr>
<tr>
<td>γ-Al(_2)O(_3)(^c), g/L</td>
<td>Balance</td>
</tr>
<tr>
<td>Total washcoat, g/L</td>
<td>225</td>
</tr>
</tbody>
</table>

\(^a\) 21.5 wt% supported on γ-Al\(_2\)O\(_3\).

\(^b\) Stabilized with 5 wt% La\(_2\)O\(_3\).

\(^c\) Stabilized with 3 wt% La\(_2\)O\(_3\).

6.2.1. Catalyst Aging.
A 1.75 cm x 2.54 cm (d x l) core was drilled from the LNT monolith and was wrapped with ceramic fiber and positioned in a quartz tube. Degreening the catalyst consisted of exposing the catalyst to neutral conditions (5% CO\(_2\), 5% H\(_2\)O, balance N\(_2\)) at 800°C for 2 h. Aging the catalyst involved subjecting the catalyst to continuous lean conditions (8% O\(_2\), 5% CO\(_2\), 5% H\(_2\)O, and balance N\(_2\)) at 800°C for 24 h. In both cases, the gas flow was adjusted to give a GHSV of 30,000 h\(^{-1}\).

6.2.2 Pulsed H\(_2\) Chemisorption.
The dispersion of precious metal (Pt + Rh) was determined using a Micromeritics AutoChem II Analyzer by means of pulsed H\(_2\) chemisorption at dry ice temperature (−78°C). This temperature was chosen in an effort to minimize H spillover from the
metal to the support material [65]. 1 g of sample (as a fine powder), including both washcoat and substrate, was loaded into the reactor. After being oxidized at 400°C in 10% O₂/He for 15 min, followed by reduction at 300°C in 10% H₂/Ar for 15 min, the catalyst was heated to 400°C (hold time 10 min) in flowing Ar to remove adsorbed H. Pulsed H₂ chemisorption was initiated using a four-way valve after the catalyst had been cooled to −78°C. During this measurement, 0.5 mL of 10% H₂/Ar was pulsed into the reactor every 2 min, while the H₂ signal at the reactor outlet was being monitored with a thermal conductivity detector (TCD). H₂ pulsing, i.e., the total precious metal (Pt + Rh) sites were saturated with H₂, was terminated after the TCD signal had reached a constant value. Assuming a 1:1 ratio of atomic hydrogen to surface Pt or Rh, the metal dispersion was calculated based on the amount of H adsorbed.

6.2.3 SpaciMS and H-Sense Mass Spectrometers.
All of the data in the experimental portion of this study were collected using either an Airsense High Speed Multi-component Gas Analyzer or an Airsense H-Sense Hydrogen Gas Analyzer. The Airsense analyzer is a chemical-ionization mass spectrometer that has been modified for SpaciMS (spatially-resolved capillary inlet chemical ionization mass spectrometry) applications by incorporating a 0.37 mm outer diameter (0.18 mm i.d.) stainless steel capillary connected to the sample chamber. The sampling rate was 14 sccm and data were collected at 3 Hz. Data pertaining to the concentrations of NO, NO₂, O₂, H₂O, and NH₃ at different positions were collected using the spaciMS, and the measurement locations are shown in Fig. 6.1. The first of these positions corresponded to the rear face of the catalyst (25.4 mm from the catalyst inlet), with successive sampling at 16.4 mm, 8.4 mm, 4.4 mm, and the front face (0 mm from the inlet). By sampling in this manner (from rear to front), the chance of contaminating the capillary with particles from the washcoat of the catalyst was decreased. Note that the “0 mm” position actually corresponds to a position of 0.1 mm; this was done in order to ensure that the capillary was correctly aligned with the selected channel.
Figure 6.1. Description of the Measurement Locations Along the Length of the Monolith Catalyst.

The other mass spectrometer employed in this study was an Airsense H-Sense Hydrogen Gas Analyzer to measure H₂ concentration only at the exit of the reactor. The H-Sense uses the principle of Electron Pulse Ionization (EIMS) mass spectrometer principle optimized for H₂-only analysis.

6.2.4. Determination of the Amount of NOₓ Stored.

Since the goal of this experiment was to study NH₃ selectivity, a repeatable starting point at the end of the lean (NOₓ storage) phase was required. To achieve this goal, both the degreened and aged catalysts were subjected to continuously lean conditions to determine the time required to reach a certain NOₓ storage level. The catalysts were subjected to a pre-treatment step consisting of fifteen 60 s lean (500 ppm NO, 5% O₂, bal. Ar) / 10 s Rich (2% H₂, 0.5% O₂, bal. Ar) cycles at 450 °C followed by exposure to 2% H₂ in Ar at 450 °C. The duration of the rich conditions at 450 °C lasted until the concentrations of NH₃ and H₂O in the effluent approached 0 ppm as measured outside the rear of the catalyst by the SpaciMS. Upon reaching this temperature, the catalyst was cooled in Ar to the experimental temperature (200 or 300 °C). Once this temperature was reached, the catalyst was exposed to continuous lean conditions (500 ppm NO, 5% O₂, bal. Ar). After the desired NOₓ storage level was attained, conditions in the reactor were switched to rich (2% H₂ bal. Ar) in order to regenerate the storage sites. This procedure was repeated to ensure the accuracy of the storage level.
6.2.5. \textit{NH}_3 Selectivity.

Once the time for a fixed level of NO\textsubscript{x} storage had been determined, the catalyst was subjected to the same pretreatment as described previously and then subjected to continuous lean conditions followed by continuous rich conditions, during which the products formed by the reduction of stored NO\textsubscript{x} were monitored using the spaciMS. Again, the lean conditions were 500 ppm NO, 5\% O\textsubscript{2}, and bal. Ar, but the rich phase was 1500 ppm H\textsubscript{2} and bal. Ar. The temperature for the lean and rich phases was either 200 or 300 °C. As during the pretreatment step, once the NH\textsubscript{3} and H\textsubscript{2}O concentrations decreased to less than 4 ppm, the temperature of the reactor was increased to 450 °C to ensure that all of the Ba storage sites were regenerated. Once the catalyst was sufficiently regenerated, it was cooled to the next temperature to be studied. These processes were first performed at the 25.4 mm position (outlet of the catalyst) and progressively moved to other measurement positions towards the front of the catalyst as described above. Again, it is worth noting again that while the SpaciMS measurements for NO, NO\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O, and NH\textsubscript{3} were collected at each of the locations previously described along the axis of the catalyst, all of the H\textsubscript{2} measurements were collected from the effluent of the catalyst.

The selectivity (6.1 and 6.2) and yield (6.3 and 6.4) are defined as:

\begin{equation}
\text{Selectivity:}
\end{equation}

\[
\frac{\text{Concentration of rich phase } \text{NH}_3 \text{ release at measurement location}}{\text{NO}_x \text{ converted on catalyst}} \times 100\%
\]

(6.1)

with:

\[
\text{NO}_x \text{ converted on catalyst} = \text{Inlet lean } \text{NO}_x - \text{Outlet lean } \text{NO}_x - \text{Concentration of rich } \text{NO}_x \text{ released at the measurement location}
\]

(6.2)
Yield:

Conversion = 

\[
\frac{\text{Feed NO}_x \text{– Lean NO}_x \text{ at measurement location} - \text{Rich NO}_x \text{ at measurement location}}{\text{Feed NO}_x \text{– Lean NO}_x \text{ at measurement location}} \times 100\%
\]  

(6.3)

Yield = Selectivity \times Conversion \tag{6.4}

In eqns. (6.14), (6.15), and (6.16), all concentrations are cycle-averaged integrated values (ppm*s).

6.3. Model Development.

The model employed in this study of NH\(_3\) selectivity resulting from the regeneration of a LNT catalyst with fixed NO\(_x\) loading was developed by Bhatia et al. [44] based on experimental work by Clayton et al. [46]. The current study is part of a collaboration between research groups at the University of Kentucky and the University of Houston. The crystallite-scale model was based on the effects that Pt dispersion and temperature have on the processes that occur at the Pt/Ba interface in LNT catalysts. During regeneration of LNT, NO\(_x\) undergoes a reverse spillover from the Ba storage phase back to at the Pt particles and then reacts with H\(_2\) that is chemisorbed onto the Pt particles. Additionally, the NO\(_x\) can be reduced by the intermediate NH\(_3\) produced as NO\(_x\) is reduced by H\(_2\). The perimeter resulting from the interface that exists between the Pt and Ba phases is subjected to changes as different Pt dispersions and loadings are used on these catalysts. This interface is also changed during the aging of the catalyst as the Pt particles are sintered.

The computer model is comprised of a localized material balance for stored NO\(_x\), species balances for H\(_2\), NH\(_3\), and N\(_2\), and a balance for the vacant sites on Pt. Along with these balances the following overall catalytic reactions are proposed to occur at the Pt/Ba interface:
Reduction of NO\textsubscript{x} by hydrogen to produce the reaction intermediate NH\textsubscript{3}, \( k_1 \) (m\textsuperscript{4}/mol s):

\[
8 \text{H}_2 + \text{Ba(NO}_3\text{)}\text{)_2} \leftrightarrow 5 \text{H}_2\text{O} + \text{BaO} + 2 \text{NH}_3
\]

(6.5)

Reduction of NO\textsubscript{x} by the intermediate NH\textsubscript{3} to produce N\textsubscript{2}, \( k_2 \) (m\textsuperscript{4}/mol s):

\[
\frac{10}{3} \text{NH}_3 + \text{Ba(NO}_3\text{)}\text{)_2} \leftrightarrow 5 \text{H}_2\text{O} + \text{BaO} + \frac{8}{3} \text{N}_2
\]

(6.6)

Consumption of H\textsubscript{2} by chemisorbed oxygen on the Pt crystallites, \( k_3 \) (m\textsuperscript{3}/mol s):

\[
\text{H}_2 + \text{O-Pt} \leftrightarrow \text{H}_2\text{O} + \text{Pt}
\]

(6.7)

For the development of the governing material balances and other equations used by the model the reader is referred to Bhatia et al. [44] or Appendix A.2. The following is a list of the assumptions made in realizing the model:

1. NO\textsubscript{x} undergoes reverse spillover from the Ba phase to Pt particles where the NO\textsubscript{x} is reduced by H\textsubscript{2} and the intermediate NH\textsubscript{3}.

2. The Pt particles are hemispherical in shape. This assumption is used to develop the relations for the total number of Pt atoms in a crystallite and number of crystallites per monolith channel. These are used to calculate the exposed surface area and total Pt/Ba interfacial perimeter. Figure 6.2 shows the radius of Pt crystallite, \( R_C \), and the effective storage radius of the NO\textsubscript{x} stored in the Ba phase, \( R_{eff} \), as supported on Al\textsubscript{2}O\textsubscript{3}. 
3. Both Pt and Ba are assumed to have a FCC crystal structure. This gives the atomic packing factor, $A_{PF}$, 0.74 for Pt. For Ba, the assumption used to calculate the surface density of BaO (BaO molecules/exposed BaO area over which NO$_x$ is stored) is from a study by Bowker et al [66].

4. All of the stored NO$_x$ is assumed to be in the form of nitrates. While nitrites are also expected to be present, this assumption only affects the quantitative aspect of the data predicted by the model, not the spatiotemporal trend of N$_2$ and NH$_3$ concentrations with respect to Pt dispersion and temperature.

5. Ba is proposed to be present in the form of Ba(OH)$_2$ on account that CO and CO$_2$ are not present in the gas phase at any time. This eliminates the need to configure the model to account for NO$_x$ storage at different phases of Ba sites.

6. The diffusion of stored NO$_x$ occurs in a radial direction only (1-dimensional). Although gradients exist due to contributions from the spillover of NO$_x$ to Pt and the adsorption/desorption at the Ba sites away from Pt, the 1-D diffusion is assumed since a model depicting these gradients does not exist in the literature.
7. The process is considered to be isothermal. This assumption is supported by the minimal increase (< 5 °C) observed by Clayton et al. [46] during the switch from lean to rich conditions during the anaerobic regeneration of a LNT.

The assumptions listed in #5 through #7 above give the following relation for the localized material balance of stored NO\(_x\):

\[
\frac{\partial c_A}{\partial t} = \frac{D_A}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_A}{\partial r} \right); \quad R_C \leq r \leq R_{\text{eff}}
\] (6.8)

where \(c_A\) is the surface concentration of stored NO\(_x\) (mol/m\(^2\) exposed BaO), \(D_A\) is the diffusivity of stored NO\(_x\) in the Ba phase (m\(^2\)/s), \(r\) is the radial coordinate (m), and \(t\) is time during regeneration (s). The initial and boundary conditions (I.C. and B.C. for (6.9) are:

I.C. At \(t = 0\) \quad c_A = c_{A0}(r), \quad R_C \leq r \leq R_{\text{eff}} \quad (6.9a)

where \(c_A\) is the surface concentration of stored NO\(_x\) (mol/m\(^2\) exposed BaO), \(c_{A0}\) is the surface concentration of stored NO\(_x\) before the start of regeneration (mol/m\(^2\) exposed BaO).

B.C.1. At \(r = R_C\) \quad D_A \frac{\partial c_A}{\partial r} = k_1 c_A c_{H_2WC} + k_2 c_A c_{NH_3WC} \quad (6.9b)

B.C.2. At \(r = R_{\text{eff}}\) \quad \frac{\partial c_A}{\partial r} = 0 \quad (6.9c)
8. BaO is assumed to be present on the Al$_2$O$_3$ surface as a monolayer. This is supported by Clayton et al., Castoldi et al., and Fanson et al. [46,67,68]. Although FT-IR studies by Dawody et al. [69] showed that all of the Al$_2$O$_3$ sites might be covered by the BaO monolayer, the contribution of the Al$_2$O$_3$ sites is not expected to change the predicted trends due to competitive adsorption of molecular H$_2$O at the Al$_2$O$_3$ sites.

The additional equations required to predict the trends of H$_2$, NH$_3$, and N$_2$ observed during regeneration are provided by a balance of each of these species in the gas and solid phases. The species balance for component $j$ ($j = H_2$, NH$_3$, or N$_2$) in the fluid phase is given by:

$$\frac{\partial c_{jm}}{\partial t} = -\bar{u} \frac{\partial c_{jm}}{\partial x} - \frac{k_{cj}(x)}{R_\Omega} (c_{jm} - c_{j,WC}) \quad (6.10)$$

where $c_{jm}$ is the cup-mixing concentration of species $j$ at the fluid-washcoat interface (mol/m$^3$), $k_{cj}(x)$ is the mass transfer coefficient of species $j$ (m/s), $c_{j,WC}$ is the concentration of species $j$ at the fluid-washcoat interface (mol/m$^3$), $x$ is the axial coordinate (m), and $R_\Omega$ effective transverse length scale (m).

H$_2$ balance:

$$\frac{\partial H_{2,WC}}{\partial t} = \frac{1}{\varepsilon_{WC}\delta_c(a+\delta_c)} \left[ ak_{C,H_2}(x)(c_{H_2,m} - c_{H_2,WC}) \right. \right.$$

$$\left. - \frac{c_{H_2,WC}N_C 2\pi R_C}{4L} \left( 4k_1c_A|_{r=R_C} + k_3c_{Pt}\theta_{O-Pt}R_C \right) \right] \quad (6.11)$$

where $\varepsilon_{WC}$ is the porosity within the washcoat, $\delta_c$ is the thickness of the washcoat (m), $a$ is the width or hydraulic diameter if the channel (m), $N_C$ is the number crystallites per channel, $R_C$ is the radius of the crystallite (m), $L$ is the length of the monolith (m), and $\theta_{O-Pt}$ is the fractional surface coverage of chemisorbed oxygen on Pt.

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9. The $4k_1c_A|_{r=R_C}$ term in equation (6.6) represents the consumption of H$_2$ by stored NO$_x$, and $k_3c_{Pt}\theta_{O-Pt}R_C$ represents the consumption of H$_2$ by chemisorbed oxygen on the exposed Pt surface. These two terms are based on the assumption that the reaction rate between H$_2$ and stored NO$_x$ is proportional to the perimeter of the Pt/Ba interface and the reaction between H$_2$ and chemisorbed oxygen is proportional to the surface area of the exposed Pt atoms, respectively.

NH$_3$ balance:

$$\frac{\partial NH_{3,WC}}{\partial t} = \frac{1}{\delta_C \delta(a+\delta_C)} \left[ ak_{C,NH_3}(x)(c_{NH_3,m} - c_{NH_3,WC}) + \frac{N_C 2\pi R_C c_A|_{r=R_C}(k_1 c_{H_2,WC} - (5/3) k_2 c_{NH_3,WC})}{4L} \right]$$

(6.12)

Finally, a species balance for N$_2$ in the solid phase:

$$\frac{\partial N_{2,WC}}{\partial t} = \frac{1}{\delta_C \delta(a+\delta_C)} \left[ ak_{C,N_2}(x)(c_{N_2,m} - c_{N_2,WC}) + \frac{N_C 2\pi R_C k_2 c_A|_{r=R_C} c_{NH_3,WC}}{3L} \right]$$

(6.13)

To complete this series of equations, a balance for the vacant sites, $\theta_V$, on Pt is necessary:

$$\frac{\partial \theta_V}{\partial t} = k_3 c_{N_2,WC} \theta_{O-Pt}$$

(6.14)

The initial and boundary conditions for equations (6.10) through (6.14) are:

I.C. At $t = 0$, $c_{i,m} = 0$, $c_{i,WC} = 0$, $\theta_V = 0$, $0 < x \leq L$ (6.15a)

B.C. At $x = 0$, $c_{i,m} = c_{i}^{in}$ (6.15b)
Equations (6.8) through (6.15) have been non-dimensionalized for use in the model and are found in Appendix A.2.

6.4. Results and Discussion.

6.4.1. Determination of the Amount of NO\textsubscript{x} Stored on the Catalysts.

One of the main features of the model employed to predict the NH\textsubscript{3} selectivity during regeneration of the LNT catalyst used in the experimental study was that regeneration commenced at the point of NO\textsubscript{x} storage at the Ba sites. This point in the lean storage phase not only needed to be repeatable but also comparable across different catalysts. As was shown by Easterling et al., the oxygen storage capacity (OSC) and NO\textsubscript{x} storage capacity (NSC) vary from one catalyst to another and these properties influence the selectivity of the N-species formed during the rich phase [47].

After several initial storage and regeneration experiments, a linear relationship became apparent between the time of the storage phase and the amount of NO\textsubscript{x} stored on the catalyst. All of the NO\textsubscript{x} stored was assumed to be in the form of nitrates for the purpose of the storage calculation and in the development of the model. As the length of the storage time and hence the amount of NO\textsubscript{x} storage increased, the relationship between time and storage gradually changed from linear to a curved resembling an exponential as shown in Fig. 6.3.
Figure 6.3. Transition from a linear to exponential relationship occurring during NOx storage on the B-225 DG catalyst. Feed gas: 500 ppm NO, 5% O2, bal Ar at 200 °C.

Additionally, it became apparent that the regeneration of the LNT with NOx storage up to this change from a linear to an exponential relationship was easily repeatable with regards to the time required to reach a subsequent specified level of NOx storage. After this transition point, the repeatability of using the same storage time across multiple experimental runs decreased. It was postulated that the change in the slope of these curves was due to NOx storage switching from easily accessible sites to bulk storage sites. The existence of multiple storage sites has been presented in the literature by several groups [46,49,70-75]. The consensus concerning the bulk storage sites is that these sites require longer and deeper purges to be regenerated. As observed in storage and regeneration trials, the level of regeneration would vary from one experiment to another, which would in turn affect the time required to reach a level of NOx storage. Based on the existence of this transition point, the amount of NOx storage for each sample was chosen to be the time required to reach the limit where the storage capacity of the easily accessible or surface sites was reached. This selection of the fixed storage amount was also in line with the assumption utilized in the model that the BaO sites exist as a monolayer on the Al2O3 surface [66].
The amounts of NO\textsubscript{x} storage selected for the degreened and aged Pt/Rh/Ba/Al\textsubscript{2}O\textsubscript{3} catalysts are provided in Table 6.2. The difference in storage capacity between these two catalysts is reflected in the greater amount of NO\textsubscript{x} stored in the degreened catalyst as compared to the aged one. This result is expected since the NSC of a catalyst is reduced after aging due to phase separation between the Pt crystallites and Ba storage phase. As discussed previously and reported in the literature, a close proximity of Pt and Ba is required for efficient NO\textsubscript{x} storage in the form of the spillover mechanism [35,39,46,47,51,71,73,76-94]. As a LNT undergoes aging, sintering of the Pt particles occurs, resulting in the growth of the crystallites and decrease in dispersion. Larger crystallites and lower dispersion results in an increase in phase segregation and decrease in proximity of the Pt and Ba, the storage capacity is reduced. This effect can be illustrated using the concept of different zones existing along the length of the catalyst as reported in the literature [35,46,47,95-99]. As these researchers proposed, upon aging, the NO\textsubscript{x} storage zone in the catalyst extends further along the length of the catalyst due to fewer Pt sites existing per length of catalyst. In other words, a greater length of catalyst is now required to store an equal amount of NO\textsubscript{x} in an aged LNT as compared to a degreened one.

Table 6.2. Amount of NO\textsubscript{x} for each of catalysts.

<table>
<thead>
<tr>
<th>Catalyst Condition</th>
<th>Temperature, °C</th>
<th>Amount of NO\textsubscript{x} stored, mol NO\textsubscript{x} / g washcoat</th>
<th>Storage Time, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-225 DEG</td>
<td>200</td>
<td>3.36 x 10\textsuperscript{-4}</td>
<td>229</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>3.36 x 10\textsuperscript{-4}</td>
<td>255</td>
</tr>
<tr>
<td>AD</td>
<td>200</td>
<td>2.47 x 10\textsuperscript{-4}</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>2.47 x 10\textsuperscript{-4}</td>
<td>150</td>
</tr>
</tbody>
</table>

Another trend visible in Table 6.2 is the effect of temperature on storage time. For the two temperatures chosen, 200 and 300 °C, it took less time to reach the fixed level of storage at the lower temperature. At first this result seemed unexpected based on the reasoning that the time needed to reach a fixed amount at the higher temperature should be less than the time needed at the lower temperature due to the kinetics of NO\textsubscript{x} oxidation being faster at higher temperatures. While the kinetics at 300 °C were faster as evidenced
by the increased amount of NO₂ detected (data not shown), it is not meaningful to compare storage times because the storage capacities are different.

6.4.2 Experimental Results: NH₃, N₂O, H₂.

6.4.2.1 B-225 DG.
As mentioned in the Introduction, the ratio of H:N:O species at the Pt sites affects the products formed during regeneration of the LNT catalyst. As a reminder, low H₂:NOₓ ratios favor N₂O formation, and high H₂:NOₓ ratios favor NH₃ formation [35-40]. An idea of the value of this ratio at any time during regeneration is provided by comparing the time required for the products (e.g., NH₃ and N₂O) and the reductants (e.g., H₂) to emerge from the catalyst outlet. Looking at Fig. 6.4, these trends are presented. The time originates at the transition from lean to rich conditions. In Fig. 6.4a, N₂O is present almost immediately in the reactor effluent. This almost instantaneous formation of N₂O is explained by examining the conditions that must be present on the catalyst surface for N₂O production. According to Lietti [100], N₂O is produced either by:

\begin{align*}
2 \text{NO (absorbed)} & \leftrightarrow \text{N}_2\text{O (g) + O (adsorbed)} \quad (6.10) \\
\text{NH}_x \text{ (adsorbed) + NO (adsorbed)} & \leftrightarrow \text{N}_2\text{O (g) + x H (adsorbed)} \quad (6.11)
\end{align*}
Figure 6.4. Relationship between the break-through times of H₂, NH₃, and N₂O for: a) B-225 DG at 200 °C, b) B-225 DG at 300 °C, c) B-225 AD at 200 °C, and d) B-225 AD at 300 °C.

Considering that Xu et al. [38] stated that low H₂:NOₓ ratios favor N₂O production, and there exists for the B-225 catalyst at 200 °C over a 60 s delay after N₂O release and before NH₃ release is present, the first reaction is more likely to occur at the lean to rich transition. As Choi et al. recently reported [97], the criteria for NOₓ release from the Ba sites back to the Pt crystallites and from the Ba sites located far from Pt is a net deficit of oxygen present in the monolith at a particular point.

As reported by many groups [35,36,38,40-46], a reductant front is present at the beginning of the rich phase at the front of the catalyst monolith. H₂ consumes any residual oxygen present in the gas stream as well as any oxygen chemisorbed on the catalyst surface. By consuming the oxygen present, the environment becomes oxygen deficient and NOₓ release begins. N₂O is favored at the leading edge of the front since
any H\textsubscript{2} present reacts with either stored oxygen or NO\textsubscript{x}. N\textsubscript{2}O production continues until enough H\textsubscript{2} is present in the reductant front to increase the H\textsubscript{2}:NO\textsubscript{x} ratio to levels that favor NH\textsubscript{3} (2.5) [38,40]. Because the hydrogen is consumed at the leading edge of the front, N-species such as N\textsubscript{2}O and unreacted NO and NO\textsubscript{2} are capable of traveling downstream in the monolith. The N\textsubscript{2}O passes through unreacted while NO and NO\textsubscript{2} can be readorsorbed at sites located further along the axis of the monolith.

Eventually, as the regeneration phase continues, the chemisorbed oxygen at the Pt sites is consumed and the amount of hydrogen present at the Pt/Ba interface increases. The actual amount of hydrogen present at this time is dependent on the rate of diffusion of NO\textsubscript{x} from Ba to the Pt sites. At 200 °C, the kinetics of the following reaction is slow enough that the rate of diffusion is controlling:

\[
\text{Ba(NO}_3\text{)}_2 + 8 \text{H}_2 \leftrightarrow 2 \text{NH}_3 + \text{BaO} + 5 \text{H}_2\text{O} \quad (6.12)
\]

The delay between H\textsubscript{2} and NH\textsubscript{3} in the effluent as shown in Fig 6.4a supports the necessity of a high ratio of H\textsubscript{2}:NO\textsubscript{x} for NH\textsubscript{3} production [35-40]. Before NH\textsubscript{3} reaches the effluent, NO\textsubscript{x} stored downstream in the catalyst must be consumed or NH\textsubscript{3} will react with NO\textsubscript{x} as follows:

\[
\text{Ba(NO}_3\text{)}_2 + \frac{10}{3} \text{NH}_3 \leftrightarrow \frac{8}{3} \text{N}_2 + \text{BaO} + 5 \text{H}_2\text{O} \quad (6.13)
\]

The yield and the selectivity of NH\textsubscript{3} increases along the length of the catalyst as shown in Fig. 6.5, because as one moves downstream, less NO\textsubscript{x} is available to react with NH\textsubscript{3} [35,36,41,57,101-103].
Figure 6.5. Comparison of yield and selectivity for B-225 DG and AD catalysts. a) NH₃ Yield, %, b) N₂O Yield, %, c) NH₃ Selectivity, %, d) N₂O Selectivity.

Using the assumption that NOₓ is stored as a monolayer and considering the results of the NOₓ storage during the lean phase in Fig 6.3, it is evident that the entire length of LNT is involved in NOₓ storage. This situation is different than the experiments reported by Easterling et al. [47] where for the degreened B-225 catalyst, only the front portion of the catalyst was used for NOₓ storage. As reported for that experiment, the maximum in NH₃ selectivity occurred after the NOₓ storage zone. This spatial relationship is present again in these experiments except the NOₓ storage zone encompasses the entire length of the catalyst.

When the temperature of the experiment is increased to 300 °C, the controlling regime during regeneration changes from diffusion to H₂ feed limited. By noticing the greater time lag before H₂ appears in the effluent at 300 °C in Figure 6.4a compared to 200 °C in Figure 6.4b, this transition between control regimes becomes apparent. N₂O again
appears shortly after the switch to rich conditions, but at 300 °C the length of time for which N₂O is present in the effluent is much shorter than at 200 °C. The production of N₂O continues until H₂ begins to be present at 200 °C, while at 300 °C, N₂O production ends well before H₂ is observed. The conditions that are favorable to N₂O exist for a shorter time in this case (H₂:NOₓ < 1) [38,40]. Additionally, as reported in the literature [36,39,41,42,46] lower temperatures (T < 200 °C) are more favorable for N₂O production. As the amount of H₂ present at the Pt/Ba interface increases, N₂ is produced until the ratio is great enough to favor NH₃. The production of N₂ has been reported by [39,41] to be favored at a ratio of H₂:NOₓ equal to ~1.

6.4.2.2. B-225 AD.
Although a direct comparison between the degreened and aged catalysts cannot be made since the amount of NOₓ stored was not the same, the following remarks are applicable. Aging of the catalyst results in less Pt crystallites per length of catalyst (lower dispersion) with a larger particle diameter. In terms of the rate at which the reduction front propagates, after the catalyst has been aged, the H₂ front propagates along the length of the catalyst faster than the rate observed with the degreened catalyst. This increased rate of travel is shown in Fig. 6.4c where H₂ breakthrough is observed ~15 s quicker for the aged catalyst than for the degreened catalyst shown in Fig. 6.4a. Because there are fewer Pt crystallites, less chemisorbed oxygen and less stored NOₓ is present per length of the catalyst to consume the H₂ in the reduction front as it travels along the catalyst.

The other effect of sintering is apparent in the yield and selectivity of NH₃ and N₂O in Fig 6.5. Although twice as much NOₓ was stored on the degreened catalyst as compared to the aged catalyst (Table 6.2), the NH₃ yield and selectivity are much greater for the aged catalyst than for the degreened catalyst. Additionally, the time between H₂ and NH₃ breakthrough is decreased for the aged catalysts. With fewer sites per length of catalyst, the stored NOₓ at the Ba sites must travel farther to reach the Pt sites during regeneration. Although the intrinsic rate of diffusion is the same, the increased distance results in an increase in diffusion time. By the time the NOₓ reaches the Pt sites, the ratio of H₂:NOₓ is expected to be higher and at a value that favors NH₃ formation. Also contributing to
NH$_3$ selectivity is the possibility of reduced rates of NO$_x$-NH$_3$ SCR and NH$_3$-O$_2$ reactions after aging [39]. If these rates of reaction are significantly reduced, the probability of NH$_3$ consumption downstream in the catalyst by these reactions increases, and therefore leads to increased NH$_3$ concentrations in the effluent from the monolith.

6.4.3 Modeling Results.
The main focus of this work was to determine the ability of a model developed by Bhatia et al. [44] to predict the NH$_3$ selectivity of LNT catalysts that included Rh. Another variation between this study and the study by Bhatia et al. is the amount of fixed NO$_x$ stored on each catalyst and the residence time in the catalyst. As reported by Easterling et al. [47], the NO$_x$ storage capacity and oxygen storage capacity varies between degreened and aged catalysts. Whereas Bhatia et al. and Clayton et al. [44,46] varied Pt dispersion by adjusting the Pt loading of the catalysts, the dispersions in this experiment were varied by exposing the catalysts to aging conditions which which sintering of the Pt occurred. The residence time in the catalyst was adjusted by using a GHSV of 30,000 h$^{-1}$ instead of 60,000 h$^{-1}$. This adjustment in GHSV is instructive in modeling the regeneration events since the residence time will vary in real world applications as the engine operates under various loads.

6.4.3.1 Model vs. Experimental Results: B-225 DG.
Simulations using the dispersion model were performed to predict the NH$_3$ production during regeneration of the two catalysts after a fixed level of NO$_x$ was stored. Table 6.3 lists the parameters used to fit the data. The only variation in parameters from the values used by Bhatia et al. [44] was the surface diffusivity of NO$_x$, $D_A$, traveling from Ba to the Pt sites. Since the model is based on PGM dispersion, the parameters that have the most impact on the model data are $D_A$ and the measured value of the PGM dispersion. While Bhatia used values of 5x10$^{-19}$ m$^2$/s and 5x10$^{-18}$ m$^2$/s for $D_A$ at 160 °C and 230 °C, respectively, a value of 9x10$^{-18}$ m$^2$/s was used for 200 °C. As mentioned in the experimental section, values for $D_A$ are not available in the literature.
Table 6.3 a. Values of $N_c$, $R_c$, and $R_{\text{eff}}$ for various Pt dispersions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt Dispersion (%)</th>
<th>$N_c$</th>
<th>$R_c$ (m)</th>
<th>$R_{\text{eff}}$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-225 Degreened</td>
<td>15.6</td>
<td>$2.95 \times 10^{14}$</td>
<td>$2.22 \times 10^{-9}$</td>
<td>$1.77 \times 10^{-8}$</td>
</tr>
<tr>
<td>B-225 Aged</td>
<td>3.34</td>
<td>$2.95 \times 10^{14}$</td>
<td>$1.03 \times 10^{-8}$</td>
<td>$1.32 \times 10^{-7}$</td>
</tr>
<tr>
<td>B-225 Aged*</td>
<td>15.5</td>
<td>$1.02 \times 10^{14}$</td>
<td>$2.23 \times 10^{-9}$</td>
<td>$2.24 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

* Using the physical properties of Rh instead of Pt (see section 6.4.3.2. for explanation)

Table 6.3 b. Parameter values to estimate $N_c$ and $R_{\text{eff}}$.

<table>
<thead>
<tr>
<th>Pt</th>
<th>A$_{PF}$</th>
<th>$D_{Pt}$ (m)</th>
<th>$M_{PtT}$ (mol/channel)</th>
<th>$n_{ch}$</th>
<th>$N_{av}$</th>
<th>$S_{BaO}$ (BaO molecules/m$^2$ exposed BaO)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$2.78 \times 10^{-10}$</td>
<td>$7.42 \times 10^{-7}$</td>
<td>125</td>
<td>$6.022 \times 10^{23}$</td>
<td>$1.89 \times 10^{18}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rh</th>
<th>A$_{PF}$</th>
<th>$D_{Rh}$ (m)</th>
<th>$M_{RhT}$ (mol/channel)</th>
<th>$n_{ch}$</th>
<th>$N_{av}$</th>
<th>$S_{BaO}$ (BaO molecules/m$^2$ exposed BaO)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$2.70 \times 10^{-10}$</td>
<td>$2.81 \times 10^{-7}$</td>
<td>125</td>
<td>$6.022 \times 10^{23}$</td>
<td>$1.89 \times 10^{18}$</td>
</tr>
</tbody>
</table>

Table 6.3 c. Variation of $M_{NOx}$ (mol) with monolith length, assuming uniform, axial NO$_x$ storage.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>25.4 mm</th>
<th>16.4 mm</th>
<th>8.4 mm</th>
<th>4.4 mm</th>
<th>0.0 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-225 Degreened</td>
<td>2.26 x 10^{-4}</td>
<td>1.46 x 10^{-4}</td>
<td>7.46 x 10^{-5}</td>
<td>3.91 x 10^{-5}</td>
<td>8.89 x 10^{-6}</td>
</tr>
<tr>
<td>B-225 Aged</td>
<td>2.26 x 10^{-4}</td>
<td>8.07 x 10^{-5}</td>
<td>4.13 x 10^{-5}</td>
<td>2.17 x 10^{-5}</td>
<td>4.92 x 10^{-6}</td>
</tr>
</tbody>
</table>

The comparisons of the experimental and model predicted data for the B-225 DG catalyst at 200 °C are shown in Fig 6.6a and b. The quality of the fit of the model was judged by comparing the spatiotemporal data as well as the relative amounts of NH$_3$ measured at each of the positions along the length of the catalyst. With these parameters (Table 6.3), the fit of the data with respect to time from the beginning of regeneration was reasonable. The model captures the delay before the onset of NH$_3$ at each of the positions. At the front of the catalyst, a value of 0.1 mm was used in the calculations for the parameters to ensure that the capillary was in a channel. Both sets of data show an increase in NH$_3$ concentrations from the front position to the remaining locations. As previously reported
[47], the decrease in NH₃ concentration at the rear position (25.4 mm) was most likely due to a slight over-sampling present in the experimental setup.

Considering the maximum values of the NH₃ concentrations attained, the model over-predicted the values. As stated previously, the model assumes that NH₃ does not readсорb downstream on the catalyst surface. In order to provide a better fit of the data, the values for the reaction rates were systematically varied. The result of this effort was that the peak values for NH₃ were decreased while changing the shape of the curve from a sharp peak to more rounded curve when the reaction rate constant of NH₃ generation from the reduction of NOₓ with H₂ was changed from 1x10⁻³ m⁴/mol*s to 1x10⁻⁵ m⁴/mol*s as shown in Fig. 6.7b. Lastly, it is apparent that a tailing effect is present in the NH₃ measurements. This tailing is due to the polarity displayed by NH₃ in the capillary. Although steps were taken to minimize this effect by using resistance heating to keep the temperature of the capillary high from inside the catalyst to the sample cell of the mass spectrometer, there is always a slight hold up of NH₃ in this type of measurement.

![Graphs showing NH₃ concentration over time at different positions](image)

**Figure 6.6.** Comparison between the a) experimental data and b) model predicted data for the B-225 DG catalyst at 200 °C.

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Figure 6.7. Comparison between the a) experimental data and b) model predicted data for the B-225 DG catalyst at 200 °C with $k_1 = 1 \times 10^{-5}$ m$^4$/mol*s instead of $1 \times 10^{-3}$ m$^4$/mol*s.

When the model was used to generate the NH$_3$ data at 300 °C, a different regime controlled the NH$_3$ selectivity. Whereas the process was diffusion controlled at 200 °C, the process is H$_2$ feed-limited at 300 °C. A value of $9 \times 10^{-17}$ m$^2$/s was used for $D_A$ at 300 °C since the model increases the diffusivity by an order of magnitude for every 100 °C temperature increase. This value of $D_A$ is almost the same as the value used by Bhatia at 300 °C, $5 \times 10^{-17}$ m$^2$/s [44]. The experimental and model data are shown in Fig. 6.8a and b.

While the peak concentrations in the model data are close to experimental values, the delay before the onset of NH$_3$ release into the gas stream is overestimated in the data provided by the model. The experimental data at 300 °C displays a sharper peak shape than the 200 °C data, and this characteristic is captured in the model data at 300 °C. The differences between a situation where NO$_x$ diffusion is controlling and one limited by the rate H$_2$ is fed to process become more visible at the measurement locations further along the length of the catalyst. At all of the locations in the experimental data, NH$_3$ release begins less than 100 s after conditions are changed to rich. However, for the model the NH$_3$ release for the 16.4 mm and 25.4 mm positions does not begin until after 100 s.
Figure 6.8. Comparison between the a) experimental data and b) model predicted data for the B-225 DG catalyst at 300 °C.

For consistency, the data were also generated using a value for $k_1$ of $1 \times 10^{-5} \text{ m}^4/\text{mol}*\text{s}$, the results being presented in Fig. 6.9a and b. This parameter adjustment did not provide an improvement in the predicted model data. The result of this change was a decrease in the peak NH$_3$ concentration. Although the reaction rate constants do not compensate for temperature in the model, based on the fits displayed in Fig. 6.7 and 6.8, a case can be made that $k_1$ does vary with the temperature from 200 °C to 300 °C. This change in rate constant could also be accounting for a process which was not accounted for by the model, i.e., NH$_3$ readsortion.

Figure 6.9. Comparison between the a) experimental data and b) model predicted data for the B-225 DG catalyst at 300 °C with $k_1 = 1 \times 10^{-5}$ instead of $1 \times 10^{-3}$. 
6.4.3.2. Model vs. Experimental Results: B-225 AD.

As discussed for the experimental data, the most prevalent change that occurs with a catalyst that has undergone aging is the reduction in the time or delay before NH$_3$ release is measured at the positions along the length of the catalyst. Using the parameters listed in Table 6.4, a comparison was made between the experimental and model data for aged B-225 catalyst at 200 °C (see Fig. 6.10a and b). The average radius of the Pt crystallites and the average radius of stored NO$_x$ around the crystallite both increased as expected after aging. The reduced lag before NH$_3$ release occurs in the aged catalyst compared to the degreened catalyst is captured by the model. Additionally, the shape of the NH$_3$ curves (sharp peaks) is also captured in the model data. However, a problem exists concerning the parameters used to predict this set of data. As mentioned earlier, the dispersion and the diffusivity values are the parameters that have the greatest effect on the data predicted by the model. Using a D$_A$ value of 9x10$^{-18}$ m$^2$/s as with the degreened data generates data that do not agree with the experimental data. The flaw in the model data set is that all of the onset of NH$_3$ releases occur at the instant conditions are switched from lean to rich in the catalyst. Although this delay is reduced after the catalyst is aged, nevertheless, a delay still exists in the experimental data for this case.

Figure 6.10. Comparison between the a) experimental data and b) model predicted data for the B-225 AD catalyst at 200 °C with D$_A$ = 9 x10$^{-18}$ m$^2$/s.
To obtain a better fit of the data, $D_A$ was increased to $9 \times 10^{-16}$ m$^2$/s, and this comparison is shown in Fig. 6.11a and b. While an improved fit is obtained from changing the value for $D_A$, an increase in the diffusivity is counter intuitive for aged catalysts since the sintering should result in phase segregation between Pt and Ba species.

**Figure 6.11.** Comparison between the a) experimental data and b) model predicted data for the B-225 AD catalyst at 200 °C with with $D_A = 9 \times 10^{-16}$ m$^2$/s.

As a way to provide a better fit, the parameters used in the model for the aged catalyst were calculated using Rh instead of Pt. When Rh is used in a Pt/Rh alloy, catalysts have been reported to be more resistant to sintering [63]. Moreover, as discussed earlier, Rh is less prone to sintering than Pt in the first place, due to the lower vapor pressure of both the metal and the oxide, as compared to Pt [64]. In addition, Rh has been reported to be a more effective reduction catalyst than Pt [59,60]. Hence, it is reasonable to assume that after aging, Rh/Pt particles are primarily responsible for the NO$_x$ reduction activity of the catalyst. For this set of generated data, the dispersion of PGM was adjusted so that the radii of the crystallites using properties of Rh were equal to the values using Pt.

With the value of $D_A$ again at $9 \times 10^{-18}$ m$^2$/s, Fig. 6.12a and b shows the comparison between experimental and model data for B-225 AD at 200 °C. The changes in the parameters involved in the model are displayed in Table 6.4a and b. The result of using Rh to predict the properties of the PGM crystallites is an improved fit of the data with regards to both the delay before the onset, peak concentration, and shape of the release curves of NH$_3$. For the experimental data, almost no delay exists for the beginning of
NH$_3$ release at the 0.0 mm, 4.4 mm, and 8.4 mm positions. As discussed, this is an expected result of a decrease in PGM dispersion due to sintering. Fewer crystallites per unit length of catalyst lead to an increase in the rate of propagation of the H$_2$ front in the catalyst. This increase also decreases the time required for H$_2$:NO$_x$ ratios to reach levels that favor NH$_3$ selectivity. However, the model fails to capture the decrease in maxima of NH$_3$ observed at the 16.4 mm and 25.4 mm positions. Although the decrease at 25.4 mm may be attributed to the method of sampling the gas species within the channel of the monolith using SpaciMS, the decrease observed at 16.4 mm leads one to conclude either that the NH$_3$ is readsoerbred on the catalyst surface or consumed by NO$_x$ downstream in the catalyst.

Figure 6.12. Comparison between the a) experimental data and b) model predicted data for the B-225 AD catalyst at 200 °C.

The same shortcomings exist in using Pt crystallites parameters for the modeling at 300 °C as at 200 °C. Again Rh was used for parameter evaluation for this data set as shown in Fig. 6.13a and b. Although this correction does provide an improved fit in terms of the spatiotemporal nature of the data, as with the degreened catalyst at 300 °C, the data from the model fails to capture all of the characteristics of the experimental data such as shape of the curves and maximum concentrations. This shortcoming is again the result of the process becoming H$_2$ feed limited at the higher temperature.
Figure 6.13. Comparison between the a) experimental data and b) model predicted data for the B-225 AD catalyst at 300 °C.

An intriguing feature of the comparison between the degreened and aged data concerns the maximum concentration of NH₃ measured at any of the points along the catalyst. Whereas the model did predict lower NH₃ levels at 200 °C than at 300 °C (Fig 6.12 and Fig 6.13) as seen for the experimental aged data, this was not the case for the degreened data (Fig 6.6 and 6.7). The model predicted a higher, maximum concentration of NH₃ for the 200 °C data as compared to the data at 300 °C, whereas the experimental data possessed the opposite trend. In fact, the slight increase selectivity as suggested by the peak NH₃ concentrations in the experimental data for the higher temperature is in agreement with the findings as reported by Bhatia et al. and Clayton et al. [44,46]. If the degreened catalyst is compared to the results Bhatia and Clayton reported for their 8% dispersion catalyst, the experimental data presented here is agreement with their results that NH₃ release increases with increasing temperature to 300 °C, while the model data presented here is contrary to their results. Similarly, if the aged data presented here is compared to Bhatia and Clayton’s data for the 3% dispersion catalyst, the trends in the experimental and model predicted data agree with their trends for the low dispersion catalyst that net NH₃ increases with increasing temperature. The slight increase in the experimental data for the higher temperature is contrary to the expected trends based on LNT catalysts usually displaying increased selectivity to NH₃ at temperatures below 250 °C.
6.5. Conclusions.
The crystallite-scale model developed by Bhatia [44] has been employed to predict the selectivity of NH$_3$ in experiments in which degreened and aged Pt/Rh/Ba/Al$_2$O$_3$ LNT catalysts underwent regeneration after a fixed amount of NO$_x$ was stored. Experiments included two catalysts at two different temperatures, whose PGM dispersions were varied by subjecting one of the catalysts to aging under lean conditions at elevated temperatures. The results from the experiments were consistent with the species observed during regeneration being a function of the PGM dispersion and the ratio of H$_2$:NO$_x$ at the Pt/Ba interface. As reported in the literature [35,38,41-47], a reductant front travels down the length of the catalyst during regeneration in which the ratio of reductant to stored NO$_x$ varies based on time and position. N$_2$O is favored at low ratios of H$_2$:NO$_x$ (at the leading edge of the front) and NH$_3$ is favored at higher ratios of H$_2$:NO$_x$ (behind the reduction front).

The modeling results indicated the use of a diffusion-based model with temperature dependent diffusivities is capable of capturing the spatiotemporal trends associated with NH$_3$ release from the LNT at low temperatures and high dispersions. The model accurately predicted the individual delay at each position before the onset of NH$_3$ release. The model was also able to predict these trends for the aged data after the parameters were adjusted using the values for the physical properties of Rh instead of Pt. This change was justified not only by the results, but also by the fact that Rh is a superior reduction catalyst and more resilient to sintering that Pt; hence, Rh is expected to be the main catalytic species active in the reduction of NO$_x$ in the aged catalyst, particularly at lower temperatures (e.g. 200 °C).

Further refinement of the model is required to account for the over prediction of the amounts of NH$_3$ measured at each location for two catalysts. The increased amounts of NH$_3$ predicted by the model are most likely due to a combination of the lack of accounting for NH$_3$ readsorption on the catalyst after it is released, and the assumption of a uniform storage of NO$_x$ along the length of the catalyst. An improved storage model that could capture the gradients in the amount of NO$_x$ stored from the front to the rear of
the monolith would be valuable to predict the phenomena observed during regeneration. Lastly, if a SpaciMS study were performed in which the amounts of reductant present at each measurement location were measured, it would be beneficial in providing insight into the conditions influencing NH₃ selectivity.
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Chapter 7. Significant Findings and Recommendations for Future Work.

The purpose of this dissertation was to determine the effects of ceria addition on the aging and sulfation characteristics of LNT catalysts for stand-alone and LNT-SCR applications. The methodology for achieving this goal was as follows:

- Investigation of the effects of ceria addition on LNT desulfation behavior using powder catalysts and fully formulated monolithic LNT catalysts.
- Elucidation of the effect of washcoat composition on LNT aging characteristics, employing fully formulated monolithic LNT catalysts containing varying amounts of Pt, Rh, and BaO after subjecting to accelerated aging on a bench reactor.
- Employment of SpaciMS to understand the factors influencing the selectivity of NOx reduction in two fully formulated LNT catalysts, both degreened and thermally aged.
- Application of a model to predict experimental SpaciMS data pertaining to NH3 selectivity during regeneration of degreened and aged LNT catalysts possessing fixed NOx storage amounts that approximated complete surface storage.

The impetus for this research was provided by the demands of consumers and auto makers alike for improved fuel economy from lean burn engines, while attaining reduced exhaust emissions, particularly NOx (NO + NO2).

7.1. Significant Findings.

7.1.1. Effect of Ceria on the Desulfation Characteristics of Model Lean NOx Trap Catalysts.

- Ceria can function as a sulfur sink in LNT catalysts, thereby helping to protect the main Ba NOx storage phase from sulfation.
- Pt and Ba proximity: when Pt and Ba are physically separated, the desulfation temperature of the surface BaSO4 is shifted by 20-40 °C towards higher temperature, i.e., towards the position characteristic of bulk BaSO4.
- Addition of La-stabilized CeO2 or CeO2-ZrO2:
- Greater resistance to deactivation during sulfation (as reflected by the NO\textsubscript{x} storage efficiency)
- Required lower temperatures to restore the NO\textsubscript{x} storage efficiency to its pre-sulfation value.

- Precious metal loadings can significantly impact desulfation efficiency, both high Rh and Pt loadings being beneficial for catalyst desulfation.

7.1.2. Effect of Aging on the NO\textsubscript{x} Storage and Regeneration Characteristics of Fully Formulated Lean NO\textsubscript{x} Trap Catalysts.

- According to H\textsubscript{2} chemisorption and TEM data, Pt sintering occurred and resulted in decreased contact between the Pt and Ba phases, this contributed to decreased first cycle NSE due to less efficient NO\textsubscript{x} spillover from Pt to Ba during NO\textsubscript{x} adsorption.

- TEM and XRD data indicate the accumulation of sulfur in the washcoat, present as BaSO\textsubscript{4} (30\% of the Ba present) providing an additional explanation for the loss in initial and cycle-averaged NSE after catalyst aging.

- Given the importance of the Pt-Ba interface, it follows that high Pt loadings are beneficial for catalyst performance since they provide one means of ensuring a high degree of Pt-Ba contact.

7.1.3. Application of SpaciMS to the Study of Ammonia Formation in Lean NO\textsubscript{x} Trap Catalysts.

- Losses in surface area, accompanied by segregation of the Pt/Rh sites and BaO storage sites, account for the decreased NO\textsubscript{x} storage efficiency of the aged catalysts.

- During lean phase NO\textsubscript{x} storage on aged catalysts, NO and NO\textsubscript{2} were required to travel further to reach storage sites due to the decreased storage site concentration. Consequently, after aging the NO\textsubscript{x} storage-reduction zone was elongated.
  - Stretching of the NSR zone results in an increase of the NO\textsubscript{x} “puff” that appears during the onset of the rich front as it travels along the length of the catalyst.
o Since NO\textsubscript{x} release from the catalyst tracks the NSR zone, for an aged catalyst the NO\textsubscript{x} concentration peaks closer to the rear of the catalyst; hence, the probability that NO\textsubscript{x} can re-adsorb downstream of the reduction front and subsequently undergo reduction by NH\textsubscript{3} is diminished, and consequently the NO\textsubscript{x} emission is higher.

o Stretching of the NSR zone causes the NH\textsubscript{3} selectivity of an aged catalyst to increase.

- Loss of OSC and NO\textsubscript{x} storage sites leads to an increase in the rate of propagation of the reductant front in the aged catalyst compared to the degreened catalyst.
- NO\textsubscript{x} is released more slowly from storage sites (due to Pt-Ba phase segregation), such that for the aged catalysts the kinetics of NO\textsubscript{x} reduction are controlled by the rate of NO\textsubscript{x} diffusion to the Pt sites (rather than being feed limited).

7.1.4. An Investigation into the Validity of a Crystallite-Scale Model to Predict the NH\textsubscript{3} Regeneration of a Pt/Rh/BaO/Al\textsubscript{2}O\textsubscript{3} Lean NO\textsubscript{x} Trap Catalyst.

- Results from the experiments were consistent with the species observed during regeneration being a function of the PGM dispersion and the ratio of H\textsubscript{2}:NO\textsubscript{x} at the Pt/Ba interface.
- N\textsubscript{2}O is favored at low ratios of H\textsubscript{2}:NO\textsubscript{x} (at the leading edge of the front) and NH\textsubscript{3} is favored at higher ratios of H\textsubscript{2}:NO\textsubscript{x} (behind the reduction front).
- Modeling results indicated the use of a diffusion-based model with temperature dependent diffusivities is capable of capturing the spatiotemporal trends associated with NH\textsubscript{3} release from the LNT at low temperatures and high dispersions.
- The model accurately predicted the individual delay at each position before the onset of NH\textsubscript{3} release.
- The model was also able to predict these trends for the aged data after the parameters were adjusted using the values for the physical properties of Rh instead of Pt.

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7.2 Suggestions for Future Research.

Although the work presented in this study of LNT catalysts as a capable technology for reducing NO\textsubscript{x} and NH\textsubscript{3} emissions (while delivering increased fuel economy resulting from the use of lean-burn engines compared to stoichiometric engines), several challenges will influence the penetration of LNT technology into the marketplace. As engines become more efficient, the resulting exhaust temperatures become cooler. In typical lean burn applications, exhaust temperatures are generally in the temperature range of 150 to 400 °C. The next generation of engines currently under development for real world use possesses exhaust temperatures as low as 100 °C. Exhaust temperatures lower than 200 °C are problematic since the activity of the PGMs are significantly reduced in regards to NO\textsubscript{x} oxidation during storage and NO\textsubscript{x} reduction to NH\textsubscript{3} and N\textsubscript{2} during catalyst regeneration. Catalyst materials besides traditional Pt, Rh, and Pd must be developed to meet this demand.

It has become apparent from the data gathered using the SpaciMS that a need exists for the capability to measure reductants in addition to the products generated from NO\textsubscript{x} reduction. For the successful implementation of an LNT-SCR system, NH\textsubscript{3} production must be tuned to the amount of NO\textsubscript{x} that slips form the LNT to the SCR catalyst. Since NH\textsubscript{3} selectivity is a function of the relative amounts of H\textsubscript{2}:NO\textsubscript{x} present at the PGM sites, the H\textsubscript{2} concentration would be an effective measurement tool in determining the H\textsubscript{2}:NO\textsubscript{x} ratios present at different locations in the catalyst rather than just measuring the N-species present (i.e., N\textsubscript{2}, NH\textsubscript{3}, and N\textsubscript{2}O). Additionally, the capability to measure H\textsubscript{2} is advantageous because H\textsubscript{2} is produced from hydrocarbons and CO during regeneration due to steam reforming and the water gas-shift reaction. An ideal SpaciMS apparatus would have the ability to measure NO\textsubscript{x} storage and regeneration with both low (NO, NO\textsubscript{2}, O\textsubscript{2}, CO, CO\textsubscript{2}, H\textsubscript{2}O) and medium (N\textsubscript{2}O, N\textsubscript{2}, O\textsubscript{2}) energy sources while simultaneously measuring H\textsubscript{2} concentrations. A system with three capillary probes attached to two chemical ionization mass spectrometers and one electron pulse ionization mass spectrometer would be able to accomplish this aim.
In regards to modeling the storage and reduction processes, the following improvements would provide a better predictive capability in LNT-SCR design. One of the assumptions used in predicting the NH₃ selectivity during regeneration from a LNT with a fixed amount of NOₓ stored was an assumed value for the diffusivity of NOₓ stored on the surface of the catalyst. While this value was adjusted with temperature, the discussion in Chapter 6 demonstrated that unaccounted processes such as NH₃ readesorption most likely occur during regeneration. Additional complications arise during aging when sintering of the PGM component occurs, resulting in changes in the diffusion of NOₓ.

Another assumption was that NOₓ was stored uniformly along the axis of the monolith catalyst. While a uniform distribution of stored NOₓ would provide a beneficial, desired proximity to PGMs essential for efficient NOₓ storage and reduction, this situation does not exist on the surface of the LNT catalyst, especially after aging. As mentioned in the preceding discussion, the distribution of the various catalyst components determines the surface area of Pt/Ba proximity which in turns governs NOₓ storage gradients, the rate of the propagation of the reductant front during regeneration, and ultimately the selectivity of the various N-species produced during regeneration of the LNT catalyst. A model capable of predicting the chromatographic-like nature of NOₓ storage existing on the surface would attain a better fit of the experimental data.
Appendix A.1. Nomenclature.

1/1 cycles: One min lean periods to one min rich periods.
5/3 cycles: Five min lean periods to three min rich periods.
a: Width/hydraulic diameter of the channel (m)
APF: Atomic packing factor
AD: Aged catalyst.
B-225: Catalyst sample where 225 refers to the washcoat loading in g/L.
BET: Surface measurement technique named after the last names of Stephen Brunauer, Paul Hugh Emmett, and Edward Teller.
$C_A$: Surface concentration of stored NO\textsubscript{x} (mol/m\textsuperscript{2} exposed BaO).
$C_{AD}$: Surface concentration of stored NO\textsubscript{x} before start of regeneration (mol/m\textsuperscript{2} exposed BaO).
$C_A^*$: Dimensionless concentration of stored NO\textsubscript{x}.
$C_{j\text{in}}$: Inlet concentration of species j in the fluid phase (mol/m\textsuperscript{3}).
$C_{j\text{in}}^*$: Dimensionless inlet concentration of species j in the fluid phase.
$C_{jm}$: Cup-mixing concentration of species j in the fluid phase (mol/m\textsuperscript{3}).
$C_{jm}^*$: Dimensionless cup-mixing concentration of species j in fluid phase.
$C_{j\text{wce}}$: Concentration of species j at the fluid–washcoat interface (mol/m\textsuperscript{3}).
$C_{j\text{wce}}^*$: Dimensionless concentration of species j at fluid–washcoat interface.
$c_{Pt}$: Surface concentration of Pt (moles exposed Pt/m\textsuperscript{2} exposed Pt).
CAFE: Corporate Average Fuel Economy.
CDC: Centers for Disease Control.
CI-MS: Chemical ionization mass spectrometer.
d: Diameter of monolith sample (cm).
d: Pt dispersion (%)
$D_A$: Diffusivity of stored NO\textsubscript{x} in the Ba phase (m\textsuperscript{2}/s).
$D_{jm}$: Diffusivity of species j in the fluid phase (m\textsuperscript{2}/s).
$D_{Pt}$: Diameter of a Pt atom (m).
DOC: Diesel oxidation catalysts.
DG: Degreened catalyst
DPF: Diesel particulate filter.
DRIFTS: Diffuse reflectance infrared Fourier transform spectroscopy.
EELS: Electron energy loss spectroscopy.
EIMS: Electron pulse ionization mass spectrometer.
EM: Electron microscopy.
ER: Eley-Rideal.
FTP: Federal testing procedure.
GHSV: Gas hourly space velocity (h⁻¹).
GVWR: Gross vehicle weight rating.
H*: Hydrogen species associated with Pt.
HC: Hydrocarbons.
HC-SCR: Selective catalytic reduction of NOx with hydrocarbon reductants.
HRTEM-EELS: High-resolution transmission electron microscopy-electron energy loss spectroscopy.
\( L_P \): Perimeter of Pt/Ba interface per channel (m).
\( k_1 \): Rate constant for NO\(_x\) regeneration by H\(_2\) (m\(^4\)/mol s).
\( k_2 \): Rate constant for NO\(_x\) regeneration by NH\(_3\) (m\(^4\)/mol s).
\( k_3 \): Rate constant for consumption of H\(_2\) by chemisorbed oxygen (m\(^3\)/mol s).
\( k_{c,j} \): Mass transfer coefficient of species j (m/s).
\( l \): Length of monolith sample (m).
\( L \): Length of the monolith (m).
LNT: Lean NO\(_x\) trap.
LNT-SCR: Lean NO\(_x\) trap coupled with a selective catalytic reduction catalyst.
LDDs: Light duty diesels.
\( m_{wc} \): Mass of washcoat (g).
\( M_{NO_x} \): Total moles of NO\(_x\) stored on the catalyst.
\( M_{Pt} \): Total moles of Pt in the washcoat per channel.
\( n_{ch} \): Total number of channels in the catalyst.
\( N_{av} \): Avogadro number.
\( N_c \): Number of crystallites per channel.
NPt: Number of atoms in a Pt particle.
N_Pt_s: Number of surface atoms.
N_T: Number of Pt atoms in the Pt crystallite.
NSC: NO_x storage capacity.
NSE: NO_x storage efficiency.
NO_x: Oxides of nitrogen.
NSR: NO_x storage and reduction.
O*: Oxygen species associated with Pt sites.
O*': Poorly active oxygen species.
ORNL: Oak Ridge National Laboratory.
OSC: Oxygen storage capacity.
PBA: Pt/BaO/Al_2O_3 catalyst.
PBAC: Catalyst containing Pt/BaO/Al_2O_3 and Pt/CeO_2 powders in a 76:24 weight ratio.
PM: Particulate matter.
PGM: Platinum group metals (Ru, Rh, Pd, Os, Ir, Pt).
r: Radial coordinate (m).
r*: Dimensionless radial coordinate.
R_c: Radius of the crystallite (m).
R_eff: Radius over which NO_x is stored on exposed BaO (m).
R_0: Effective transverse length scale (m)
S_{BaW}: Total surface area of active BaO per unit mass of washcoat (m^2/g washcoat)
S_{BaO}: Surface density of BaO (BaO molecules/m^2 exposed BaO surface)
S_E: Exposed Pt surface area per channel (m^2)
SCR: Selective catalytic reduction.
SFTP: Supplementary federal testing procedures.
SpaciMS: Spatially resolved capillary inlet mass spectrometry.
STEM: Scanning transmission electron microscopy.
t: Time during the regeneration (s).
TAP: Temporal analysis of products reactor.
TCD: Thermal conductivity detector.
TEM: Transmission electron microscopy.
TPR: Temperature programmed reduction.

TWC: Three-way catalytic converter.

\( \bar{u} \): Average fluid velocity in the fluid phase (m/s).

\( W_a \): Atomic weight.

WGS: Water gas shift reaction.

\( x \): Axial coordinate (m).

XRD: X-ray diffraction.

XPS: X-ray photoelectron spectroscopy.

\( z \): dimensionless axial coordinate.

\( \delta_c \): Thickness of the washcoat on a monolith catalyst (m).

\( \varepsilon_{wc} \): Porosity within the washcoat.

\( \theta_v \): Fractional surface coverage of vacant sites on Pt.

\( \theta_{O-Pt} \): Fractional surface coverage of chemisorbed oxygen on Pt.

\( \lambda \): Dimensionless radial distance.

\( \lambda_{Pt} \): Total interfacial perimeter per gram of Pt.

\( \sigma \): Particle density (g/nm\(^3\))

\( \tau \): Dimensionless time.

\( \omega \): Average atom density of Pt particle surface.

\( \Sigma p \): Number of particles per gram of Pt.
Appendix A.2. Development of the Material Balances Used the Dispersion Model.

This is the model developed by Bhatia et al [1]. The model has been modified for this study.

A.2.1. Parameter Development.
Assumption #1: stored NO\textsubscript{x} species (represented by ‘A’ here) undergoes reverse-spillover via diffusion in the Ba phase towards the Pt/Ba interface, where it is reduced by H\textsubscript{2} as well as the reaction network intermediate, NH\textsubscript{3}.

Figures A.2.1 shows the Pt crystallite and the NO\textsubscript{x} stored around it. Figure A.1. is a bird-eye’s view. \( R_C \) is the radius of the crystallite, and \( R_{\text{eff}} \) is the radius of NO\textsubscript{x} stored around the crystallite.

Figure A.2.1. Illustration of down-looking view of Pt on exposed BaO supported on Al\textsubscript{2}O\textsubscript{3}.

\[ \text{Al}_2\text{O}_3 \]
\[ \text{Ba(NO}_3\text{)}_2 \]
\[ \text{Pt} \]
\[ R_C \]
\[ R_{\text{eff}} \]
Assumption #2: the Pt crystallites have a hemispherical shape.

Let \( N_T \) be the total number of Pt atoms in the Pt crystallite.

\[
N_T = \frac{\text{volume of Pt crystallite (hemisphere)} \cdot A_{PF}}{\text{volume of Pt atom}} = \frac{1/2 \frac{4}{3} \pi R_T^3 A_{PF}}{\frac{4}{3} \pi \left(\frac{D_{PT}}{2}\right)^3} = \frac{2/3 \pi R_T^3 A_{PF}}{1/6 \pi D_{PT}^3} \tag{A.2.1}
\]

where \( A_{PF} \) is the atomic packing factor. For Pt with a FCC structure, \( A_{PF} \) is equal to 0.74. \( D_{PT} \) is the diameter of the Pt atom.

Using equation (A.1), the number of crystallites in a monolith channel, \( N_C \), is calculated from:

\[
N_C = \frac{M_{Pt} N_{AV}}{N_T} \tag{A.2.2}
\]

where \( M_{Pt} \) is the total number of moles of Pt in the washcoat per channel, and \( N_{AV} \) is Avogadro’s number. Substituting (A.2.1) into (A.2.2):

\[
N_C = \frac{M_{Pt} N_{AV} \frac{1}{6} \pi D_{Pt}^3}{\frac{2}{3} \pi R_T^3 A_{PF}} = \frac{M_{Pt} N_{AV} D_{Pt}^3}{4 R_T^3 A_{PF}} \tag{A.2.3}
\]

The total exposed surface area, \( S_E \), is equal to:

\[
S_E = \frac{1}{2} \text{ surface area (sphere) } N_C = \frac{1}{2} \cdot 4 \pi R_C^2 N_C = 2 \pi R_C^2 N_C \tag{A.2.4}
\]

The total Pt/Ba interfacial perimeter for a single channel, \( I_P \):\[
I_P = \text{perimeter (circle)} \cdot N_C = 2 \pi R_C N_C \tag{A.5}
\]
Substituting (A.2.3) into (A.2.4) and (A.2.5):

\[ S_E = \frac{M_{Pt}N_{AV}D_{Pt}^2 \pi}{2A_{PF}R_C} \]  \hspace{1cm} (A.2.6)

\[ I_P = \frac{M_{Pt}N_{AV}D_{Pt}^2 \pi}{2A_{PF}R_C^2} \]  \hspace{1cm} (A.2.7)

The overall catalytic reactions occurring at the Pt/Ba interface are:

Assumption #3: NO\(_x\) is stored in the form of nitrates

\[ 8\, H_2 + Ba(NO_3)_2 \leftrightarrow 5\, H_2O + BaO + 2\, NH_3 \]  \hspace{1cm} (A.2.8)

\[ 10/3\, NH_3 + Ba(NO_3)_2 \leftrightarrow 5\, H_2O + BaO + 8/3\, N_2 \]  \hspace{1cm} (A.2.9)

In addition, some of the H\(_2\) is consumed by chemisorbed oxygen on the Pt crystallites:

\[ H_2 + O-Pt \leftrightarrow H_2O + Pt \]  \hspace{1cm} (A.2.10)

Assumption #4: One-dimensional diffusion of NO\(_x\) within the Ba phase (R\(_C\) \leq r \leq R_{eff}).

A localized material balance for stored NO\(_x\) gives:

\[ \text{input} - \text{output} + \text{generation} = \text{accumulation} \]

\[ P\, N_A|_r - P\, N_A|_{r+\Delta r} + 0 = \frac{\partial n_A}{\partial t} \]  \hspace{1cm} (A.2.11)

where P is the perimeter and equal to P = 2\(\pi\), \(N_A\) is the flux of NO\(_x\), and \(n_A\) is the moles of NO\(_x\) present. Utilizing \(n_A = C_A P \Delta r\) where \(C_A\) is the concentration of NO\(_x\). The above equation reduces to \(\frac{\partial N_A}{\partial r} = \frac{\partial n_A}{\partial t}\). Substituting \(N_A = D_A \frac{\partial C_A}{\partial r}\) where \(D_A\) is the diffusivity of NO\(_x\) into (A.2.11):
\[
\begin{align*}
\frac{\partial}{\partial r} \left( N_A P \right) &= \frac{\partial C_A P}{\partial t} \\
2\pi \frac{\partial}{\partial r} \left( r D_A \frac{\partial C_A}{\partial r} \right) &= 2\pi r \frac{\partial C_A}{\partial t} \\
\frac{\partial C_A}{\partial t} &= \frac{D_A}{r} \left( r \frac{\partial C_A}{\partial r} \right) \quad R_C \leq r \leq R_{\text{eff}}
\end{align*}
\]  

(A.2.12)

The following conditions apply to (A.2.12):

I.C. at \( t = 0, C_A = C_{AO}(r) \) for \( R_C \leq r \leq R_{\text{eff}} \)  

(A.2.13)

B.C. 1. Assumption #5, diffusional limitations in the washcoat (transverse to axial flow) are negligible, and the diffusive flux of stored NO\(_x\) at the Pt/Ba interface is equal to consumption of NO\(_x\) by NH\(_3\) and H\(_2\):

\[
N_A = D_A \frac{\partial C_A}{\partial r} = k_1 C_A C_{H_2,WC} + k_2 C_A C_{NH_3,WC}
\]

(A.2.14)

where \( k_1 \) is rate constant for NO\(_x\) regeneration by H\(_2\) (m\(^4\)/mol s), and \( k_2 \) is rate constant for NO\(_x\) regeneration by NH\(_3\) (m\(^4\)/mol s). The rate expression is derived from the fact that the consumption at the interface is dependent on the amount of NO\(_x\) at the surface and the amount of H\(_2\) or NH\(_3\) present.

B.C.2. at \( r = R_{\text{eff}}, \frac{\partial C_A}{\partial r} = 0 \)  

(A.2.15)

Assumption #6, NO\(_x\) is stored uniformly in the washcoat as a monolayer of BaO and all Al\(_2\)O\(_3\) sites are covered.
$R_{\text{eff}}$ is an estimate of the BaO that is utilized for NO\textsubscript{x} storage. $R_{\text{eff}}$ is determined from equating the total moles of NOx stored on the catalyst ($M_{NOx}$) to 2x the number of moles of exposed area around the Pt crystallite $[\pi \ast (R_{eff}^2 - R_c^2)]$.

$$M_{NOx} = \frac{2n_{ch}NcS_{BaO}\pi(R_{eff}^2 - R_c^2)}{N_{av}} \quad (A.2.16)$$

Substituting the expression for $Nc$ (A.2.3) into (A.2.16), the value for $R_{\text{eff}}$ is:

$$R_{eff} = R_c \sqrt{1 + \frac{2 Appendix NOx R_c}{n_{ch}\pi S_{BaO}D_{Pt}M_{Pt}}} \quad (A.2.17)$$

where $S_{BaO}$ surface density of BaO (BaO molecules/m$^2$ exposed BaO surface). The total surface area of active BaO per unit mass of washcoat, $S_{BaW}$ is:

$$S_{BaW} = \frac{n_{ch}Nc\pi(R_{eff}^2 - R_c^2)}{m_{wc}} \quad (A.2.18)$$

where $m_{wc}$ is the mass of the washcoat loading (g).

Using (A.2.16) and (A.2.18), we can relate the active BaO surface area to mol of NO\textsubscript{x} stored:

$$\frac{S_{BaW}}{M_{NOx}} = \frac{N_{av}}{2m_{wc}S_{BaO}} \rightarrow S_{BaW} = \frac{M_{NOx}N_{av}}{2m_{wc}S_{BaO}} \quad (A.2.19)$$

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A.2.2. Species Balance.

For a transient diffusion-reaction model of a porous catalyst with reaction, an overall mole balance gives:

\[
F_{jx} \bigg|_{x} - F_{jx} \bigg|_{x + \Delta x} - RA_{\Omega_1} \Delta x = \frac{\partial n_j}{\partial t}
\]  

(A.2.20)

where  
\( F_{jx} \bigg|_{x} \) is the molar rate in, mol/s  
\( F_{jx} \bigg|_{x + \Delta x} \) is the molar rate out, mol/s  
\( R \) is the molar rate of disappearance of component \( j \), mol/m\(^3\) catalyst  
\( A_{\Omega_1} \) is the cross sectional area of the fluid phase, m\(^2\)  
\( x \) is the axial coordinate  
\( n_j \) is the mol of \( j \)

Using \( n_j = c_j A_{\Omega_1} \Delta x \varepsilon_{wc} \), dividing by \( A_{\Omega_1} \Delta x \), and taking the limit as \( \Delta x \to 0 \):

\[
\frac{1}{A_{\Omega_1}} \left( - \frac{\partial F_{jx}}{\partial x} \right) - R = \varepsilon_{wc} \frac{\partial c_j}{\partial t}
\]  

(A.2.21)

where \( \varepsilon_{wc} \) is the porosity of the washcoat. If we assumed that the amount of material transported by diffusion in the axial direction is negligible compared with bulk flow Knudsen diffusion):

\[
\frac{\partial F_{jx}}{\partial x} = \bar{u} A_{\Omega_1} \frac{\partial c_j}{\partial x}
\]  

(A.2.22)

so (A.2.21) becomes

\[
\varepsilon_{wc} \frac{\partial c_j}{\partial t} = -\bar{u} \frac{\partial c_j}{\partial x} - R
\]  

(A.2.23)
A.2.2.1. Gas Phase Species Balance (Diffusion from the Bulk to the Interface).

Assumption #7: Assuming the entire resistance for mass transfer in the gas phase resides in a stagnant film of a certain thickness, a balance for the diffusion of component \( j \) from the bulk phase to the fluid washcoat interface gives:

\[
A_{\Omega_1} \bar{u} C_{jm} \Big|_x - A_{\Omega_1} \bar{u} C_{jm} \Big|_{x+\Delta x} - P_{\Omega} \Delta x k_{c,j}(x) \left( c_{jm} - c_{s,avg} \right) = 0 \tag{A.2.24}
\]

where

- \( A_{\Omega_1} = \) cross-sectional area of the fluid phase, m\(^2\)
- \( c_{jm} = \) cup-mixing concentration in the fluid phase, mol/m\(^3\)
- \( c_{s,avg} = \) circumferentially averaged concentration at the fluid-washcoat interface, mol/m\(^3\)
- \( P_{\Omega} = \) the wetted fluid-washcoat interfacial perimeter, m
- \( k_{me}(x) = \) position dependent mass transfer coefficient from the bulk of the fluid to the fluid-washcoat interface, m/s
- \( \bar{u} = \) average fluid velocity, m/s

Dividing by \( A_{\Omega_1} \Delta x \) and taking the limit as \( \Delta x \to 0 \):

\[
\bar{u} \frac{\partial c_j}{\partial x} = - \frac{1}{R_{\Omega_1}} k_{me}(x) \left( c_{jm} - c_{s,avg} \right) \tag{A.2.25}
\]

and \( R_{\Omega_1} \) is the effective transverse diffusion length for the fluid phase, m (\( R_{\Omega_1} = \frac{A_{\Omega_1}}{P_{\Omega}} \))
A.2.2.2. Washcoat Species Balance.
Assumptions #8 and #9: Assuming a hypothetical film in the washcoat describes the intra-phase or internal mass transfer resistance and no diffusional limitations exist in the bulk washcoat (the concentration of \( j \) drops from \( c_{s,avg} \) to constant value of \( c_{j,wc} \), we get the following:

\[
P_{\Omega} \Delta x k_{ml}(x) (c_{s,avg} - c_{j,wc}) = R_{\Omega_2} R(c_{j,wc})
\]  
(A.2.26)

\( k_{me}(x) \) = position dependent internal mass transfer coefficient between the interior of the washcoat and fluid-washcoat interface, m/s
\( c_{j,wc} \) is the volume-averaged concentration in washcoat weighed with respect to activity, mol/m \(^3\)

\( A_{\Omega_2} = \) cross-sectional area of the washcoat, m \(^2\)

\( R_{\Omega_2} \) is the effective transverse diffusion length for the washcoat, m \((R_{\Omega_2} = \frac{A_{\Omega_2}}{p_{\Omega}})\)

\( R \), reaction rates evaluated at \( c_{j,wc} \).

Dividing (A.2.26) by \( P_{\Omega} \Delta x \) and taking the limit \( \Delta x \to 0 \):

\[
k_{ml}(x) (c_{s,avg} - c_{j,wc}) = R_{\Omega_2} R(c_{j,wc})
\]  
(A.2.27)

A.2.2.3. Interface between the Fluid Phase and Washcoat.
At the interface between the fluid phase and the catalyst washcoat, no accumulation of mass can occur. This means that the external mass flux from the bulk gas phase to the interface must be the same as the interface to the bulk.

\[
k_{me}(x) (c_{jm} - c_{s,avg}) = k_{ml}(x) (c_{s,avg} - c_{j,wc})
\]  
(A.2.28)
Using the idea of the overall, position dependent mass transfer coefficient, \( k_{c,j}(x) \) is equal to the total individual resistances:

\[
\frac{1}{k_{c,j}(x)} = \frac{1}{k_{me}(x)} + \frac{1}{k_{ml}(x)} \tag{A.2.29}
\]

Using (A.2.29) in (A.2.25) and (A.2.28), the \( c_{s,avg} \) term can be eliminated. So (A.2.28) into (A.2.25):

\[
\bar{u} \frac{\partial c_j}{\partial x} = -\frac{1}{R_{\Omega_1}} k_{c,j}(x) \left( c_{jm} - c_{j,wc} \right) \tag{A.2.30}
\]

and (A.2.29) into (A.2.28):

\[
k_{c,j}(x) \left( c_{jm} - c_{j,wc} \right) = R_{\Omega_2} R \left( c_{j,wc} \right) \tag{A.2.31}
\]

or

\[
R \left( c_{j,wc} \right) = \frac{k_{c,j}(x)}{R_{\Omega_2}} \left( c_{jm} - c_{j,wc} \right) = \tag{A.2.32}
\]

A.2.2.4. The Species Balance for Component \( j \) in the Fluid Phase.

The final expression for the species balance for component \( j \) in the fluid phase is obtained by substituting (A.2.31) and (A.2.32) into (A.2.23):

\[
\frac{\partial c_j}{\partial t} = -\bar{u} \frac{\partial c_{jm}}{\partial x} - \frac{k_{c,j}(x)}{R_{\Omega}} \left( c_{jm} - c_{j,wc} \right) \tag{A.2.33}
\]

where the fluid velocity (m/s) and the transverse diffusion length scale (m) are represented by \( \bar{u} \) and \( R_{\Omega} \), respectively. The position-dependent mass-transfer coefficients for each species \( j \), represented by \( k_{c,j}(x) \), are used to account for the transverse gradients. The position dependence obtained from Ramanathan et al. [2] is used here for a square channel of uniform washcoat thickness (Figure A.2), its development is described in Section A.3.5.
Figure A.2.2. Square channel of uniform washcoat thickness.

\[ R_{\Omega_1} = \frac{\text{flow area (} A_{\Omega_1} \text{)}}{\text{fluid washcoat perimeter } p_{\Omega}} = \frac{R}{2} \]  

(A.2.34)

and

\[ R_{\Omega_2} = \frac{\text{washcoat cross-sectional area (} A_{\Omega_2} \text{)}}{\text{interfacial perimeter } p_{\Omega}} = \frac{(a+2\delta_c)^2 - a^2}{4a} = \frac{\delta_c(a+\delta_c)}{a} \]  

(A.2.35)

where

\[ R_{\Omega_1} = \text{effective transverse length scale (m) in the fluid phase, m} \]
\[ R_{\Omega_2} = \text{effective transverse length scale (m) in the washcoat, m} \]
\[ a = \text{width/hydraulic diameter of the channel, m} \]
\[ \delta_c = \text{thickness of the washcoat (m)} \]

The reaction rate term, \( R(c_{j,wc}) \), is comprised of the reactions that occur at the fluid-washcoat interface and the catalyst surface.
At the interface (1):

\[ R(c_{j,wc}) = \text{interfacial reaction rate} \times \frac{l_p}{\text{surface area } R_{\Omega_1}} \]  

(A.2.36)

At the surface (2):

\[ R(c_{j,wc}) = \text{surface reaction rate} \times \frac{l_p}{\text{surface area } R_{\Omega_1}} \]  

(A.2.37)

where \( S_{E} \) and \( l_p \) are defined in (A.2.4) and (A.2.5).

### A.2.3. Washcoat Species Balance.

#### A.2.3.1. Hydrogen Surface Balance.

For a square channel of uniform cross-section, the species balance for H\(_2\) is given by:

\[ \varepsilon_{wc} \frac{\delta c_{H_2,wc}}{\delta t} = \frac{k_{c_{H_2}}(x)}{R_{\Omega_2}} k_{c,j}(x) \left( c_{H_2m} - c_{H_2,wc} \right) - R_{\Omega_2} R \left( c_{H_2,wc} \right) \]  

(A.2.38)

The reaction rate of H\(_2\) reacting with stored NO\(_x\) at the Pt/Ba interface (A.8), \( r=R_c \), is given by:

\[ 8 \text{H}_2 + \text{Ba(NO}_3\text{)}_2 \leftrightarrow 5 \text{H}_2\text{O} + \text{BaO} + 2 \text{NH}_3 \]  

(A.2.8)

\[ R(\varepsilon_{wc}) = 4k_1c_A|_{r=R_c}c_{H_2,wc} \times \frac{N_c2\pi R_c}{4aL_{\Omega_2}} \]  

(A.2.39)

For H\(_2\) reacting with chemisorb oxygen on the surface of the Pt crystallite (A.2.10):

\[ \text{H}_2 + \text{O-Pt} \leftrightarrow \text{H}_2\text{O} + \text{Pt} \]  

(A.2.10)

\[ R(\varepsilon_{wc}) = k_3c_{pt}\theta_{O-Pt}c_{H_2,wc} \times \frac{N_c2\pi R_c^2}{4aL_{\Omega_2}} \]  

(A.2.40)
The total reaction rate expression for the consumption of H$_2$:

\[
R(c_{wc}) = \frac{c_{H2,we}N_c2\pi R_c}{\delta_c(a+\delta_c)} * \left(4k_1 c_A|_{r=R_c} + k_3 c_{Pt} \theta_{O-Pt} R_c\right)
\]  (A.2.41)

The diffusion of H$_2$ is expressed as:

\[
\frac{k_{CH_2}(x)}{R_{Pt}} (c_{H2m} - c_{H2,wc}) = \frac{a}{\delta_c(a+\delta_c)} k_{CH_2}(x) (c_{H2m} - c_{H2,wc})
\]  (A.2.42)

Substituting (A.40) and (A.41) into (A.37):

\[
\frac{\delta c_{H2,wc}}{\delta t} = \frac{1}{e_{wc}\delta_c(a+\delta_c)} \left[\frac{ak_{CH_2}(x)(c_{H2m} - c_{H2,wc})}{c_{H2,wc}N_c2\pi R_c} \left(4k_1 c_A|_{r=R_c} + k_3 c_{Pt} \theta_{O-Pt} R_c\right)\right]
\]  (A.2.43)

Assumption #10: (A.2.43) assumes the reaction rate between H$_2$ and the stored NO$_x$ is proportional to the perimeter of the Pt/Ba interface, whereas the reaction between H$_2$ and chemisorbed O$_2$ is proportional to the surface area of exposed Pt atoms. Hence, the term “4$k_1 c_A|_{r=R_c}$” represents the consumption of H$_2$ by NO$_x$, whereas the term “$k_3 c_{Pt} \theta_{O-Pt} R_c$” represents the consumption of H$_2$ by chemisorbed oxygen on the exposed Pt surface.

A.2.3.2. NH$_3$ Surface Balance.

The diffusion of NH$_3$ on the surface is similar to that of H$_2$:

\[
\frac{k_{CNH_3}(x)}{R_{\Omega_2}} (c_{NH3m} - c_{NH3,wc})
\]  (A.2.44)
As for the reaction rate expression, NH₃ only reacts at the Pt/Ba interface and not on the Pt surface. NH₃ is produced in (A.2.8) and consumed in (A.2.9):

\[
8 \text{H}_2 + \text{Ba(NO}_3)_2 \leftrightarrow 5 \text{H}_2\text{O} + \text{BaO} + 2 \text{NH}_3 \quad (\text{A.2.8})
\]

\[
\frac{10}{3} \text{NH}_3 + \text{Ba(NO}_3)_2 \leftrightarrow 5 \text{H}_2\text{O} + \text{BaO} + \frac{8}{3} \text{N}_2 \quad (\text{A.2.9})
\]

The rate expression for (A.2.8):

\[
R(c_{\text{wc}}) = k_1 c_A|_{r=R_e} c_{H_2\text{wc}} \frac{N_c 2\pi R_c}{4aLR_{\Omega_2}} \quad (\text{A.2.45})
\]

The rate expression for (A.2.9):  

\[
R(c_{\text{wc}}) = -(\frac{5}{3})k_2 c_A|_{r=R_e} c_{\text{NH}_3\text{wc}} \frac{N_c 2\pi R_c}{4aLR_{\Omega_2}} \quad (\text{A.2.46})
\]

Using the expression for \( R_{\Omega_2} \) (A.2.34), the total rate of reaction for NH₃ is:

\[
\text{total } R(c_{\text{wc}}) = k_1 c_{H_2\text{wc}} \frac{c_A|_{r=R_e} N_c 2\pi R_c}{4L} \frac{1}{\delta_c(a+\delta_c)} \left[ k_1 c_{H_2\text{wc}} - \left( \frac{5}{3} \right) k_2 c_{\text{NH}_3\text{wc}} \right] 
\quad (\text{A.2.47})
\]

Substituting (A.2.36), (A.2.37), (A.2.44), and (A.2.47) into (A.2.33):

\[
\frac{\delta c_{\text{NH}_3\text{wc}}}{\delta t} = \frac{1}{\epsilon_{\text{wc}} \delta_c(a+\delta_c)} \left\{ \frac{a k_{c_{\text{NH}_3}}(x)(c_{\text{NH}_3m} - c_{\text{NH}_3\text{wc}})}{c_A|_{r=R_e} N_c 2\pi R_c} \left[ k_1 c_{H_2\text{wc}} - \left( \frac{5}{3} \right) k_2 c_{\text{NH}_3\text{wc}} \right] \right\} \quad (\text{A.2.48})
\]

Assumption #11: NH₃ does not react with chemisorbed oxygen on Pt. The term “\( k_1 c_{H_2\text{wc}} \)” is the generation of NH₃, whereas “\( \left( \frac{5}{3} \right) k_2 c_{\text{NH}_3\text{wc}} \)” is the consumption of NH₃ by stored NOₓ.
A.2.3.3. $N_2$ Surface Balance.

The diffusion of $N_2$ on the surface is similar to that of $H_2$ and $NH_3$:

$$\frac{k_{CN_2}(x)}{R_{\Omega_2}} \left( c_{N_{2m}} - c_{N_{H3,wc}} \right)$$ \hspace{1cm} (A.2.49)

The reaction rate expression for the generation of $N_2$ at the interface is (A.2.9):

$$^{10/3}NH_3 + Ba(NO_3)_2 \leftrightarrow 5 H_2O + BaO + \frac{8}{3} N_2$$ \hspace{1cm} (A.2.9)

$$R(c_{wc}) = \left(\frac{4}{3}\right)k_2c_A|_{r=R_c}c_{NH_3,wc} * \frac{N_c2\pi R_c}{4aLR_{\Omega_2}}$$ \hspace{1cm} (A.2.50)

Using the expression for $R_{\Omega_2}$ (A.2.34):

$$R(c_{wc}) = * \frac{k_2c_A|_{r=R_c}c_{NH_3,wc}N_c2\pi R_c}{3L\delta_c(a+\delta_c)}$$ \hspace{1cm} (A.2.51)

Substituting (A.2.49) and (A.2.51) into (A.2.25):

$$\frac{\delta c_{N_2,wc}}{\delta t} = \frac{1}{\epsilon_{wc}\delta_c(a+\delta_c)} \left[ ak_{c_{H_2}}(x) \left( c_{N_{2m}} - c_{N_{2,wc}} \right) + \frac{N_c2\pi R_c k_2c_A|_{r=R_c}c_{NH_3,wc}}{3L} \right]$$ \hspace{1cm} (A.2.52)

A.2.3.4. Vacant Site Balance.

Lastly, a vacant site balance is required using (A.2.10):

$$H_2 + O-Pt \leftrightarrow H_2O + Pt$$ \hspace{1cm} (A.2.10)

Here, generation is equal to accumulation:

$$\frac{\partial \theta_v}{\partial t} = k_3c_{H_2,wc}\theta_{O-Pt}$$ \hspace{1cm} (A.2.53)
The initial and boundary conditions for (A.2.43), (A.2.48), (A.2.52), and (A.2.53):

I.C. \( @ \ t = 0, \quad c_{j,m} = 0, \quad c_{jwc} = 0, \quad \theta_v = 0 \) for \( 0 < x \leq L \) \hspace{1cm} (A.2.54)

B.C. \( @ \ x = 0, \quad c_{j,m} = c_{j}^{in} \) \hspace{1cm} (A.2.55)

where \( c_{j}^{in} \) is the inlet concentration of species \( j \) in the fluid phase, mol/m\(^3\).

**A.2.4. Dimensionless Expression for Use in the Model.**

The above expressions are non-dimensionalized for their use in the model using the following expressions:

- **Dimensionless axial coordinate**
  \[ z = \frac{x}{L} \] \hspace{1cm} (A.2.56)

- **Dimensionless radial coordinate**
  \[ r^* = \frac{r - R_c}{R_{eff} - R_c} \] \hspace{1cm} (A.2.57)

- **Dimensionless time**
  \[ \tau = \frac{t D_A}{(R_{eff} - R_c)^2} \] \hspace{1cm} (A.2.58)

- **Dimensionless radial distance**
  \[ \lambda = \frac{R_c}{R_{eff} - R_c} \] \hspace{1cm} (A.2.59)

Using \( \lambda \), \( r^* \) becomes
\[ r^* = \frac{r}{R_{eff} - R_c} - \lambda \] \hspace{1cm} (A.2.60)

- **Dimensionless cup-mixing concentration of species \( j \) in the fluid phase**
  \[ C_{j,m}^* = \frac{c_{j,m}^{in}}{c_{in}^{H_2}} \] \hspace{1cm} (A.2.61)

- **Dimensionless cup-mixing concentration of species \( j \) in the fluid-washcoat interface**
  \[ C_{j,wc}^* = \frac{c_{j,wc}^{in}}{c_{in}^{H_2}} \] \hspace{1cm} (A.2.62)

- **Dimensionless concentration of stored NO\(_x\)**
  \[ C_{A}^* = \frac{C_A}{c_{AO}} \] \hspace{1cm} (A.2.63)
With these expressions, the following expressions can be non-dimensionalized:

A localized material balance for stored NO:

\[
\frac{\partial c_A}{\partial \tau} = \frac{D_A}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_A}{\partial r} \right) \quad (A.2.12)
\]

\[
\frac{\partial c_A^*}{\partial \tau} = \frac{\partial^2}{\partial \tau^2} + \left( \frac{1}{r^{*-\lambda}} \right) \frac{\partial c_A^*}{\partial r^*} \quad (A.2.64)
\]

I.C. at \( \tau = 0 \), \( C_A^* = 1 \), \( 0 \leq r^* \leq 1 \) \( (A.2.65) \)

B.C.1. at \( r^* = 0 \),

\[
\frac{\partial c_A^*}{\partial r^*} = \frac{(R_{\text{eff}} - R_c)C_{\text{in}}^{\text{H}_2}}{D_A} \left( k_1 C_{\text{H}_2 \text{wc}} + k_2 C_{\text{NH}_3 \text{wc}}^* \right) \quad (A.2.66)
\]

B.C.2. at \( r^* = 1 \), \( \frac{\partial c_A^*}{\partial r^*} = 0 \) \( (A.2.67) \)

Washcoat Species Balance (A.2.25) becomes:

\[
\frac{\partial c_{\text{j,m}}}{\partial \tau} = \frac{(R_{\text{eff}} - R_c)}{D_A} \left[ \frac{\bar{u}}{L} \frac{\partial c_{\text{j,m}}^*}{\partial z} - \frac{k_c(z)}{R_\Omega} \left( c_{j,m}^* - C_{j,\text{wc}}^* \right) \right] \quad (A.2.68)
\]

The H\(_2\) surface balance (A.2.43) becomes:

\[
\frac{\partial C_{\text{H}_2 \text{wc}}}{\partial \tau} = \frac{(R_{\text{eff}} - R_c)^2}{D_A \varepsilon_w \delta_c(a + \delta_c)} \left[ \frac{\alpha k_{\text{c,H}_2}(z)\left( C_{\text{H}_2 \text{in}}^* - C_{\text{H}_2 \text{wc}}^* \right)}{4L} + \frac{k_1 C_{\text{A}} C_{\text{A}}^* |_{r^*=0} + k_3 C_{\text{Pt}} \theta_{0 - \text{Pt}} R_c}{4L} \right] \quad (A.2.69)
\]

The NH\(_3\) surface balance (A.2.48) becomes:

\[
\frac{\partial C_{\text{NH}_3 \text{wc}}^*}{\partial \tau} = \frac{(R_{\text{eff}} - R_c)^2}{D_A \varepsilon_w \delta_c(a + \delta_c)} \left[ \frac{\alpha k_{\text{c,NH}_3}(z)\left( C_{\text{NH}_3 \text{in}}^* - C_{\text{NH}_3 \text{wc}}^* \right)}{4L} + \frac{k_1 C_{\text{H}_2 \text{wc}}^* \left( \frac{5}{3} \right) k_2 C_{\text{NH}_3 \text{wc}}^*}{4L} \right] \quad (A.2.70)
\]
The \( N_2 \) surface balance (A.2.52) becomes:

\[
\frac{\partial C_{N_2}^*}{\partial \tau} = \frac{(R_{\text{eff}} - R_c)^2}{D_A e_{\text{wc}} \delta_e (a + \delta_e)} \left[ a k_c N_2 (z) (C_{N_2}^* - C_{N_2}^*_{\text{WC}}) + \frac{N_c 2\pi R_c c_{\text{AO}} \lambda_{\text{wc}} \rho = 0 c_{N_3 \text{WC}}^*}{3L} \right]
\]  
(A.2.71)

Finally, the vacant site balance (A.2.53) becomes:

\[
\frac{\partial \theta_v}{\partial \tau} = \frac{(R_{\text{eff}} - R_c)^2}{D_A} k_{3H_2} c_{H_2 \text{WC}}^* \theta_{O - Pr}
\]  
(A.2.72)

The initial and boundary conditions for the species balances become:

I.C. at \( \tau = 0 \), \( C_{jm}^* = 0 \), \( C_{jwc}^* = 0 \), \( \theta_v = 0 \) for \( 0 < z \leq 1 \) (A.2.73)

B.C. at \( z = 0 \), \( C_{jm}^* = C_{j}^{\text{in}} \)  
(A.2.74)

where \( C_{j}^{\text{in}} \) is the dimensionless inlet concentration of species \( j \)

A.2.5. Determination of the Overall Mass Transfer Coefficient.

From Ramanathan et al. [2], position dependent mass transfer coefficient for species \( j \) at axial position \( x \), \( k_c j(x) \), is calculated for the case of fully developed laminar flow with the velocity field developing along with the concentration boundary layer using the following expression:

\[
Sh_\Omega(x) = \frac{k_c j(x) R_\Omega}{D_m e(j)}
\]  
(A.2.75)
If
\[ z(j) < \frac{R_{\Omega_2} \bar{u}}{D_{me}(j) Sc^{1/3} \left( \frac{1.4}{Sh_{\infty}} \right)^2} \]  \hspace{1cm} (A.2.76)
then:
\[ k_{c,j}(x) = \frac{0.35 D_{me}(j)}{R_{\Omega} Sc(j)^{1/6} \varepsilon(j) D_{me}(j)} \left( \frac{R_{\Omega}}{R_{\Omega} + \frac{D_{me}(j)}{4}} \right)^{1/2} \]  \hspace{1cm} (A.2.77)
else:
\[ k_{c,j}(x) = \frac{D_{me}(j)}{R_{\Omega} \left( \frac{D_{me}(j)}{4} \right)} \]  \hspace{1cm} (A.2.78)

where:
\[ Sh_{\Omega}(x) = \text{Sherwood Number, defined by (A.2.75)} \]
\[ k_{c,j}(x) = \text{position dependent mass transfer coefficient for species } j \text{ at axial position } x \text{ (m/s)} \]
\[ R_{\Omega} = \text{effective transverse length scale in the fluid phase (m), in this case: one-half the channel hydraulic radius (m) (A.2.34)} \]
\[ D_{me}(j) = \text{diffusion coefficient in the fluid phase (m}^2/\text{s)} \]
\[ z(i) = \text{dimensionless coordinate along the length of the channel} \]
\[ R_{\Omega_2} = \text{effective transverse length scale in the washcoat (m) (A.2.35)} \]
\[ \bar{u} = \text{average fluid velocity (m/s)} \]
\[ Sc = \text{Schmidt Number} = \frac{v}{D_{me}(j)} \]
\[ v = \text{kinematic viscosity (m}^2/\text{s)} = \frac{\mu}{\rho} \]
\[ \mu = \text{dynamic viscosity (kg/m}^\text{s}) \]
\[ \rho = \text{density (kg/m}^3) \]
\[ Sh_{\infty} = \text{asymptotic Sherwood(Nusselt) numbers for the channel (with constant flux boundary condition). Here } Sh_{\infty} = 3.608 [2] \]
A.2.6. References.


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J. Wang, M. Crocker, unpublished data.


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