Environmental Technology Management (ETM):
Performance and Reaction Activity Changes of a NO\textsubscript{X} Storage/Reduction Catalyst as a Function of Regeneration Mixture and Thermal Degradation

by

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A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of

Master of Applied Science
in
Chemical Engineering

Waterloo, Ontario, Canada, 2008

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Meshari AL-Harbi
Abstract

With steadily increasing emissions regulations being imposed by government agencies, automobile manufacturers have been developing technologies to mitigate NOX emissions. Furthermore, there has been increasing focus on CO2 emissions. An effective approach for CO2 reduction is using lean burn engines, such as the diesel engine. An inherent problem with lean-burn engine operation is that NOX needs to be reduced to N2, but there is an excess of O2 present. NOX storage and reduction (NSR) is a promising technology to address this problem. This technology operates in two phases; where in the lean phase, normal engine operation, NOX species are stored as nitrates, and in a reductant rich phase, relative to O2, the NOx storage components are cleaned and the NOX species reduced to N2.

In this study, the effects of reductant type, specifically CO and/or H2, and their amounts as a function of temperature on the trapping and reduction of NOX over a commercial NSR catalyst have been evaluated. Overall, the performance of the catalyst improved with each incremental increase in H2 concentration. CO was found ineffective at 200°C due to precious metal site poisoning. The addition of the H2 to CO-containing mixtures resulted in improved performance at 200°C, but the presence of the CO still resulted in decreased performance in comparison to activity when just H2 was used. At 300-500°C, H2, CO, and mixtures of the two were comparable for trapping and reduction of NOX, although the mixtures led to slightly improved performance.

Although NSR technology is very efficient in reducing NOX emissions, a significant challenge that questions their long-term durability is poisoning by sulfur compounds
inherently present in the exhaust. Therefore, during operation, NSR catalysts require an intermittent high-temperature exposure to a reducing environment to purge the sulfur compounds from the catalyst. This desulfation protocol ultimately results in thermal degradation of the catalyst. As a second phase of this study, the effect of thermal degradation on the performance of NSR technology was evaluated. The catalyst performance between a 200 to 500°C temperature range, using H₂, CO, and a mixture of both H₂ and CO as reductants was tested before and after different high-temperature aging steps. Tests included water-gas shift (WGS) reaction extent, NO oxidation, NOₓ storage capacity, oxygen storage capacity (OSC), and NOₓ reduction efficiency during cycling. The WGS reaction extent was affected by thermal degradation, but only at low temperature. NO oxidation did not show a consistent trend as a function of thermal degradation. The total NOₓ storage capacity was tested at 200, 350 and 500°C. Little change was observed at 500°C with thermal degradation and a steady decrease was observed at 350°C. At 200°C, there was also a steady decrease of NOₓ storage capacity, except after aging at 700°C, where the capacity increased. There was also a steady decrease in oxygen storage capacity at test temperatures between 200 and 500°C after each increase in thermal degradation temperature, except again when the sample was degraded at 700°C, where an increase was observed. In the cycling experiments, a gradual drop in NOₓ conversion was observed after each thermal degradation temperature, but when the catalyst was aged at 700°C, an increase in NOₓ conversion was observed. These data suggest that there was redispersion of a trapping material component during the 700°C thermal degradation treatment while the oxygen storage capacity data indicate redispersion of oxygen storage components. It therefore seems
likely that it is these oxygen storage components that are becoming “activated” as trapping materials at low temperature.
Acknowledgements

All thanks and praise for ALLAH (GOD) for his guidance and support throughout my study.

I would like to express my deep and sincere gratitude to my supervisor Prof. William Epling for his unlimited advice, guidance, and encouragement throughout my study. Prof. William Epling has the best intentions in mind for the development of his students and he is the best educator I have ever seen.

I would like to express my immense appreciation to Prof. Ali Elkamel who was always around to help and his constructive comments in reviewing this thesis. I would also like to thank Prof. Ting Tsui for his beneficial comments and time spent in reviewing this thesis.

I would like to express my deepest gratitude for my beloved parents, brothers, and sisters for their infinite encouragement throughout my study. Special thanks and appreciation to my wife, who is a source of love, inspiration, and support.

I am extremely grateful for endless and continuous support and advice of my friend Ibrahim AL-Hajri. My deep appreciation also goes to all my friends in Catalysis Research Groups, and secretaries and technicians at chemical engineering department.

Finally, I would like to express my appreciation to Natural Sciences and Engineering Research Council of Canada Discovery Grants Program, Cummins Inc. and Kuwait University for financial support.
Dedication

To my families especially

my beloved parents

and

my beloved wife
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Chapter 1: Introduction

1.1 Overview

Environmental Technology Management (ETM) focuses on providing a comprehensive understanding of the environmental issues for air, water, and land and solutions for those issues. The focus of this research is on a technology for controlling NOX pollution and preventing its introduction into the environment.

Climate change is a significant environmental issue facing the world today. Global warming and climate change have created need for reducing automotive emissions of greenhouse gases. Globally, concerns have been raised about the increase in carbon dioxide level, the principal greenhouse gas, in the atmosphere. There is approximately 30 percent more carbon dioxide in the atmosphere today than there was in 1750 [1]. This increase in carbon dioxide concentration has caused, and is causing, the earth's atmosphere to warm up. Carbon dioxide is emitted to the atmosphere from either natural sources such as volcanic eruptions, or human-related sources such as the combustion of fossil fuels such as coal, oil and gas in power plants, automobiles, industrial facilities and other sources. For automobiles, one of the suggested approaches for mitigation and reduction of CO2 emissions is the use of lean burn engines, such as diesel engines.

Despite the fact that using diesel engines can contribute to a reduction of carbon dioxide relative to gasoline engine use, their NOX emissions require special attention. The inherent challenge is reducing NOX to N2 in the oxidizing environment of lean-burn engine exhaust gas. Several technologies have been proposed to mitigate such diesel
engine emissions. These include three way catalytic (TWC) converters, continuous selective catalytic reduction (SCR), and nitrogen storage/reduction (NSR) catalysis. Each of these technologies will be described in this chapter.

1.2 Air Pollutants

Air pollutants are any substances, particles, liquids, or gaseous, that are released into the air and lead to a deterioration of the atmosphere, which in turn will affect the life of humans, plants, and animals. Pollutants are classified as either primary or secondary.

Primary pollutants are substances that are released directly into the air from their sources. Common examples of primary pollutants include sulfur dioxide (SO₂), carbon monoxide (CO), nitrogen oxides (NOₓ), particulate matter less than 10 µm in diameter (PM-10), particulate lead (Pb), and volatile organic compounds (VOCS). In table 1, some primary pollutants are listed, starting from 1970, as cited by the Environmental Protection Agency (EPA)[2].

Secondary pollutants are not directly emitted from sources, but form in the atmosphere as a result of chemical and photochemical reactions of other emitted molecules. Common examples of secondary pollutants are ground level ozone (O₃), peroxy acetyl nitrate (PAN), and hydrogen peroxide (H₂O₂).

These pollutants, whether primary or secondary, have harmful effects on human, plant, and animal life. SO₂, for example, can react with water to form sulfuric acid which can corrode buildings, statues, and bridges as well as lead to lower pH levels in bodies of water. Also, sulfur dioxide is irritating to the respiratory system, eyes, and can result in
severe diseases[3]. Another example is CO, which is a poisonous gas that can be produced as a result of incomplete combustion of hydrocarbons in motor vehicle engines. It has significant effects on human health. It can cause shortage of breath, dizziness, severe headaches, and at high concentration can cause death.

Table 1-1 National air pollutant emissions estimates for major pollutants (EPA)

<table>
<thead>
<tr>
<th></th>
<th>Millions of Tons Per Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>197</td>
</tr>
<tr>
<td>Nitrogen Oxides (NOx)</td>
<td>27</td>
</tr>
<tr>
<td>Particulate Matter (PM)</td>
<td></td>
</tr>
<tr>
<td>PM10</td>
<td>12</td>
</tr>
<tr>
<td>PM2.5</td>
<td>12</td>
</tr>
<tr>
<td>Sulfur Dioxide (SO2)</td>
<td>31</td>
</tr>
<tr>
<td>Volatile Organic Compounds (VOC)</td>
<td>34</td>
</tr>
<tr>
<td>Lead</td>
<td>0.221</td>
</tr>
<tr>
<td>Totals</td>
<td>302</td>
</tr>
</tbody>
</table>

1.2 Regulations and Standards

With a dramatic increase in the number of cars world wide over the last several decades, government environmental agencies have been continuously imposing tighter regulations
to mitigate emissions from vehicle engines. Overall, automobile manufacturers have made remarkable progress in reducing pollutant emissions via advanced engine design and advanced exhaust aftertreatment technologies.

Basically, air quality standards are set by accounting for the assessment of the effects of each pollutant on public health and the environment. In fact, since the Clean Air Act (CAA) legislation began in 1955, there have been noteworthy reductions in emission levels.

Table 1-2 California (CARB) Emissions Standards

<table>
<thead>
<tr>
<th>Year</th>
<th>HC</th>
<th>NOₓ</th>
<th>CO</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1993</td>
<td>0.25</td>
<td>0.40</td>
<td>3.40</td>
<td></td>
</tr>
<tr>
<td>1994</td>
<td>0.25</td>
<td>0.40</td>
<td>3.40</td>
<td></td>
</tr>
<tr>
<td>2003</td>
<td>0.25</td>
<td>0.40</td>
<td>3.40</td>
<td></td>
</tr>
<tr>
<td>2004</td>
<td>0.125</td>
<td>0.40</td>
<td>3.40</td>
<td>0.08</td>
</tr>
<tr>
<td>2005</td>
<td>0.075</td>
<td>0.40</td>
<td>3.40</td>
<td>0.08</td>
</tr>
<tr>
<td>2006</td>
<td>0.04</td>
<td>0.20</td>
<td>1.70</td>
<td>0.04</td>
</tr>
<tr>
<td>2007</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Although public awareness related to air pollutants regulation has been gradually increasing over the last decade, statistics show that more than thousands die yearly because of air pollutants[4]. Therefore, public and governments efforts are still focused on reducing air pollution to protect human health. In table 2, a summary of some common pollutant legislation history is listed.
1.4 NO\textsubscript{X}

NO\textsubscript{X} is a generic term pertaining to compounds of nitric oxide (NO), nitrogen dioxide (NO\textsubscript{2}), and other oxides of nitrogen, all of which are highly reactive gases. Most of the nitrogen oxides are colorless and odorless, except for NO\textsubscript{2}, which appears as a yellowish-brown cloud with a biting odor. In our research, NO\textsubscript{X} is used as a generic term for mono-nitrogen oxides, NO and NO\textsubscript{2}.

1.5 Effect of NO\textsubscript{X}

NO\textsubscript{X} is one of the major contributors to ground-level ozone, which forms when NO\textsubscript{X} reacts with highly reactive VOCs in the presence of sunlight. Ozone damages vegetation, kills trees, irritates the respiratory system, throat, eyes, or nose, and causes severe headaches.

\[ \text{VOCs} + \text{NO\textsubscript{X}} + \text{Sunlight} \rightarrow \text{Ozone} \]

In addition, NO\textsubscript{X} is a major component of smog. Smog is a mixture of poisonous gases caused by a reaction between sunlight and pollutants such as ozone, NO\textsubscript{X}, and VOCs. Smog has adverse effects on plants, animals, and humans.

Furthermore, NO\textsubscript{X} can react with atmospheric water to form acid which falls to earth as rain, fog, or dry particles. This acid rain leads to corrosion of statues and buildings, damages crops and forests, and changes the acidity of lakes and streams, consequently,
killing fishes and other plants and animals. The following figures illustrate the effect of acid rain on statues:

**Figure 1-1 Effect of acid rain on statues**

1.6 Sources of NO\textsubscript{x}

The major sources of NO\textsubscript{x}, as shown in Figure 2, are combustion of fuel at high temperature in motor vehicles, electric utilities, and other industrial, commercial, and residential sources.
1.7 Diesel Engine

Diesel engines operate via internal combustion. Combustion of the fuel and air takes place in enclosed space called a combustion chamber. Air is forced and compressed into the cylinder, and then the fuel is injected into it. The compressed air is hot enough to ignite the diesel fuel without the use of a sparkplug, unlike gasoline engine which needs a spark to initiate fuel ignition. The resulting combustion causes increased heat and expansion in the cylinder via increased pressure from the combustion process, which moves the piston downward creating power. The remaining gases are vented through an exhaust valve. This piston motion is transmitted by means of connecting rods to the crankshaft that converts linear motion to rotary motion for use as power in a variety of applications. A picture of diesel engine operation is shown in Figure 3.
1.8 NO\textsubscript{X} Reduction Technologies

Although diesel engine use is promising from a fuel economy standpoint, the high NOx emissions remains an important technical issue for its use today. Fortunately, numerous technologies have been developed to reduce NO\textsubscript{X} emissions from diesel and/or lean-burn engine exhaust. Examples of the most common technologies that have been applied are summarized in Figure 4.

Figure 1-4 NO\textsubscript{X} emission control technologies
1.8.1 Three way catalytic (TWC) converter

The three way catalytic (TWC) converter is a device equipped in the exhaust pipe of most gasoline vehicles. It has a honeycomb structure, as shown in Figure 5. The TWC converter contains precious metals, such as platinum and rhodium, for chemically converting some pollutants in the exhaust gases, such as carbon monoxide, unburned hydrocarbons, and oxides of nitrogen, into harmless compounds. The chemical reactions occurring on the TWC can be described as follows:

\[
2 \text{NO}_x \rightarrow x\text{O}_2 + \text{N}_2
\]

\[
2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2
\]

\[
2\text{C}_x\text{H}_y + (2x + y/2) \text{O}_2 \rightarrow 2x\text{CO}_2 + y\text{H}_2\text{O}
\]

TWC converters have been used in cars since 1970 and have had a significant impact in the reduction of NO\textsubscript{x}, CO and hydrocarbons emitted in engine exhaust. The TWC converter is designed for use in exhaust that is free of oxygen, in other words the engine operates with a stoichiometric air to fuel ratio.

Figure 1-5 Three way catalytic converter (TWC)
Although the TWC can reduce a small fraction of lean-burn engine NO\textsubscript{X} emissions, the reduction is not significant enough to meet today’s regulations. This is due to its design focus on operation at the stoichiometric air/fuel ratio; where little to no oxygen is present during reaction. Another issue associated with TWC technology is its sensitivity toward lead, zinc, and sulfur. Thus, this catalyst can be poisoned when using fuels that have high amounts of these impurities. Due to its low conversion in lean-burn exhaust, alternate technologies have been developed to reduce NO\textsubscript{X} emissions in oxygen-containing environments.

### 1.8.2 Selective catalytic reduction (SCR)

Selective catalytic reduction (SCR) is a process where a reductant such as (1) ammonia, either injected as ammonia or injecting urea as a precursor which decomposes to ammonia, or (2) a hydrocarbon, is added to the engine’s exhaust gas as shown in Figure 8. These reductants react selectively with NO\textsubscript{X} to form N\textsubscript{2} and H\textsubscript{2}O. Ammonia-based SCR can meet the regulations being imposed, however there is currently no catalyst for hydrocarbon-based SCR to meet the efficiencies required to meet today’s regulations. Ammonia SCR reactions take place in the presence of a catalyst, which is commonly a platinum catalyst when operating at low temperature, <573 K, a vanadium based catalyst at medium temperatures, <700 K, or metal-doped zeolites at higher temperatures, < 863 K. The basic stoichiometric reactions that occur in an ammonia SCR system are shown below:

\[ 4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \]
$4 \text{NH}_3 + 2 \text{NO}_2 + \text{O}_2 \rightarrow 3 \text{N}_2 + 6 \text{H}_2\text{O}$

Although this technology has proven to achieve significant reductions in NO$_X$ emissions, it has some associated problems:

- SCR catalysts with precious metals only operate well within narrow temperature bands [5] [6]. Thus, tight control and adjustment of exhaust gas temperatures are required, which is not practical for a wide range of driving conditions.
- SCR technology would require a distribution network for urea or ammonia. In addition, there are toxicity, storage and refueling problems with these reductants[7].
- Another common problem with SCR is ammonia slip and odor[8]. Consequently, it requires a very accurate injection system for urea or ammonia to assure that all the ammonia is consumed by NO$_X$ to prevent ammonia slip.

![Figure 1-6 Selective Catalytic Reduction Technology](image-url)
1.8.3 NSR Catalyst Technology

Nitrogen storage/reduction (NSR) catalyst technology is a new and promising technology for NO\textsubscript{X} emission abatement from diesel engines. Reduction of NO\textsubscript{X} to N\textsubscript{2} over a NSR catalyst, as described in Figure 9, is accomplished in five sequential reaction steps [9]:

1. Oxidation of NO to NO\textsubscript{2},
2. Adsorption of NO\textsubscript{2} onto alkali and/or alkaline earth components in the form of nitrate or nitrite species,
3. Reductant evolution,
4. NO\textsubscript{X} release from nitrate or nitrite sites, and
5. Reduction of NO\textsubscript{X} to N\textsubscript{2}.

![Diagram of NSR Catalyst Technology](Figure 1-7 Overall Nitrogen Storage/Reduction reactions)
This technology operates in two phases; called lean and rich. The lean phase is normal engine operation and the exhaust gas in this phase includes CO₂, H₂O, O₂, N₂ and NOₓ species, as shown in Table 1-3. The NSR catalyst contains alkali and alkaline metal earth components, such as BaO, as NOₓ storage materials. These have the ability to store the entering NOₓ species in the form of a nitrate, Ba(NO₃)₂ and/or nitrite, Ba(NO₂)₂, during lean conditions. With time, the storage materials become saturated with NOₓ species.

Table 1-3 Diesel engine exhaust for both lean and rich phase

<table>
<thead>
<tr>
<th>Phase</th>
<th>Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean</td>
<td>H₂O, CO₂, NOₓ, O₂, and N₂</td>
</tr>
<tr>
<td>Rich</td>
<td>H₂O, CO₂, reductants (for example H₂ and CO), and N₂</td>
</tr>
</tbody>
</table>

Thus, the rich phase is needed to clean the storage materials from adsorbed NOₓ and complete the cycle, thereby beginning a new cycle where the storage species are nitrate-free and are able to adsorb entering NOₓ species again. This rich phase is also described in Table 1-3, where a key factor is the presence of reductants.

In NSR, reductants have the ability to react with NOₓ and convert it to N₂. The most commonly used reductants in NSR catalyst testing are H₂, CO, and propylene. These reductants are present in gasoline and diesel engine exhaust as a result of combustion of extra fuel and air. H₂ is the most effective reductant at low temperature, while all other reductants are comparable at high temperature[10]. When the engine switches to the rich
phase, NO\textsubscript{X} species release from the storage materials, migrating to adjacent precious metal sites, such as Pt. On metallic Pt, NO\textsubscript{X} can be reduced to N\textsubscript{2}. Proposed reactions that occur between NO\textsubscript{X} and reductants are listed below:

\[ 2H_2 + 2NO \rightarrow N_2 + 2H_2O \]

\[ 2CO + 2NO \rightarrow N_2 + 2CO_2 \]

\[ C_3H_6 + 9NO \rightarrow 4.5 N_2 + 3CO_2 + 3H_2O \]

In NSR, one cycle takes approximately \( \frac{1}{2} \) to 2 minutes, with 1 to 5 seconds for the rich phase. Overall, NSR catalysts contain both NO\textsubscript{X} storage materials, such as alkali and alkaline earth components, and precious metals, such as Pt, which account for oxidation of NO to NO\textsubscript{2} and reduction of NO\textsubscript{X} to N\textsubscript{2}. All these materials are supported on alumina (Al\textsubscript{2}O\textsubscript{3}).

Figure 1-8 Structure of a NSR catalyst
An NSR catalyst, like the TWC, is supported on a ceramic honeycomb structure to expose the maximum surface area of catalyst to the exhaust stream while minimizing the back pressure and amount of catalyst required. Figure 10 illustrates the structure of a honeycomb catalyst.

**1.8.3.1 Deactivation of NSR Catalysts**

Catalyst deactivation is a generic term used to describe a decrease in the activity of a catalyst. Catalyst deactivation is typical in most catalytic processes, but hopefully a slow phenomenon. A catalyst can be deactivated via five standard mechanisms. Each one is defined briefly in Table 1-4. These mechanisms are classically categorized into three main types: chemical, thermal and mechanical[11].

Thermal aging and sulfur poisoning are the two major mechanisms for deactivation of NSR catalysts [9]. SO$_2$ is always found in the exhaust of diesel engines. Sulfates can then form on the alkali or alkaline-earth species just as nitrates do from NO$_X$. These sulfates are more stable than the nitrates and therefore they result in less NO$_X$ storage sites available on the catalyst.

Therefore, it is critical to keep the surface sulfate concentration low, or to periodically remove sulfate build-up. The latter is called desulfation and is the accepted solution as complete S removal from fuel is not currently practical. Desulfation can be achieved by introducing a reductant such as hydrogen, but at much higher temperatures than that required to reduce the surface nitrates. The sulfur is removed via the reaction of hydrogen
with sulfur to form hydrogen sulfide \((H_2S)\). However, the requirement of high temperature ultimately results in thermal degradation of the catalyst.

Table 1-4 Mechanisms of catalyst deactivation

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Type</th>
<th>Problem</th>
<th>Cause</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fouling</td>
<td>Mechanical</td>
<td>Loss of catalytic surface sites due to formation of carbon or coke films</td>
<td>Physical deposition of species from fluid phase onto the catalyst surface and pores</td>
</tr>
<tr>
<td>Poisoning</td>
<td>Chemical</td>
<td>Loss of catalytic surface sites</td>
<td>Blockage of sites by strong adsorption of Impurity</td>
</tr>
<tr>
<td>Thermal degradation</td>
<td>Thermal</td>
<td>Loss of catalytic surface area, supported area, and transformation of catalytic phases to noncatalytic phases</td>
<td>Migration of metal particle, crystallization and/or structural modification or collapse, and active phase-support reaction</td>
</tr>
<tr>
<td>Vapor Formation</td>
<td>Chemical</td>
<td>Loss of catalytic phases</td>
<td>Reaction of gas with catalyst phase to form volatile compound</td>
</tr>
<tr>
<td>Attrition</td>
<td>Mechanical</td>
<td>Loss of catalytic materials</td>
<td>Loss of catalyst surface area due to mechanical crashing of catalyst particle</td>
</tr>
</tbody>
</table>

Thermal degradation of NSR catalysts is inevitable at the temperatures required for desulfation \((T>650^\circ C)\)[12]. Thermal degradation of NSR catalysts occur via the loss of precious metal dispersion (sintering), the loss of surface area of the NO\(_X\) storing components, and the loss of surface area of oxygen storage capacity (OSC) components. Pt and Rh, and sometimes Pd, are commonly used in NSR catalysts. They are known to
sinter easily in an oxidizing atmosphere (O₂, H₂O, in N₂) and in reducing atmospheres (H₂, H₂O, in N₂) at high temperatures [13].

Overall, a decrease in NOₓ storage capacity upon exposure to high temperature can be attributed to the following reasons. First, the storing materials, the most common example being Ba, can react with the washcoat ingredients, such as alumina resulting in a loss of trapping sites. A second reason is the loss of interface contact area between the precious metals and adsorbents because of particle growth of both [14]. Simple agglomeration of the trapping site components is another reason.

The OSC of the catalyst can be decreased as a result of particle size growth of OSC components such as ceria (Ce)[15]. These losses are on top of the loss in activity due to precious metal sintering.

1.9 Research objectives

In the research to be described, the goals were to:

1. Evaluate the effect of amount, and ratio of H₂ and CO reductants on the trapping and reduction performance of a commercial NSR catalyst.

2. Investigate the effect of thermal degradation on the performance of a commercial NSR catalyst.
Chapter 2: Literature Review

As stated, the research project had two main goals:

1. Evaluating the effect of amount and ratio of H₂ and CO reductants on the trapping and reduction performance of a commercial NSR catalyst.

2. Investigating the effect of thermal degradation on the performance of a commercial NSR catalyst.

In this section, a literature review focused on the five sequential reaction steps for NSR catalysis and the effect of thermal degradation on the performance of a commercial NSR catalyst is presented.

2.1 Overview of the NSR cycle

The NSR process cycles through two phases; a lean phase and a rich phase. In one step of the lean phase NO is oxidized to NO₂. Subsequently, NO₂ can be adsorbed by trapping materials such as Ba, in the form of Ba(NO₃)₂ and/or Ba(NO₂)₂. In operation, the lean phase continues until NOₓ starts to slip, which is an indication that the trapping materials are becoming saturated. At this point, the second phase of the cycle is typically started. In the rich phase, reductants are introduced to reduce the NOₓ species to N₂. The entire process takes approximately ½ to 2 minutes. Overall, the reduction of NOₓ to N₂ over an NSR catalyst can be described, as shown in Figure 2-1, with five sequential reaction steps.
Figure 2-1 Overall NO\textsubscript{X} cycle

2.1.1 Oxidation of NO to NO\textsubscript{2} over the noble metal component

The majority of NO\textsubscript{X} emitted in diesel engine exhaust is NO, usually around 90%, with the rest NO\textsubscript{2}. The NO oxidation reaction to NO\textsubscript{2} is the first step in the NSR process. Since NO\textsubscript{2} is trapped more readily than NO, this step is important.

\[ \text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2 \]

NO oxidation occurs on the surface of the catalyst precious metal species. Typically Pt, Pd, and/or Rh are used. Pt is the most common used due to its high red-ox activity. A comparative study [16] showed that when using Pt, the maximum conversion to NO\textsubscript{2} was 20% while no conversion was detected when using a Pd based catalyst under the conditions of the test. Although Pd and Rh have less NO oxidation activity, they have a
significant impact on NO\textsubscript{x} reduction, thus their addition [17]. Not only can the type of precious metal affect NO oxidation, but also their particle size. It has been demonstrated that as the particle size of Pt increases, NO oxidation surprisingly increases, demonstrating structure dependence. For example, as a model catalyst was exposed to high temperature treatment, to approximately 750°C, NO oxidation increased [9]. As shown in Figure 2-2, NO oxidation is a function of temperature. At low temperature, the NO oxidation rate increases as the temperature increases. The conversion under the conditions of the test described reached its maximum at approximately 350°C and then started to decrease.

![Figure 2-2](image)

**Figure 2-2** Effect of Temperature on NO oxidation. The inlet gas contained 10% O\textsubscript{2}, 330 ppm NO, 5% H\textsubscript{2}O, 5% CO\textsubscript{2} and a balance of N\textsubscript{2} and the experiment was run with a commercial NSR sample at a space velocity of 30,000 hr\textsuperscript{-1}
The decrease at high temperature is due to thermodynamic limitation; the equilibrium conversion was reached. The storage component can also hinder NO oxidation over Pt. Its presence can decrease Pt activity by covering some portion of the Pt particles[18].

2.1.2 Adsorption of NO/NO\textsubscript{2} on the trapping sites

After NO is oxidized to NO\textsubscript{2}, the NO\textsubscript{2} is adsorbed by the storage materials, which are usually alkali and alkaline earth components, such as BaO. Numerous studies [19][21] have suggested that NO\textsubscript{2} is a precursor for adsorption and nitrate formation. However, NO can also be adsorbed by trapping materials in the presence of oxygen (O\textsubscript{2}), although to a lesser extent and at slower rates. Overall, NO\textsubscript{X} is adsorbed in the form of nitrate (NO\textsubscript{3}) and/or nitrite (NO\textsubscript{2}) species on the alkali and alkaline earth components. Nitrate species, for example, have been detected when introducing NO\textsubscript{2} to Pt/Ba/Al\textsubscript{2}O\textsubscript{3} [21] while nitrites and nitrates have been detected when NO + O\textsubscript{2} was introduced at low temperature [22].

The selection of trapping materials is obviously an important factor and several have been tested, such as mixed oxides, perovskites, and inorganic oxides [20]. However, alkali and alkaline earth components show better trapping capacity due to their higher basicity. BaO for instance, is the most commonly used in NSR catalyst testing as a storage material.

Although NO\textsubscript{2} is adsorbed by trapping materials, it can also be adsorbed by the catalyst support, which is typically Al\textsubscript{2}O\textsubscript{3}. A Fourier Transform Infrared (FTIR) study [23] has shown that NO\textsubscript{2} sorbed on Al\textsubscript{2}O\textsubscript{3} when Pt/Al\textsubscript{2}O\textsubscript{3}, BaO/Al\textsubscript{2}O\textsubscript{3}, and Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalysts
were used. However, the amount of NO₂ adsorbed is small; approximately 1% of the NOₓ trapped by Ba [24].

Temperature also impacts NOₓ sorption. With increasing temperature, the thermal stability of nitrate and/or nitrite species decrease, and therefore, at temperatures greater than ~350°C, typically NOₓ storage capacity decreases. For example, in thermogravimetric analyzer (TGA) experiments, where the weight change measured represents an amount of NOₓ trapped, at 200 ºC the total change in catalyst weight was 0.431 g while, at 450°C the total change in catalyst weight was 0.135 g [9]. But, as shown in Figure 2-3, NOₓ sorption increases with temperature, until reaching approximately 350°C where it then starts to decrease. One reason for the low temperature increase is NO oxidation. As mentioned, as the amount of NO₂ increases, storage increases. NO conversion to NO₂ typically reaches a maximum at around 350ºC, helping to increase storage rates to this temperature as well. The increase in capacity as the temperature increases, at low test temperatures, also coincides with improved regeneration as temperature increases. Thus, at low temperatures, the amount of NOₓ trapped is limited by NO oxidation and efficiency in removing nitrate or nitrite species during regeneration. At high temperatures, the trapping capacity is limited by nitrate or nitrite stability.

Another factor that influences NOₓ trapping capacity is the gas composition, including components like CO₂, H₂O, and O₂, since the storage capacity is affected by the sorbate surface state. A common assumption is that BaO is the easiest to form nitrates, relative to hydroxides or carbonates [9]. The presence of CO₂ in the gas stream can produce BaCO₃ which is more stable than BaO. This increased stability can hinder nitrate and/or nitrite
species formation, which in turn will affect the trapping capacity. In one example with a Pt/K/Al₂O₃ catalyst, the trapping capacity decreased by 45% when CO₂ was added to the gas mixture[25].

Similarly, the presence of H₂O can cause decreased trapping capacity by Ba(OH)₂ formation. In the same study described above, the addition of 5% H₂O to a dry mixture caused a 16% loss in trapping capacity[9]. However, when both CO₂ and H₂O are added, the H₂O had a positive impact on NOₓ storage capacity, via the equilibrium reaction BaCO₃ + H₂O → Ba(OH)₂ + CO₂. The carbonate is more stable than the hydroxide, so additional hydroxide relative to carbonate resulted in better trapping performance.

The presence of O₂ also can influence the trapping capacity via oxidation of NO to NO₂ as well as oxidation of surface NOₓ to nitrates. It has been shown [26] that as O₂ concentration increases, the NOₓ storage capacity increases.

Several mechanisms have been suggested for NOₓ adsorption. In the below listed mechanisms, Ba has been taken as an example for alkali and alkaline earth components. It does not necessarily mean that Ba is the only component that can adsorb NOₓ; but is used as a representative trapping component. Hydroxide and carbonates are also present, but the oxide is selected as an example.

- NO reacts with Ba oxide to form nitrate [24]
  \[ \text{BaO} + 2\text{NO} + 3\text{O} \rightarrow \text{Ba(NO}_3\text{)}_2 \]

- NO₂ reacts with barium peroxide to form nitrate [27]
  \[ \text{BaO}_2 + 2\text{NO}_2 \rightarrow \text{Ba(NO}_3\text{)}_2 \]
- NO₂ reacts with BaO to form nitrate and nitrite species [28]

\[ 2\text{BaO} + 4\text{NO}_2 \rightarrow \text{Ba(NO}_2)_2 + \text{Ba(NO}_3)_2 \]

- NO₂ reacts with BaO to form nitrate and NO [9]

\[ \text{BaO} + 3\text{NO}_2 \rightarrow \text{Ba(NO}_3)_2 + \text{NO} \]

![Graph](image)

**Figure 2-3** NOₓ Storage Capacity. The reactant gas was composed of 10% O₂, 330 ppm NO, 5% H₂O, 5% CO₂ and a balance of N₂ at a space velocity of 30,000 hr⁻¹ using a commercial NSR catalyst.

### 2.1.3 Reductant evolution

Trapping decreases with time as the trapping sites become saturated as nitrate and/or nitrite species. Consequently, the catalyst needs to undergo periodic regeneration to remove the adsorbed NOₓ, and hopefully reduce these to N₂. This can be achieved by
introducing reductants and removing the O₂, resulting in a net-reducing environment. The reductants can be introduced in a few ways. One is via adjusting combustion so that they exit with the rest of the exhaust. Thus, for the rich phase, more fuel is injected into the engine, which in turn increases the amount of reductant. Enough fuel must be added so that more reductant exits than O₂, thus the stream is reductant rich. The most widely used reductants in NSR catalyst testing are hydrogen, carbon monoxide, and propylene, the former two observed in rich engine exhaust and the last representing hydrocarbons, also observed. Hydrogen is superior for NOₓ reduction with NSR catalysts at lower temperatures compared to carbon monoxide and propylene; however, they are all comparable at higher temperature.

Carbon monoxide has been tested as a reductant for NOₓ due to its presence in diesel engine exhaust when the engine is run rich[29]. Carbon monoxide can reduce NOₓ directly or indirectly. It can be used directly via reaction with NOₓ: 2 CO + NO \rightarrow N₂ + CO₂. While indirectly it can participate in the water gas shift (WGS) reaction; CO + H₂O \rightarrow CO₂ + H₂. The produced H₂ then reacts with the NOₓ. It has been demonstrated [11],[30] that the WGS reaction occurs over precious metals and is therefore expected to occur over NSR catalysts as well [31].

Although CO is a reductant for NOₓ at higher temperatures, it can poison Pt at lower temperatures. Therefore, NO oxidation and NOₓ reduction steps can be affected at low temperature when CO is present.
Propylene can break down to smaller components that in turn can act as reductants. Propylene is comparable with hydrogen and carbon monoxide at higher temperature in NSR regeneration.

The effect of reductant mixtures on the overall performance of a NO\textsubscript{X} trap catalyst has been investigated by Szailer and coworkers\cite{32}. They found that when mixtures of CO and H\textsubscript{2} were used at low temperature (~147\textdegree C), low NO\textsubscript{X} reduction was achieved in comparison with using only H\textsubscript{2}. They attributed the poor NO\textsubscript{X} reduction when using the mixture to reductant competition for adsorption sites on Pt particles. With stronger CO bonding, the surface H\textsubscript{2} concentration would be lower in the presence of CO and if conditions favor reduction with H\textsubscript{2} instead of CO, the NO\textsubscript{X} reduction rate would be lowered. They also showed that NO\textsubscript{X} conversion was higher with mixtures of H\textsubscript{2} and CO in comparison to just CO as the reductant under otherwise identical conditions. With only CO as the reductant, NCO and CO\textsubscript{2} species were formed. And in the presence of H\textsubscript{2}, the resultant H\textsubscript{2}O hydrolyzed the NCO to form the intermediate that ultimately decomposed to N\textsubscript{2} and H\textsubscript{2}O. Overall, as would be expected, literature evidence suggests that the reduction efficiency of the different reductants depends on its activation on the surface.

The amount of reductant also of course has an impact on NO\textsubscript{X} reduction. Furthermore, reductants are not only required to reduce the trapped NO\textsubscript{X}, but they are also consumed by stored oxygen as will be discussed in further detail in the results section. Consequently, the amount of reductant needed is dependent on surface oxygen, the more stored oxygen, the more reductant required.
2.1.4 NO\textsubscript{X} release

Release of NO\textsubscript{X} from the catalyst surface occurs via two paths [9]. The first is due to heat caused by the exothermic reaction between the entering reductant and any surface oxygen. The more oxygen on the surface, the more heat will be generated. The associated temperature rise may be enough to decrease the stability of the surface nitrate or nitrite species. The second reason for NO\textsubscript{X} release is the change in gas composition with the switch to the rich phase. With an absence of NO and O\textsubscript{2}, the stability of nitrate and/or nitrite species are reduced.

NO\textsubscript{X} release is a function of temperature. For example, at lower temperatures, the release of NO\textsubscript{X} is strongly dependent on the degree that the catalyst can activate the reductants [9]. As the temperature increases, the capability of reductants to reduce NO\textsubscript{X} to N\textsubscript{2} should increase and the release of observed NO\textsubscript{X} in the outlet gas should decrease. While, at higher temperatures, around 350°C and above, where the activation of reductant is not an issue, the weak stability of nitrate species is the main cause for observed NO\textsubscript{X} release [9].

Realize that for reduction to occur, release must occur first. So, observed NO\textsubscript{X} in the outlet during regeneration is actually released and unreduced NO\textsubscript{X}, whereas even if none is observed being released in the outlet gas, a substantial amount might have been released but most reduced.

As mentioned above, another factor that can affect the release of NO\textsubscript{x} is the exhaust gas composition. Via thermodynamic-based calculations, it has been predicted [33] that there is a direct correlation between the amount of carbon dioxide and the stability of NO\textsubscript{X} species. The more carbon dioxide present, the more NO\textsubscript{X} released from trapping sites
under otherwise identical conditions. This could be due to the competition between carbonate and nitrate formation/stability.

Oxygen also has an impact on the release of NO\textsubscript{X}. It was demonstrated by Liu and Anderson [34] that oxygen enhances the stability of nitrate and/or nitrite species. Therefore, upon switching to the rich phase, where little or no oxygen is introduced, the nitrate and/or nitrite species will destabilize. This leads to nitrate and/or nitrite species decomposition and NO\textsubscript{X} release to hopefully be reduced on adjacent precious metal sites or find their way out of the catalyst without being reduced. If O\textsubscript{2} remains present, then some nitrate species may remain stable enough to not decompose and not result in NO\textsubscript{X} release.

Water also has a significant influence on NO\textsubscript{X} release [33][35]. Epling et al [35] have investigated the influence of the presence and absence of H\textsubscript{2}O in the gas stream. They found that the presence of H\textsubscript{2}O in the gas stream lowered the magnitude of NO\textsubscript{X} release in the outlet gas. This could be related to displacement of carbonate groups by hydroxyl groups.

Impacting the overall conversion of NO\textsubscript{X} is the release of any unconverted NOx. Overall, the observed unconverted NO\textsubscript{X} is due to slower reduction at precious metal sites, compared to Ba nitrite/nitrate decomposition[36]. This is more significant at higher temperatures due to nitrate stability.

Contributing to this is the proximity of Pt sites to the alkali and alkaline earth components [8]. It is speculated that it is easier to reduce NO\textsubscript{X} molecules that are released
from trapping sites near to the Pt. For trapping sites further from Pt, NO\textsubscript{X} can readsorb after release or will exit with the gas stream.

### 2.1.5 Reduction of NO\textsubscript{X} to N\textsubscript{2}

Reduction of NO\textsubscript{X} to N\textsubscript{2} is the last step in the overall NSR cycle description. In this step, the NO\textsubscript{X} stored during the lean phase and then released at the onset of the rich phase is reduced to N\textsubscript{2} over the precious metals. Two main mechanisms have been proposed for reduction of NO\textsubscript{X} to N\textsubscript{2} on the precious metal sites of NSR catalysts. The first mechanism postulates that the reductant reduces the precious metal site. Afterward, the reduced precious metal site participates in NO decomposition. As part of this mechanism, James et al [37] suggested that Pt size can plays an important role in NO\textsubscript{X} reduction. They postulated that small Pt particles are unable to dissociate NO effectively because they form the oxide species more readily. The second mechanism, supported by Olsson et al [38], proposes that the reductant is activated on the precious metal and reacts directly with NO\textsubscript{X}:

\[
\begin{align*}
C_3H_6 (g) + Pt & \rightarrow Pt-C_3H_6 \\
Pt-C_3H_6 +2Pt & \rightarrow 3 Pt- CH_2 \\
Pt-CH_2 + 3Pt-NO & \rightarrow 4 Pt + CO_2 (g) + H_2O (g) + 1.5 N_2 (g)
\end{align*}
\]

Reductant type and amount, temperature, and lean/rich time ratio are known to affect NO\textsubscript{X} reduction. Abdulhamid et al [39] did a comparative study between H\textsubscript{2}, CO, C\textsubscript{3}H\textsubscript{6}, and C\textsubscript{3}H\textsubscript{8} for reduction of NO\textsubscript{X} over BaO/Al\textsubscript{2}O\textsubscript{3} samples containing Pt, Pd, or Rh. The results of this study showed that H\textsubscript{2} and CO are superior for NO\textsubscript{X} reduction in comparison
to hydrocarbons, C₃H₆, and C₃H₈, especially when Pt/BaO/Al₂O₃ was used. Another comparative study between H₂, CO, and a mixture of H₂ and CO as a reductant source over Pt/Al₂O₃ and Pt/BaO/Al₂O₃ catalysts was performed by Szailer et al [30] using FT-IR and X-ray Diffraction (XRD) measurements. The results showed that H₂ was more efficient than CO and a mixture of H₂ and CO on NOₓ reduction, especially at a temperature of 150°C. Furthermore, as mentioned above, CO is inefficient at lower temperature likely due to Pt site poisoning, hindering the release and reduction of NOₓ. Experiments have been performed to investigate the effect of combining CO with H₂ [40]. In their first experiment, where 2.25% CO was introduced with 0.75% H₂ as a reductant source at 200°C, the overall conversion attained was approximately 40% while in the second experiment when only 3% CO was used, the overall conversion was achieved was 22%. Furthermore, it has been shown that [41] combining CO with H₂ at lower temperatures also hampers the effect of H₂ on NOₓ reduction over a Pt-Rh/Ba-based NSR catalyst.

The amount of reductant of course has an effect on NOₓ reduction. Bailey et al [42] demonstrated that increasing the amount of CO during the regeneration phase resulted in an improvement in overall NOₓ reduction under the conditions tested.

2.2 Effect of thermal degradation

NSR is a promising technology to mitigate NOₓ emissions. However, a significant challenge that questions their long-term durability is poisoning by sulfur compounds present in the exhaust[43]-[49]. The problem is that sulfur will lead to sulphates on the
catalyst surface, with these sulphates forming where nitrates should form during trapping/storage. Furthermore, these sulphates are thermodynamically more stable than nitrates [50][51].

Several studies have evaluated the influence of sulfur on the performance of NSR catalysts. For Ba-based NSR catalysts, it has been shown that the presence of SO₂ and O₂ in the lean phase forms surface sulfates on storage components, which later migrate into the bulk phase [52]. These sulphates hinder the adsorption of NOₓ species on the surface of Ba [53] and hence NOₓ storage capacity decreases during subsequent cycles. H₂S and COS that are present in the rich phase are also harmful and under certain conditions are even worse for decreasing the performance of trapping materials [43]. H₂S and COS will be oxidized to SO₂ in the lean phase where the oxygen is in excess, but they reside on the precious metal sites during the rich phase. With their oxidation, they poison sites next to the Pt, which is proposed as more efficient in trapping than sites further away [54]. Sulfur was also found to interact strongly with alumina on alumina-based NSR catalysts to form Al₂(SO₄)₃ [55]. SO₂ can react with other catalyst components, such as ceria, and has a negative effect on water gas shift and steam reforming reactions [56].

Beyond forming sulphates, via interaction with the trapping materials, sulfur influences precious metal activity as well. For example; sulfur characterization studies have shown that during rich conditions, Pt can interact with sulfur forming a layer of sulfur on Pt [44]. With sulfur in the gas feed in testing a Pt-based NSR catalyst, the NO oxidation and reduction were activity decreased after a few cycles at 350°C [56]. The authors attributed the drop in the oxidation and reduction activity to poisoning of Pt by
SO\textsubscript{2} and SO\textsubscript{2} derived species. Such site blocking had been previously proposed [57]. NO oxidation is more severely affected by sulfur at lower temperatures than higher temperatures. This has been attributed to two possible reasons [9]. First, the rate of Pt-S decomposition increases as the temperature increases, so the impact of S on NO oxidation will diminish since there is less Pt-S interaction. Second, between 350 and 400ºC, the stability of S species on the alumina support decreases, such that S desorption would take place. But, S species could be readorsbed, forming stronger bonds on Pt or Ba.

To maintain performance, sulfur compounds need to be removed from the catalyst in order to regain its activity. To remove sulfur compounds, NSR catalysts require an intermittent high-temperature exposure to a reducing environment[48][51]. This desulfation protocol ultimately, however, results in thermal degradation of the catalyst. The thermal degradation can include the loss of precious metal dispersion (sintering), the loss of surface area of NO\textsubscript{X} storing components, and the loss of surface area of oxygen storage capacity (OSC) components.

Desulfation temperatures can reach 700ºC [12], resulting in deactivation by sintering of the noble metals that are present in NSR catalyst formulations for oxidation and reduction of NO\textsubscript{X}. For example, Graham and coworkers [58] investigated the effect of temperature and exposure to oxidizing versus reducing conditions on Pt particle size changes with a Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst. The authors found that Pt agglomeration occurred when the sample was exposed to an oxidizing atmosphere for three hours at temperatures as low as 600ºC. On the other hand, no significant change in Pt size was observed even when the catalyst was exposed to high temperature at 950ºC but in a reducing
atmosphere. Another study also investigated the effect of reducing versus oxidizing conditions on Pt/Al₂O₃ and Pt/Ba/Al₂O₃ model catalysts [59]. A Pt/Al₂O₃ catalyst was exposed to both reducing and oxidizing conditions at temperatures between 670 and 1041°C. The increase in the Pt particle size was observed after exposure to oxidizing conditions beginning at 763°C and increased with temperature, while less change in particle size was observed under reducing conditions in comparison with oxidizing environment. On the Pt/Ba/Al₂O₃ model catalyst, the sample was exposed to both reducing and oxidizing conditions at 900°C for 7 hours. Again, little change in Pt size was observed with reducing conditions while growth in Pt size was readily observed with oxidizing conditions. Furthermore, a Pt/Rh based NSR catalyst was evaluated after aging at 800 and 900°C with 10% H₂O and 90% air [60]. The authors found severe sintering of Pt. The above discussion shows that Pt particle size is affected by high temperature exposures; however, oxidizing environments seems to have more effect on Pt size than reducing environment.

Another reason for the degradation in the performance of NSR catalysts with high temperature exposure is the loss of surface area of the NOₓ storage components. Studies with a Pt/Ba/Al₂O₃ catalyst have shown that when the catalyst was thermally aged at 750°C for 24 hrs, the NOₓ conversion dropped from 86% to 55% due to a decrease in the storage capacity. They reported that the decrease in the storage capacity could occur via two possible pathways. The first is due to the reaction of the trapping component with the washcoat material[61][62]. For example, in testing four catalysts types, Pt/Al₂O₃, Ba/Al₂O₃, Pt–Ba/Al₂O₃, and a physical mixture of Pt/Al₂O₃ + Ba/Al₂O₃, Jang et al [63] found that the deterioration in the catalyst NSC capacity arising from thermal aging in all
Ba-based catalysts was attributed to a phase transition of BaO into a Ba–Al solid alloy. That transition occurred above 600°C and ultimately became more stable BaAl₂O₄ at above 950°C. Another study investigated the effect of lean/rich thermal cycling on a Pt / “Ba+K” based NSR catalyst at 700, 800, 900 and 1000°C [64]. It was found that as the thermal aging temperature increased, the catalyst performance decreased. The drop in the catalyst performance after each incremental increase in aging temperature was attributed to several reasons. For example, at 700 and 800°C, the transition of \( \gamma \)-Al₂O₃ to \( \delta \)-Al₂O₃, which has lower specific area, as well as agglomeration of both K and Ba, were observed. At 830°C, a significant amount of K migrated toward the cordierite substrate. As the temperature increased to 1000°C, even more severe deterioration in catalyst performance was observed. The authors attributed this final effect to the reaction of BaCO₃ with the catalyst washcoat to form BaAl₂O₄. Such a transformation to BaAl₂O₄ has actually been reported as low as 800ºC [65]. The second reason for decrease in the storage capacity is a loss in interface contact between the precious metals and trapping components because of particle size growth of both[51][63]. Toops et al [51] investigated the thermal aging of a Pt/Rh/Ba/\( \gamma \)-Al₂O₃ catalyst under lean/rich cycling at 600, 700, and 800°C. They reported that the catalyst capacity to store NOx decreased when the catalyst was exposed to 800°C due to agglomeration of adsorbent materials such as Ba. Thermal aging can also induce a decrease in the catalyst OSC[66], likely due to a loss in the surface area of the OSC components. Ceria, for example, is a well-known OSC component that is present in three-way catalysts (TWC) and has been shown to promote NSR catalyst performance[67]. The loss in OSC via thermal aging can occur via growth of OSC component crystallites [15] when they are exposed to high temperature, which would lead to less oxygen stored on
the ceria[65]. Another possibility is again the reaction of OSC components with the catalyst support. For example [68]in characterizing CeO$_2$/Al$_2$O$_3$ samples, the formation of CeAlO$_3$ upon reduction in H$_2$ at temperatures higher than 600°C has been observed.
Chapter 3: Experimental work

3.1 Experiment Description

3.1.1 Feed and delivery system

For the research done, the typical operating conditions and gas compositions of diesel engine exhaust have been simulated, excluding particulate matter and sulfur compounds. The gas compositions were obtained by mixing gases from gas cylinders supplied by Praxair. The experiments were carried out with a total flow of 14.32 L/min or a space velocity of 30000 h\(^{-1}\). The typical compositions of the lean and rich flows are listed in Tables 3-1 and 2.

As mentioned in the previous two sections, this technology cycles through two phases; a lean and a rich phase. The lean phase is the normal diesel engine operation where the NO\(_X\) is trapped while the rich phase is the regeneration phase where the reductant is introduced to reduce stored NO\(_X\) to N\(_2\). Each of the two gas compositions was set using Bronkhorst mass flow controllers controlled via a LabVIEW program.

The gas mixtures entered a four-way solenoid valve that was also controlled by the LabVIEW program. Simply, this valve allows either the lean or the rich mixture to flow to the reactor while the other is vented to an exhaust. The mixture directed to the reactor is mixed with water vapor downstream of the 4-way valve. The water was introduced as steam using a Bronkhorst vaporizing system. After water introduction the gas mixture is directed through an insulated line, which is also wrapped by a heating cord to compensate...
for heat loses to the environment. A pre-heater section after the water introduction is used to heat the gas to the target test temperature, prior to entering the reactor itself.

### 3.1.2 Reactor

The experiments were performed in a bench-scale reactor. The catalyst was wrapped with high-temperature Zetex insulation and inserted into a quartz tube. The insulation was used to cover the gap between the catalyst and the wall of the tube to ensure that no gas slipped around the sample. The quartz tube was then inserted into a horizontal tube furnace. Two K-type thermocouples were placed at the radial center of the catalyst; one just inside the inlet face of the catalyst and one just inside the outlet face of the catalyst. Another two were placed ~ ½ inch upstream and downstream of the sample. A picture of the reactor and the catalyst is shown in Figure 3-1. The gases exiting the reactor were maintained at >190°C to avoid condensation and NH₃ hold-up. The outlet gas mixture concentrations were constantly detected with an FT-IR analyzer described below.

![Figure 3-1 Reactor and catalyst section](image-url)
3.1.3 Gas analysis:

Fourier Transform Infrared (FT-IR) spectroscopy was used to measure outlet gas concentrations. The instrument used is a MKS MultiGas™ 2030. It has four main components; a fourier transform infrared spectrometer, a gas cell, an optics box containing an infrared detector, and associated transfer optics, and supporting electronics. In our experiments, CO, CO₂, NO, NO₂, N₂O, NH₃, and H₂O gas concentrations were measured.

Principle of Operation

When the gas sample passes through the gas cell, some of infrared radiation is absorbed by the gas molecules. For each gas in the sample, molecular bonds vibrate at various frequencies based on the type of chemical bond and the strength of that bond. The absorption spectrum is different for each infra-red-active gas. The MultiGas analyzer converts these absorption spectrums to concentrations using its analysis algorithms and pre-loaded calibrations.

3.1.4 Catalyst

A commercial NOₓ storage/reduction catalyst was used in these experiments, supplied by a catalyst vendor who requested their name not be used yet in public communications. The catalyst was supported on a ceramic honeycomb cordierite structure. The sample was removed from a larger monolith block which had a cell density of 300 cpsi. The sample used was 0.912” in diameter with a length of about 3”. 

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3.2 Process Flow Schematic

Figure 3-2 Process Flow schematic
3.3 Experiments Types:

3.3.1 Influence of reductant type and amount on the performance of a commercial NSR catalyst

The objective of this set of experiments was to evaluate the effect of amount and ratio of CO and H\textsubscript{2} on the trapping and reduction of NO\textsubscript{X} at different temperatures; 200 to 500\degree C. The compositions of the lean and rich flows for these experiments are listed in Tables 3-1 and 2.

**Table 3-1 Typical composition of the lean and rich flows**

<table>
<thead>
<tr>
<th>Flow conditions</th>
<th>Sorption (lean)</th>
<th>Regeneration (rich)</th>
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</thead>
<tbody>
<tr>
<td>Space velocity</td>
<td>30,000/h</td>
<td>30,000/h</td>
</tr>
<tr>
<td>NO</td>
<td>330 ppm</td>
<td>0 ppm</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>10%</td>
<td>0%</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>0%</td>
<td>see table 5</td>
</tr>
<tr>
<td>CO</td>
<td>0%</td>
<td>see table 5</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>Balance</td>
<td>Balance</td>
</tr>
<tr>
<td><strong>Temperature (\degree C)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>60 sec</td>
<td>5 sec</td>
</tr>
<tr>
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<td>150 sec</td>
<td>5 sec</td>
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<tr>
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</tr>
<tr>
<td>500</td>
<td>120 sec</td>
<td>5 sec</td>
</tr>
</tbody>
</table>
Table 3-2 Hydrogen and carbon monoxide concentrations and ratios

<table>
<thead>
<tr>
<th>Hydrogen (H₂) %</th>
<th>Carbon monoxide (CO) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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</tr>
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<td>2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

Before each experiment, the sample temperature was ramped to 500°C with 5% H₂O, 5% CO₂, and a balance of N₂ and then the catalyst was cleaned with a regeneration mixture consisting of 5% H₂O, 5% CO₂, 1% H₂, and a balance of N₂ for 15 min. The reactor was then cooled to the target test temperature. Experiments were performed at 200, 300, 400 and 500°C with a space velocity, at standard conditions, of 30,000 hr⁻¹.

3.3.2 Effect of thermal degradation on the performance of a commercial NSR catalyst

The aim of this set of experiments was to investigate the effect of thermal degradation on the performance of a commercial NSR catalyst. The performance changes were evaluated
after exposing the sample to air with 2% H₂O at 600, 650, 700 and 750°C. Performance change measures include NOₓ storage capacity, water-gas-shift reaction extent, NO oxidation, oxygen storage capacity, and NOₓ conversion under cycling conditions.

3.3.2.1 NOₓ storage capacity

After the sample was cleaned at 500°C and then cooled to the test temperature, the sample was exposed to the same conditions as those of the lean phase in the cycling experiments. This was ended once a steady value of 330 ppm NO + NO₂ was measured at the outlet. The number of moles of NOₓ stored in the catalyst at each temperature can then be calculated:

- Stored NOₓ (ccm) = Total NOx in – Total NOₓ out

3.3.2.2 Water-gas-shift reaction

In this set of experiments, 10 to 15 cycles were repeated at the 4 standard test temperatures. A lean period of 60 seconds and a rich period of 30 seconds were used, with the lean composition containing 10% O₂, 5% CO₂, 5% H₂O and a balance of N₂ and the rich phase containing 1% CO, 5% CO₂, 5% H₂O and a balance of N₂. The water-gas-shift reaction extent values were calculated after steady-state CO and CO₂ values were reached:

\[
\text{CO Conversion} = \frac{\text{Inlet CO} - \text{Outlet CO}}{\text{Inlet CO}} \times 100
\]
3.3.2.3 NO oxidation to NO₂

The objective of this set of experiments was to evaluate NO to NO₂ oxidation as a function of temperature. The experiments were carried under the same lean phase conditions as those used in the cycling experiments. The temperature was stepped upward in 25°C increments from 150 to a temperature where equilibrium limitations were reached. This occurred approximately between 375 and 425°C. The NO₂ conversion was calculated after a steady value of 330 ppm NO + NO₂ was reached:

\[
\text{NO}_2 \text{ conversion} = \frac{\text{NO}}{\text{NO} + \text{NO}_2} \times 100
\]

3.3.2.4 Oxygen storage capacity

The objective of this set of experiments was to evaluate the oxygen storage capacity (OSC) of the catalyst. In this set of experiments, 10 to 15 cycles were repeated at the 4 standard test temperatures. A lean period of 60 seconds and a rich period of 30 seconds were used, with the lean composition containing 10% O₂, 5% CO₂ and a balance of N₂ and the rich phase containing 1% CO, 5% CO₂ and a balance of N₂. To remove the effect of the water-gas-shift reaction on the oxygen storage capacity, water was not used in these experiments. Oxygen storage capacity was calculated from the amount of CO converted:

- \( \text{CO (moles)} = \frac{\text{CO pulse} \times 143200 \text{ ccm} \times 1 \text{ min} \times 1 \text{ mole}}{1000000 \text{ ccm} \times \text{ min} \times 60 \text{ sec} \times 22400 \text{ ccm}} \)
- \( \text{CO Converted (moles)} = \text{Inlet CO} - \text{Outlet CO} \)
- \( \text{O}_2 \text{ Stored (moles)} = \frac{\text{CO Converted (moles)}}{2} \)
4.1 Effect of regeneration phase H₂ concentration on the storage and reduction of NOₓ

Outlet NOₓ (the sum of NO + NO₂) concentrations obtained using different H₂ concentrations with an inlet temperature of 200°C are shown in Figure 4-1. For this set of experiments, the lean, or trapping, time was 60 seconds and the rich, or regeneration, time was 5 seconds. The conversions and amounts of NOₓ trapped and released for these experiments are listed in Table 4-1. All reported values and plotted data were obtained once steady cycle-to-cycle performance was observed. With no reductant added, and after a steady cycle-to-cycle trend was attained, the calculated conversion was 0.25%, close to the expected nil conversion with no reductant at such a low temperature. With the addition of reductant, 1.5% H₂ in the first step, the overall NOₓ conversion reached 77% and with 3% H₂, the NOₓ conversion increased to 85%. With further H₂ addition, little change in performance was observed; the conversion increased from 85 to 86.5% with the increase from 3 to 5% H₂. With each increase in H₂ concentration in the regeneration phase, the amount of NOₓ trapped increased. This is due to increased catalyst regeneration with additional H₂. Thus, since the catalyst is being more deeply regenerated, more NOₓ can be trapped in the subsequent lean phase, resulting in the increased trapping observed once steady performance was obtained. And although more NOₓ was trapped in the lean phase, with additional H₂, the amounts released during the regeneration also decreased, to an extent that with 5% H₂, 99% of the NOₓ trapped in the
previous lean phase was reduced. This is explained by the excess amount of H₂ relative to inlet NOₓ. The total inlet NOₓ was 0.21 m mole. With 5% H₂, 2.66 m moles of H₂ were introduced to the catalyst during the 5 second regeneration period. The reduction equation is assumed as follows; Ba(NO₃)₂ + 5H₂ → N₂ + BaO + 5H₂O. Therefore for 2 moles of NOₓ trapped, 5 moles of H₂ are required for reduction to N₂, or 0.53 m moles to reduce all the entering NOₓ. However, at 200°C, 0.99 m moles of H₂ are also needed to consume surface oxygen on this sample, which is considered associated with oxygen storage capacity (OSC). The OSC values in the range of 200 and 500°C are listed in Table 4-2, as O₂ equivalent. As a result, 1.67 m moles of H₂ remain for nitrate reduction, still in excess amount relative to the inlet NOₓ. However, 1.5% H₂ is insufficient to account for both the OSC and entering NOₓ, one factor contributing to the lower efficiency observed.

\[ \text{Ba(NO}_3\text{)}_2 + 5\text{H}_2 \rightarrow \text{N}_2 + \text{BaO} + 5\text{H}_2\text{O} \]

**Figure 4-1** NOₓ outlet concentrations obtained when testing the sample at 200°C with 0, 1.5, 3 and 5% H₂ in the regeneration phase.
Similar experiments were carried out at 300°C and 500°C to investigate the influence of temperature on the storage and reduction of NO\textsubscript{X} as a function of reductant level. The outlet NO\textsubscript{X} concentration profile for a set of 150 second storage and 5 second regeneration periods at 300°C are shown in Figure 4-2. The changes in overall NO\textsubscript{X} performance, trapping and reduction as a function of H\textsubscript{2} concentration are also listed in Table 4-1.

In the absence of reductant, and after steady cycle-to-cycle performance, the calculated conversion was 1%, again close to the expected value of 0. With the addition of 1.5% H\textsubscript{2}, the NO\textsubscript{X} conversion attained was 50.5%. The calculated inlet NO\textsubscript{X} during the 150 second lean period was 0.53 mmoles and the required H\textsubscript{2} to reduce this amount if all was trapped, assuming nitrate formation, should be 1.33 mmole. Therefore, 1.5 % H\textsubscript{2}, or about 0.8 mmoles input during 5 seconds, is insufficient amount to reduce inlet NO\textsubscript{X}. This also does not account for that needed to consume the OSC.

Some conversion is observed though, due to the integral nature of such a catalyst system. The entering H\textsubscript{2} does likely first interact with the OSC at the inlet of the sample. Once that OSC is consumed, the entering reductant can reduce nitrates at the inlet portion, where no remaining reactive surface oxygen exists. With the addition of 3% H\textsubscript{2}, the NO\textsubscript{X} conversion increased to 98%. When the H\textsubscript{2} concentration was increased from 3% to 5%, little overall performance change was observed. The NO\textsubscript{X} conversion, trapping and release were all similar.
The outlet NO\textsubscript{X} concentration profiles obtained at 500°C are shown in Figure 4-3. In the absence of reductant, the NO\textsubscript{X} reduction efficiency was calculated to be 2.5%, slightly higher than our typical error and therefore may be due to NO decomposition on the surface at the onset of the lean phase when Pt is reduced. When the H\textsubscript{2} concentration was increased to 1.5%, the overall performance of the catalyst increased to 32% and was further improved to 52% and 66.5% with 3% and 5% H\textsubscript{2}, respectively. It is apparent from the data in Figure 4-3 that the primary differences in observed outlet NO\textsubscript{X} concentration occur during the early stages of trapping for the three tests that included H\textsubscript{2}. At the end of the storage period, upon switching to the regeneration period, the difference in outlet NO\textsubscript{X} concentrations are small, as all the available trapping material, for 500°C trapping, has become saturated and the outlet concentration has approached the inlet value. In addition, at the beginning of the trapping phase, the NO\textsubscript{X} level did not reach 0 ppm for
the 1.5 and 3% H₂ levels. This indicates that although the rates of reaction are rapid due to the elevated catalyst temperature, the reductant amount is apparently still critical for the trapping performance. Previous work has demonstrated that Ba nitrates on Ba/Al₂O₃ samples decompose between approximately 350 and 475°C [69]. Furthermore, Pt catalyzes the decomposition of nitrate species [70], at least those in close proximity to the precious metal site, suggesting that even lower temperatures would be needed to release surface NOₓ. However, the catalyst maintained some performance at 500°C, indicating that the catalyst being tested has some high-temperature performance built into the formulation. The rate of decomposition is still rapid however, and therefore the rate of reductant delivery should be critical. Indeed, NOₓ release decreased when the H₂ concentration increased indicating that delivery rate was important.

![Graph](image)

**Figure 4-3** NOₓ outlet concentrations obtained when testing the sample at 500°C with 0, 1.5, 3 and 5% H₂ in the regeneration phase.
Table 4-1 calculated performance characteristics as a function of temperature, and amount of CO and/or H₂

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reductant (%)</th>
<th>NOₓ Conversion (%)</th>
<th>NOₓ Trapped (μmoles)</th>
<th>NOₓ Released (μmoles)</th>
<th>NH₃ Released (μmoles)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
<td>H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
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<tr>
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</table>
When the H\textsubscript{2} concentration was increased from 3\% to 5\% at 200 and 300°C, little difference in NO\textsubscript{X} trapping was observed, while at 500°C a significant difference was noted.

At 500°C, the weaker stability of nitrate species and higher OSC contribute to the observation that increasing the reductant amount from 3 to 5\% still has a pronounced effect. For example, at 500°C, the OSC was 1.10 mmoles and the amount of NO\textsubscript{X} trapped was 0.36 mmoles during 5\% H\textsubscript{2} tests. With 5\% H\textsubscript{2}, 2.66 mmoles of H\textsubscript{2} were introduced to the catalyst during the 5 second regeneration period. 0.72 mmoles of H\textsubscript{2} are needed for reduction of the nitrate and 2.2 mmoles are needed to consume surface oxygen. Using 3\% H\textsubscript{2} obviously leads to even less sufficient reductant delivery.

The NO\textsubscript{X} trapping and reduction performance at 500°C was poor in comparison with 200 and 300°C. As observed in Figure 4-3, NO\textsubscript{X} breakthrough increased sharply after just 50 seconds of trapping time. The poorer performance of the catalyst at 500°C can be primarily attributed to the thermal stability of nitrate and/or nitrite species[71]. Although NO oxidation is also thermodynamically limited at this high test temperature, NO\textsubscript{2} was observed in the outlet, indicating this should not limit trapping. Similar to adsorption/desorption rates, the formation and decomposition rates of the nitrates have different dependencies on temperature, and as the temperature is increased the decomposition rate gains significance. Therefore, although there is no inhibition to nitrate formation at such high temperatures, less of the trapping material is used due to the rapid establishment of surface nitrate/gas-phase NO\textsubscript{X} equilibrium. At lower temperatures the decomposition rate is not as significant, shifting equilibrium between the surface and gas-
phase species, thus allowing more availability of the trapping material. Therefore, at lower temperatures an equilibrium would also eventually be achieved, but at higher usage than that observed at 500°C.

At 500°C, a significantly higher amount of NO\textsubscript{X} was released in comparison to 200 and 300°C. For example, with 3% H\textsubscript{2}, 2 μmoles were released at 200°C, 0.1 μmoles at 300°C and 98.7 μmoles at 500°C. Nitrate instability, or rapid nitrate decomposition at the elevated temperature, caused this performance loss[72]. Furthermore, upon switching from the lean to rich phase, the partial pressure of oxygen drops to zero in these experiments, decreasing the stability of the nitrates further[34].

Compounding this loss in performance, via a loss in stability, heat is generated via the exothermic reaction between the reductants entering and stored oxygen on the catalyst surface upon the switch from lean to rich. This generated heat raises the surface temperature, further affecting the thermal stability of the nitrate species. Release of the NO\textsubscript{X}, or decomposition of the nitrates to an intermediate NO\textsubscript{X} species, is ideally accompanied by reduction on adjacent noble metal sites.

The rate of NO\textsubscript{X} reduction also increases with temperature, but there is competition for the reductant between OSC consumption and the NO\textsubscript{X} reduction reaction and therefore the actual delivery rate of the reductant to the NO\textsubscript{X} reduction sites are not high enough. Therefore, the rapid decomposition of the nitrates at the higher operating temperature results in the observed, large release in Figure 4-3, because enough reductant is not immediately available coincident with the large and rapid release from the surface.
The increase in temperature from 200 to 300°C did result in increased NO\textsubscript{X} conversion. This has been attributed to several reasons. First, from a kinetics perspective, NO oxidation to NO\textsubscript{2} increases with temperature \cite{73}. In general, a maximum in NO oxidation is attained between 300 and 400°C over these catalyst types, being ultimately limited by thermodynamics. As a result, going from 200 to 300°C, the NO\textsubscript{2} amount will be increased at the catalyst surface resulting in higher adsorption rates, as NO\textsubscript{2} has been demonstrated as more favorable for trapping by the alkali and alkaline earth species. A second reason for the higher NO\textsubscript{X} storage and reduction performance at 300°C is the decreased thermal stability of nitrate species. When the nitrate species are too stable, NO\textsubscript{X} may not be released upon switching from the lean to rich phase. Without release from the trapping sites, reduction and regeneration is not as easy.

Also, the activity for not only oxidation by precious metals is higher, but reduction rates are also higher; therefore, the rate of reduction might be faster than or as fast as NO\textsubscript{X} release. Another possible contributing factor is increased activity toward the water-gas-shift reaction as the temperature is increased. Finally, another reason that has been proposed is increased surface diffusion rates with temperature. The nitrates formed around the precious metal sites can act as a barrier toward further trapping, but if these species can diffuse to sites further from the oxidation or precious metal sites, then more trapping availability is realized. Individually, or in parallel, these explain the increased performance between 200 and 300°C.
Table 4-2 Oxygen storage capacities

<table>
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<th>Temperature (°C)</th>
<th>OSC (mmole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
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</tr>
<tr>
<td>300</td>
<td>0.628</td>
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<td>0.901</td>
</tr>
<tr>
<td>500</td>
<td>1.10</td>
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</tbody>
</table>

4.2 Effect of regeneration phase CO concentration on the storage and reduction of NOX

Figure 4-4 compares the NOX storage and reduction performance as a function of CO concentration at 200°C under otherwise the same conditions as described in Figure 4-1. The conversions and amounts of NOX trapped and released for these experiments are also listed in Table 4-1. It is clear from these data that increasing the CO concentration in the regeneration period at 200°C, beyond the first addition of 1.5%, actually results in a decrease in the overall NSR catalyst performance. With 1.5% CO in the regeneration phase, the overall NOX conversion was 23%. However, when the CO concentration was increased from 1.5% to 3%, the NOX conversion decreased to 14.8% and decreased further to 10% with 5% CO. With the increase from 1.5 to 5% CO, the amount trapped decreased from 79 to 59 μmoles, while the amount released increased from 30.8 to 37.5 μmoles demonstrating that these drops in conversion are related to both decreased trapping and increased released NOX. A likely explanation is that when CO is added at low temperature, it poisons the precious metal sites[74]. This will directly affect the NO oxidation and NOX reduction reaction steps, as they are dependent on the precious metal activity. However, the additional CO impacts the amount released as well. This conclusion is based on the lower amounts trapped in subsequent trapping phases when
additional CO was used. Previous research has indicated that the precious metals catalyze not only NOX reduction, but also nitrate decomposition [70], and apparently CO poisoning affects this reaction process as well.

![Figure 4-4](Image)

**Figure 4-4** NOX outlet concentrations obtained when testing the sample at 200°C with 0, 1.5, 3 and 5% CO in the regeneration phase.

The little NOX storage and reduction performance observed may have actually originated from the water-gas-shift (WGS) reaction. The H₂ formed may have been the ultimate reducing agent or may have led to NH₃ formation, where NH₃ has been termed a hydrogen carrier or the reductant itself [8][75]. WGS reaction experiments were performed, and at 200°C, the maximum conversion attained was only ~10%, but enough to possibly account for some of the observed conversion. During the NOX cycling experiments, upon switching from the lean to rich phase when CO was being used, there was a slight increase in the CO₂ outlet concentration and a simultaneous decrease in the
H$_2$O concentration. This is also an indication that some H$_2$O was consumed to form H$_2$ during the regeneration period.

The data obtained at 300°C with CO as the reductant are shown in Figure 4-5. The cycle time was again 150 seconds for storage and 5 seconds for regeneration, as in Figure 4-2. The conversion and trapped and released amounts are listed in Table 4-1. It is obvious that the increased temperature results in very different trends than those observed at 200°C. When 1.5% CO was used in the regeneration, the NO$_X$ conversion was 52%, with 3% CO it was 96% and with 5% CO 97% conversion was attained. The NO$_X$ release decreased from 6.2 to 2 to 0.9 μmoles with 1.5, 3 and 5% CO, respectively. Although the amounts released decreased, it was primarily the trapping performance that increased when the CO concentration was increased. The trapping efficiency increased from 54% to 98% between 1.5 and 5% CO. The slight improvement in the performance of the catalyst when the CO concentration was increased from 3% to 5% was not observed when the H$_2$ concentration was increased from 3% to 5%. This indicates, as does the actual calculated values, that even at 300°C, CO may not be quite as effective as H$_2$ in regenerating the catalyst or reducing the trapped NO$_X$ before ultimate release, however, this is difficult to conclude with such a small change. Equivalent performance was observed with 1.5% of either reductant, but this can be interpreted as the easier, or more efficient, sites being regenerated first, and not enough reductant available to regenerate more distant or more difficult to regenerate sites.

Another possibility is that CO is still having to go through the water-gas-shift reaction and at higher levels of CO; the reaction is not driven to completion, thereby
limiting the amount of H₂ available. This however, should not fully explain the trend since at 1.5% reductant, both performed similarly. It is apparent from these data that the catalyst performance using CO was overall similar to that when H₂ was used at 300°C. There are slight differences, such as the overall conversion mentioned above, where both slightly improved trapping and decreased NOₓ released was observed when H₂ was used in regeneration period.

The improvement in the catalyst performance at 300°C versus 200°C was again observed but obviously much more significant than the improvement observed when using H₂. Several reasons for the improvement were discussed above in conjunction with the H₂ reductant data. Most importantly, when CO is used, decreased CO poisoning occurred as the temperature was increased above 200°C, which caused the significant improvement observed.

Figure 4-5 NOₓ outlet concentrations obtained when testing the sample at 300°C with 0, 1.5, 3 and 5% CO in the regeneration phase.
The data obtained at 500°C when using CO as the reductant are shown in Figure 4-6. The test conditions are the same as those used for the data shown Figure 4-3. Catalyst performance increased monotonically with each increase in the CO concentration. With the addition of 1.5 % CO, the NO\textsubscript{X} conversion was 35%, with 3% CO it was 53%, and with 5% it was 64%. The increase between 1.5 and 3% was attained via improved NO\textsubscript{X} trapping, as shown in Figure 4-6. There was some change in release with the increase from 1.5 to 3%, but only 5 \(\mu\)moles. The improved performance with the change from 3 to 5% CO was again not observed at the 200 and 300°C test points. This is again evidence that the NO\textsubscript{X} release rate and OSC consumed increased faster than the reduction rate as a function of temperature.

**Figure 4-6** NO\textsubscript{X} outlet concentrations obtained when testing the sample at 500°C with 0, 1.5, 3 and 5% CO in the regeneration phase.
The slightly higher amount of unconverted NOX observed when CO was used as the reducing agent at 500°C can be attributed to a few factors. One possibility is the increased amounts of CO₂ leading to increased competition between nitrate species and carbonate on the trapping materials. As barium carbonate is more stable than barium nitrate [33], the presence of CO₂ should, and has been observed to[35], lead to the decomposition of nitrates at lower temperatures than in its absence. This would in turn lead to even more rapid NOX release. H₂O, leading to hydroxyls, could have a similar effect, but its impact has been reportedly less significant [33], [35], [76].

Another possibility is the slightly higher exothermic nature of CO oxidation compared to H₂ oxidation, leading to higher surface temperatures when using CO upon the switch from lean to rich. Due to the very sensitive stability as a function of temperature at these higher temperatures, even a small increase would lead to measurable differences in release. Lastly, any limitation in WGS activity could also result in less reduction, without much if any difference in subsequent trapping. Overall however, the performance of the catalyst was primarily affected by the reductant concentrations rather than type of the reductant at 500°C.

4.3 Effect of H₂ and CO mixtures (CO + H₂ = 3%) on the storage and reduction of NOX

NSR catalyst performance was also evaluated using mixtures of CO and H₂. No significant differences were observed in the catalyst performance when either the CO or H₂ reductant amount was increased from 3 to 5% at 200 and 300°C. Therefore, when
testing with the mixtures, 3% as the total amount (CO + H₂ = 3%) was chosen. Selected data obtained at 200°C with 3% total reductant, but different CO/H₂ ratios, are shown in Figure 4-7. Like the data presented in Figures 4-1 and 4-4, the lean phase was 60 seconds and the regeneration phase was 5 seconds. The calculated NOₓ trapped, released and reduced are listed in Table 4-1. It is clear that H₂ was better at 200°C; however, it is also apparent that the CO poisoning effect was still significant. For example, with 1.5% H₂ and no CO, see Figure 4-1, 77% NOₓ conversion was attained. However, with 1.75% H₂ and 1.25% CO, twice the total reductant amount, and at least more H₂ than was available with just 1.5% H₂, only 41% was attained. Overall however, as the amount of H₂ in the regeneration phase was increased, the conversion did increase, but not in proportion to the amount being added due to CO poisoning. This improvement occurred via both increased trapping during the lean phase and decreased release during regeneration. The addition of the H₂ to the CO-containing mixtures resulted in improved performance, but when CO was completely removed, a large jump in trapping performance was observed.

The addition of CO poisons the precious metal sites to not just reduction of released NOₓ, but also toward the catalyzed decomposition of the nitrates leading to released NOₓ, further supporting the mechanism that includes reductant and the precious metal both inducing decomposition of the nitrate species [77]. Some trapped NOₓ was released (here released means NOₓ observed as unreduced and in the outlet, as well as that released and reduced) when only CO was used, or even when CO was present, but it is less than when H₂ was included, as is demonstrated by improved trapping in subsequent lean phases when H₂ was added. The increased performance with decreasing CO addition can be attributed to a decrease in CO poisoning, via simple competition with H₂ present.
Figure 4 -7 NOX outlet concentrations obtained when testing the sample at 200°C with 3% mixtures of CO and H2 in the regeneration phase.

Selected data obtained at 300°C using two of the mixtures, and also re-plotting the data with just H2 or CO, are shown in Figure 4-8. The cycling experiment again consisted of a 150 second storage phase and a 5 second regeneration phase. The increase in operating temperature from 200 to 300°C resulted in higher NOX removal efficiency with the CO/H2 mixtures as well. The reasons for such improvement are the same as those discussed above with the individual reductants.

As shown in Figure 4-8 and Table 4-1, with each incremental addition of H2, improvement in trapping performance was observed. However, the maximum difference in the overall NOX conversion, and trapping, among all the reductant mixtures was only in a range of 1-2%. Both reductants are similar in efficiency, with the differences
observed real, but quantitatively not very significant under the conditions of this test. Longer lean-phase times may have resulted in different conclusions. The differences in trapping are still due to better regeneration of the catalyst by the H₂ reductant in a prior regeneration phase. The amount of NOₓ released during the regeneration did not follow a clear trend, although it is obvious that with H₂ less was released than in the case where just CO was the reductant source.

![Figure 4-8](image)

**Figure 4-8** NOₓ outlet concentrations obtained when testing the sample at 300 with 3% mixtures of CO and H₂ in the regeneration phase.

Selected data obtained at 400°C are shown in Figure 4-9. A complete set of data at this temperature was not obtained due to difficulty in obtaining comparable breakthrough data as a function of chosen trapping time. In other words, with shorter trapping times, 0 ppm slip was observed, and when slip was finally observed by going to longer trapping times, the outlet NOₓ level would not reach 0 ppm at the beginning of the lean phase during subsequent trapping cycles. As a balance, the cycle time was 140
seconds for trapping and again 5 seconds for regeneration. Calculated conversions and amounts trapped and released are also listed in Table 4-1 for the few experiments done. There was little difference in the overall catalyst performance when either of 3% H₂ or CO was used separately; 88% with 3% H₂ and 87% with 3% CO. However, when mixtures of the two reductants were used, but still maintaining a total of 3% reductant, there was an improvement in the performance. The NOₓ conversion rose to 91% when 1.25% H₂ and 1.75 % CO was used and to 92% when 1.75% H₂ and 1.25% CO was used. Although not definite, there are a couple of possibilities that could explain this observation. First, CO oxidation is more exothermic than H₂ oxidation whereas the activation of H₂ on precious metals is much easier than CO. When mixtures of the two reductants were used, it is possible that these two effects occurred simultaneously. The heat generated from the more exothermic CO oxidation reaction via its interaction with OSC resulted in more nitrate decomposition and NOₓ release coupled with the presence of H₂ resulted in better regeneration. Another possible reason for the improved performance relates to the formation and reduction ability of NH₃, which will be discussed in further detail below. Briefly, however, higher concentrations of NH₃ were observed in the outlet when using the CO and H₂ mixtures at 300 and 500°C and NH₃ has been proposed as the reductant or at least as a H₂ carrier during regeneration.

The performance of the catalyst at 400°C, regardless the reductant, was lower than that with the 300°C tests. Again, this is due to the poorer thermal stability of the nitrate species on the trapping materials, as discussed above. Coupled to this is insufficient reductant to account for the trapped NOₓ. The total trapped NOₓ was around 0.46 mmoles and OSC was 0.90 mmoles. 1.16 mmoles of reductant are needed to reduce
the nitrate species and 1.8 mmoles of reductant are needed to consume the surface oxygen. Therefore, even with 3% or 1.6 mmoles of reductant, there is an insufficient amount of reductant. Again, shorter trapping times which would alleviate this problem, led to 0 ppm breakthrough during the trapping period.

![Figure 4-9](image)

**Figure 4-9** NOX outlet concentrations obtained when testing the sample at 400°C with 3% mixtures of CO and H2 in the regeneration phase.

The data obtained at 500°C are shown in Figure 4-10. As was discussed previously, no significant changes were observed in the overall performance of the catalyst when using H2 or CO in the regeneration period. The NOX conversion when 3% H2 was used was 52% while 53% conversion was achieved with 3% CO. Again, however, when mixtures of the two reductants were used, the performance was better. For example, with 1.25% H2 and 1.75 % CO, the NOX conversion was 56% and 57% when 1.75% H2 and 1.25% CO was used. In addition, the NOX release associated with using the mixtures of the two reductants was slightly lower than using either H2 or CO.
separately. Reasons for such improvement in the catalyst performance when using mixtures of the two reductants were discussed above.

![Graph](image)

**Figure 4-10** NOX outlet concentrations obtained when testing the sample at 500°C with 3% mixtures of CO and H2 in the regeneration phase.

### 4.4 NH3 formation

Ammonia is a common byproduct in NSR experiments[76]-[81]. NH3 formation has been observed when H2 was used as a reducing agent in the regeneration period overPt/Ba-based catalysts [77] as well as with mixtures of H2 and CO [79], and pure CO [80]. In this study, NH3 was observed when H2, CO, and the mixtures of H2 and CO were used at all temperatures. Cumaranatunge et. al. [75] have demonstrated equivalent reduction efficiency of H2 and NH3 in NSR catalysis, and facile formation of NH3 from a
feed of NO and H₂ over a Pt/Al₂O₃ catalyst. NH₃ has therefore been proposed as a hydrogen carrier or even the reductant participating in the NOₓ reduction reaction.
Figure 4-11 NH₃ outlet concentration data obtained when testing the sample at 200°C with regeneration-phase (A) H₂ concentrations of 0, 1.5, 3, and 5%, (B) CO concentrations of 0, 1.5, 3, and 5%, and (C) mixtures of H₂ and CO of 3%.

Ammonia can be formed directly from reaction of H₂ with NO on the catalyst, with the H₂ added to the regeneration mixture or produced from the WGS reaction when CO and H₂O are available in the regeneration mixture[9]. NO can be easily dissociated to atomic nitrogen and oxygen over precious metals at higher temperatures[82]. Subsequently, the N atom would react with dissociated H₂ to form NH₃. In comparing the data at the different test temperatures listed in Table 4-1, it is apparent that NH₃ in the outlet increased as the temperature was decreased. At 200°C, the NOₓ-to-NH₃ reduction mechanism is rapid, relative to the reduction reaction that results in N₂. The NOₓ-to-N₂ reduction mechanistic path increases with temperature until it is more comparable to the
NH₃ formation mechanism and/or surpasses it. And finally as the temperature is further increased, the weak stability of NOₓ species causes the release of unconverted NOₓ and hence NH₃ formation, as well as NOₓ reduction to N₂ will be limited.

The NH₃ outlet concentration data obtained from the 200 and 300°C experiments described above are shown in Figures 4-11 and 4-12. It is clear from these that NH₃ formation at 200 and 300°C, when H₂ was used as the reductant source, is proportional to H₂ concentration in the regeneration mixture; as the H₂ concentration increased, the NH₃ in the exhaust increased. Similarly, when CO was used at 300°C, NH₃ in the outlet increased with increasing CO concentration from 3 to 5%. This NH₃ must originate from H₂ generated via the WGS reaction. At 200°C however, NH₃ formation was found to decrease as the CO concentration increased, as shown in Figure 4-11b. This is again attributed to the negative impact of CO poisoning on the precious metals at 200°C. Little or no NH₃ was observed during the tests at 400 and 500°C. However, the small amounts that did form changed proportionally to the inlet reductant concentrations; as the reductant concentrations increased, the NH₃ outlet concentration increased.

At 300°C, NH₃ was not observed with the lower reductant concentrations, 0% and 1.5%. This is due to insufficient reductant, relative to trapped NOₓ, delivered during regeneration. This does not suggest NH₃ is not formed along the catalyst, but that any NH₃ that is formed is used downstream in nitrate or released NOₓ reduction. NSR catalysts operate as integral devices and spatial resolution of the chemistry along the axial length of channel is evolving. However, there are several publications that suggest NH₃...
formation is constantly occurring, but the NH₃ formed can easily react with downstream nitrates of surface NOₓ species to form product N₂[74][76].
Figure 4-12 NH₃ outlet concentration data obtained when testing the sample at 300°C with regeneration-phase (A) H₂ concentrations of 0, 1.5, 3, and 5%, (B) CO concentrations of 0, 1.5, 3, and 5%, and (C) mixtures of H₂ and CO of 3%.

As can be seen in Figure 4-12c, at 300°C using H₂ surprisingly led to lower levels of NH₃ in the outlet gas composition in comparison to the amount evolved when using the mixtures. This coincides with the slightly higher conversion observed with the mixtures as well. It is likely that this is due to a combination of effects observed at 200°C. It is apparent that CO hinders NOₓ release from the surface at 200°C, and this effect may be reduced at 300°C, but still present. H₂, as noted, induces release. With just H₂, NOₓ release occurs and the local H₂: NOₓ ratio determines the amount of NH₃ made. When CO is added with the H₂, the CO slows the release of NOₓ, or decomposition of the surface NOₓ species, relative to H₂ such that the local H₂: NOₓ ratio must be higher than with just H₂, leading to more NH₃ evolved. With just CO, the local amount of H₂
generated from the WGS reaction relative to the surface NO\textsubscript{X} species determines the amount of NH\textsubscript{3} made, and although the CO would still slow NO\textsubscript{X} release, the extent of the WGS reaction is only 62% at the catalyst outlet at 300°C, indicating less at the inlet where most trapped NO\textsubscript{X} resides at the end of the lean phase. The CO slowing the release, combined with the presence of H\textsubscript{2} results in more NH\textsubscript{3} formed. A similar argument can be made for the 500°C operating condition, where slightly more NH\textsubscript{3} was also made when using the mixtures. Here, however, and likely at 400°C also although no significant NH\textsubscript{3} was observed in the outlet, the extra NH\textsubscript{3} made down the axial length of catalyst could also result in the slight improvement in NO\textsubscript{X} conversion observed, as shown in Table 4-1 and discussed in section 4.3 above.
Chapter 5: The Effects of Thermal Degradation on the Performance of a Commercial NSR Catalyst.

To obtain a detailed understanding of the effect of chronic thermal aging on the overall performance of NO\textsubscript{X} storage/reduction catalysts, a vendor-supplied catalyst was exposed to different temperatures in air with 2% H\textsubscript{2}O in the range of 500 to 750°C. After each exposure temperature, the catalyst performance was evaluated at different operating temperatures in the range of 200 to 500°C. Performance measures included NO\textsubscript{X} storage capacity, water-gas-shift reaction extent, NO oxidation, oxygen storage capacity, and NO\textsubscript{X} conversion under cycling conditions. For cycling experiments using an unaged sample, 0-5% of either H\textsubscript{2}, CO, or a mixture of H\textsubscript{2} and CO were used as a reductant source. However, no significant changes were observed in catalyst performance when either the CO or H\textsubscript{2} reductant amount was increased from 3 to 5% at 200 and 300°C. Therefore, in this study only 3% of either H\textsubscript{2}, CO, or mixtures with 3% as the total amount (CO + H\textsubscript{2} = 3%) were chosen.

5.1 Effect of thermal degradation on NO\textsubscript{X} reduction efficiency during cycling

5.1.1 Effect of thermal degradation on NO\textsubscript{X} reduction efficiency with H\textsubscript{2}

The outlet NO\textsubscript{X} (NO + NO\textsubscript{2}) concentrations obtained using the unaged catalyst and thermally aged catalysts during cycling experiments with 3% H\textsubscript{2} as the reductant in the regeneration phase at an inlet temperature of 200°C are shown in Figure 5-1. For this set of experiments, the lean, or trapping, time was 60 seconds and the rich, or regeneration, time was 5 seconds. The conversions and amounts of NO\textsubscript{X} trapped and released for these
experiments are listed in Table 5-1. All reported values and plotted data were obtained once steady cycle-to-cycle performance was observed. With the unaged catalyst, the calculated NOX conversion was 85%. With the first two degradation steps, at 600 and 650°C for 2 hours each, the NOX conversion decreased to 81 and 71%, respectively. The NOX trapped decreased from 0.182 mmoles for the unaged sample, to 0.154 mmoles after aging at 650°C. The amount released was relatively small, but increased from 0.002 mmoles with the unaged catalyst to 0.005 mmoles after the 650°C degradation step. However, when the catalyst was aged for 2 hrs at 700°C, the NOX conversion actually increased to 88%. The trapped amount increased and the release decreased. With further exposure at 700°C, for 8 hours total, the NOX conversion decreased to 81% and further decreased to 67% with the 750°C degradation step. The NOX release increased from 0.002 mmoles after 2 hours at 700°C to 0.004 and 0.008 mmoles after 8 hours at 700°C and 2 hours at 750°C, respectively.

To obtain further understanding about the improvement that occurred after the sample was aged at 700°C for 2 hours; a new sample was aged with different exposure times at 700°C. Exposure times of ½, 2, 5, 8 and 15 hours were tested. This was done with one sample, with the times being the cumulative time spent at 700°C. The data obtained are listed in Table 5-2 and shown in Figure 5-2. It is apparent from Figure 5-2 that the catalyst performance or NOX conversion improved after exposure to ½ and 2 hrs at 700°C. However, after exposure for 5 hours, the NOX conversion decreased. No further changes in the catalyst performance were observed when the catalyst was aged for 8 and 15 hours.
Figure 5-1 NO\textsubscript{X} outlet concentrations as a function of thermal degradation obtained when testing the sample at 200°C with 3 % H\textsubscript{2} in the regeneration phase.

Figure 5-2 NO\textsubscript{X} outlet concentrations after different aging times at 700°C obtained when testing the sample at 200°C with 3 % H\textsubscript{2} in the regeneration phase.
Table 5-1 calculated performance characteristics as a function of temperature, thermal aging, and type of reductant, CO and/or H₂.

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<th>Aged at 650°C</th>
<th>Aged at 700°C (2hrs)</th>
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Table 5-2 NO\textsubscript{X} conversions at 200°C after different aging times at 700°C

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</table>

Similar experiments were carried out at 300, 400 and 500°C to investigate the effects of thermal aging on NO\textsubscript{X} storage and reduction at different operating temperatures. Figure 5-3 shows the outlet NO\textsubscript{X} concentration profile for a set of 150 second storage and 5 second regeneration periods at 300°C. Summary data are listed in Table 5-1. With the unaged catalyst, and after steady cycle-to-cycle performance was reached, the calculated conversion was 98%. This high conversion is due to a combination of factors, including nitrate stability, decent NO oxidation kinetics, and sufficient regeneration/cleaning during the rich phase due to sufficient reductant delivered, coincident with lower OSC at 200 and 300°C as shown in Table 5-3. However, as shown in Table 5-1 and Figure 5-3, the performance drops after just the 600°C degradation temperature. The amount of NO\textsubscript{X} trapped decreased from 0.518 to 0.477 mmoles while the NO\textsubscript{X} release also increased from 0.001 to 0.003 mmoles as a result of this thermal aging step. With exposure at 650°C and higher, little if any change in performance occurred.
Figure 5-3 NO\textsubscript{X} outlet concentrations as a function of thermal degradation obtained when testing the sample at 300°C with 3 % H\textsubscript{2} in the regeneration phase.

The outlet NO\textsubscript{X} concentration profiles obtained at 400°C are shown in Figure 5-4. For this set of experiments, the trapping time was 180 seconds and the regeneration time was 5 seconds. The conversions and amounts of NO\textsubscript{X} trapped and released for these experiments are listed in Table 5-1. With the unaged catalyst, the calculated NO\textsubscript{X} conversion was 81%. Although the NO\textsubscript{X} conversion at 400°C was less than that at 200 and 300°C, a longer NO\textsubscript{X} trapping period was used, convoluting the comparison. It is of course possible to improve the NO\textsubscript{X} reduction ability or conversion by using shorter trapping times; for example with a 140 second trapping period, the conversion attained was 88%. Decreased nitrate thermal stability, combined with higher OSC, and insufficient reductant amounts are the main reasons for this lower conversion.
The NO\textsubscript{X} observed in the outlet reached a minimum value of about 25 ppm 11 seconds after the rich-phase ended and the trapping phase began. Then, the NO\textsubscript{X} slip increased to a maximum value of about 45 ppm, 42 seconds after the minimum value was reached, and then again decreased until the regeneration phase began. This NO\textsubscript{X} slip profile can be explained by the heat being generated via the exothermic reactions during the regeneration phase, as shown in Figure 5-5. NO\textsubscript{X} trapping is a function of catalyst temperature and hence changes in the temperature will affect the trapping ability. With the increase in catalyst temperature as result of the exothermic regeneration reactions, nitrate stability decreased, and as the catalyst cooled, taking many seconds, the trapping ability increased. This increase becomes apparent with the decrease in NO\textsubscript{X} slip noted 42 seconds after the minimum was reached. Previous work has discussed this trend, specifically in the 400 to 475°C range [71][83].

![Figure 5-4](image)

**Figure 5-4** NO\textsubscript{X} outlet concentrations as a function of thermal degradation obtained when testing the sample at 400°C with 3 % H\textsubscript{2} in the regeneration phase.
Figure 5-5 Temperature data obtained in the radial center, just inside the inlet and outlet faces of the catalyst. These data were obtained when testing the sample at 400°C with 3 % H₂ in the regeneration phase.

It is clear from Figure 5-4 and Table 5-1 that no significant changes were observed with the first two thermal degradation temperatures; 600 and 650°C. A significant change was however observed when the catalyst was aged for 2 hours at 700°C. The NOₓ conversion decreased sharply from 83% after aging at 650°C to 70% after aging at 700°C. The NOₓ trapped decreased from 0.562 to 0.49 mmoles at 650 and 700°C respectively. With the longer exposure at 700°C, the catalyst slightly improved in performance relative to performance observed after the 700°C degradation for two hours. After degradation at 750°C, the observed conversion was less than that at observed after the aging at 700°C for 8 hours.
The data obtained at 500°C with H₂ as the reductant are shown in Figure 5-6. The cycle time was 120 seconds for storage and 5 seconds for regeneration. The conversion and trapped and released amounts are listed in Table 5-1. With the unaged catalyst, the calculated NOₓ conversion was 52%. It is apparent from Figure 5-6 and Table 5-1 that the performance at 500°C was less than 200, 300, and 400°C tests. The weak stability of nitrate species, insufficient reductant amount with 3% H₂, and higher OSC at 500°C are the reasons for this low performance, which was also observed in the data discussion presented in the previous chapter.

With 500°C performance, the first degradation temperature resulted in no significant change observed. Degradation was observed with the degradation step at 650°C. The NOₓ conversion decreased from 53.5% to 46% at 600 and 650°C, respectively. Again, there was a slight drop in the NOₓ conversion after first exposure at 700°C, but with longer exposure, there was a slight increase in the performance of the catalyst. With the exposure at 750°C, no significant conversion changes were relative to the performance observed after degradation at 700°C, although both trapping and release amounts changed. It is noticeable from the data in Figure 5-6 that there were changes in observed outlet NOₓ concentration after the different degradation steps, apparent during the early stages of trapping. However, the amount of NOₓ released changed as well and balanced the effect of thermal degradation on the trapping phase catalyst. Therefore, little change was observed in the overall NOₓ conversion. The improvement observed with the longer 700°C exposure originates from differences at the very early lean-phase times. The amount of NOₓ slip was actually higher at the end of the lean time after the 700°C 8-hour exposure in comparison to after the 2-hour exposure. This indicates that if the lean-phase
time were to have been increased, the observed performances may have been more similar, or even led to the conclusion of a different trend.

![Graph showing NOx outlet concentrations as a function of thermal degradation](image)

**Figure 5-6** NOx outlet concentrations as a function of thermal degradation obtained when testing the sample at 500°C with 3 % H₂ in the regeneration phase.

The data shown demonstrate an overall negative effect of thermal aging on catalyst performance. This degradation can be attributed to several mechanisms. The first is a loss in precious metal dispersion via sintering and/or pore closure. Upon exposure to high temperature (at least 600°C), sintering of precious metals on TWC and NSR catalysts is considered typical [9], [84]-[86]. For example, a change in Pt particle size after aging in air, for 4 hrs in the range of 600 and 900°C has been reported on a Pt/Ba-based catalyst and a Pt/γ-Al₂O₃ catalyst [62]. The calculated Pt particles sizes the Ba-containing catalyst were 2.6, 21.3, 37.2, and 48.4 nm after aging at 600, 700, 800, and 900°C, respectively. Similar observations were also seen on the Pt/γ-Al₂O₃ catalyst where the calculated Pt particles sizes are 3.4, 17.1, 26.1, and 39.5 nm after the same aging
temperatures. In this study, the aging temperatures were in the range of 600 and 750°C, therefore, some growth in precious metal particle sizes is expected based on the literature data discussed. The growth in precious metal particle sizes could have a negative effect on NSR activity by limiting oxidation and reduction reactions. Precious metal sintering also leads to a reduction in precious metal to storage component contact surface area, which is thought important in NSR performance[54].

Another possible reason for NSR performance loss with high-temperature exposure is reaction of the storage components with the support or other washcoat components to form mixed oxides, such as BaAl$_2$O$_4$ and BaCeO$_3$ if Ba, Al$_2$O$_3$ and CeO$_2$ are present. Jang et. al. reported the interaction between Ba and Al to form a Ba-Al solid alloy during aging above 600°C, and subsequently the transformation into stable BaAl$_2$O$_4$. Casapu et. al. [87] have also reported formation of both BaAl$_2$O$_4$ and BaCeO$_3$ when Ba/CeO$_2$ and Ba/Al$_2$O$_3$ based NSR catalysts were tested, however, the aging was done above 850°C. Such a transformation would lead to a reduced number of available trapping sites and hence would lower the storage capacity. Still other possibilities include the loss in surface area or dispersion of NO$_X$ and oxygen storage components. This will be discussed in more detail below.

The data above suggest redistribution and/or redispersion of one or more trapping materials when the catalyst was aged at 700°C, resulting in more available trapping sites during subsequent NSR cycling tests. Furthermore, it appears that some of the “activated” trapping materials are more active at low temperatures whereas others are more active at higher temperatures. With the first exposure at 700°C for 2 hours, the trapping materials
that are active at low temperatures were redistributed/redispersed. Hence, an improvement in the catalyst performance was observed during low temperature tests. While the trapping materials that are more active at high temperatures, were redistributed/redispersed with the longer exposure, 8 hours, at 700°C.

5.1.2 Effect of thermal degradation on NOX reduction efficiency with CO

NOX breakthrough and release profiles for a 60 second trapping and 5 second regeneration cycle using 3% CO as a reductant source at 200°C are shown in Figure 5-7. The conversions and amounts of NOX trapped and released for these experiments are also listed in Table 5-1. It is apparent from these data that using CO as a reductant source at 200°C results in poorer overall NSR catalyst performance compared to H2. With the unaged catalyst, and after steady cycle-to-cycle performance, the calculated conversion was only 15%. The drop in NOX conversion in comparison with using H2 as a reductant source under the same conditions is related to both decreased trapping and increased NOX release. The total inlet NOX was 0.21 mmole and the amount trapped when H2 was used as reductant source was 0.181 mmoles while only 0.0624 mmoles were trapped with CO. The amount released, on the other hand, with CO was 0.0314 mmoles whereas 0.0025 mmoles were released with H2. The drop in NOX conversion is likely related to precious metal site poisoning by CO at these low operating temperatures[88]. As a result, this will affect the oxidation and reduction steps since both are reliant on precious metal activity. When the catalyst was aged at 600 and 650°C, there was a decrease in trapping performance. The NOX release during regeneration also decreased, as expected since less was trapped. Thus, no significant change was observed on the overall NOX conversion.
When the catalyst was further aged at 700°C for 1/2 hour, a similar trend as that with H₂ was observed. The NOₓ conversion increased from 15% to 85%. Beyond the first ½ hour of aging, however, no consistent trend was observed. A further drop in catalyst performance was observed with the degradation step at 750°C.

![Graph showing NOₓ outlet concentrations as a function of thermal degradation obtained when testing the sample at 200°C with 3 % CO in the regeneration phase.](image)

**Figure 5-7** NOₓ outlet concentrations as a function of thermal degradation obtained when testing the sample at 200°C with 3 % CO in the regeneration phase.

The data obtained at 300°C with CO as the reductant are shown in Figure 5-8. Like the data presented in Figure 5-3, the lean phase was 150 seconds and the regeneration phase was 5 seconds. The conversion and trapped and released amounts are listed in Table 5-1. The NOₓ conversion with the fresh catalyst was 96%. It is apparent that there is a significant improvement in the catalyst performance at 300°C versus 200°C. There are several reasons for the improvement in catalyst performance at 300°C versus 200°C.
as discussed above, but the most important reason is that the impact of CO poisoning on precious metal activity decreased as the temperature was increased to 300°C.

After the degradation step at 600°C, there was a drop in catalyst performance, as the NO\textsubscript{X} conversion decreased from 96% to 89%. The trapping amount decreased from 0.507 to 0.474 mmoles and the NO\textsubscript{X} release slightly increased from 0.002 mmoles to 0.003 mmoles. With further degradation, through 700°C, no significant change was observed in the catalyst performance. With the degradation step at 750°C, there was another drop in the performance of the catalyst. The NO\textsubscript{X} conversion decreased from 88% after the aging at 700°C to 82% after the aging at 750°C.

![Figure 5-8](image)

**Figure 5-8** NO\textsubscript{X} outlet concentrations as a function of thermal degradation obtained when testing the sample at 300°C with 3 % CO in the regeneration phase.

Several reasons for the deactivation of the catalyst were discussed above in conjunction with the H\textsubscript{2} data. The trends observed with using CO were similar to those with H\textsubscript{2}. There
were differences, such as the overall conversion, especially at 200°C, as mentioned above. The NO\textsubscript{X} released when using CO was always higher than with H\textsubscript{2} for both the unaged and aged catalysts. But, the NO\textsubscript{X} release, when CO was used as the reductant source, did decrease after each thermal degradation step.

The data obtained at 400°C when using CO as the reductant source are shown in Figure 5-9. The conditions are otherwise the same as those used for the data shown in Figure 5-4. The conversions and amounts of NO\textsubscript{X} trapped and released for these experiments are listed in Table 5-1. It is apparent that both CO and H\textsubscript{2} are comparable as reductants at 400°C. The NO\textsubscript{X} slip pattern upon switching from rich to lean at approximately t = 1909 seconds was discussed above in conjunction with H\textsubscript{2} data at 400°C.

With the first two thermal degradation temperatures, 600 and 650°C, there was little if no change observed. However, when the catalyst was aged at 700°C for 2 hours, there was a sharp drop in conversion, decreasing from 86% to 64%. The NO\textsubscript{X} release increased from 0.050 to 0.067 mmoles after aging at 650 and 700°C for 2 hours. With further exposure at 700°C, the catalyst performance improved, with the NO\textsubscript{X} conversion increasing from 64% to 75%. Such data again suggest redistribution and/or redispersion of trapping materials. A similar trend was observed with the H\textsubscript{2} data. However, there was again a sharp decrease in catalyst performance with degradation at 750°C, where the NO\textsubscript{X} conversion decreased to 45%. The reasons for this drop were discussed above.
Figure 5-9 NO\textsubscript{X} outlet concentrations as a function of thermal degradation obtained when testing the sample at 400°C with 3 % CO in the regeneration phase.

The outlet NO\textsubscript{X} concentration profiles obtained at 500°C are shown in Figure 5-10. For this set of experiments, the trapping and the regeneration times were the same as those used in Figure 5-6. The conversion and trapped and released amounts are again listed in Table 5-1. At this high operating temperature, it is clear that the performance with CO is comparable when H\textsubscript{2} was used in regeneration phase. The calculated NO\textsubscript{X} conversion with the unaged catalyst was 53%. With the degradation exposure at 600°C no significant change in conversion was observed. With the degradation at 650°C, the NO\textsubscript{X} conversion decreased from 56% to 47%. No significant change was observed with the next thermal degradation step. With the longer exposure at 700°C, the catalyst performance again improved, with the NO\textsubscript{X} conversion increasing to 53%. Such an
improvement was also seen with the H\textsubscript{2} reductant data. This consistent trend with both CO and H\textsubscript{2} further supports the idea of a redistribution/redispersion of a trapping material, in this case trapping components with activity at higher temperature. The catalyst performance decreased after the final degradation step at 750\textdegree C, for the reasons discussed above.

![Graph showing NO\textsubscript{X} outlet concentrations as a function of thermal degradation](image)

**Figure 5-10** NO\textsubscript{X} outlet concentrations as a function of thermal degradation obtained when testing the sample at 500\textdegree C with 3 \% CO in the regeneration phase

### 5.1.3 Effect of thermal degradation on NO\textsubscript{X} reduction efficiency with mixtures of CO and H\textsubscript{2}

The outlet NO\textsubscript{X} concentrations obtained when using the unaged and aged catalysts while using 1.75\% CO and 1.25\% H\textsubscript{2} at 200\textdegree C are shown in Figure 5-11. The cycling experiment again consisted of a 60 second storage phase and a 5 second regeneration
phase. The calculated conversion of NO\textsubscript{X} and the amounts trapped and released are listed in Table 5-1. It is apparent that the CO poisoning effect is still significant and using only H\textsubscript{2} results in better performance at 200\textdegree{}C. For example, with 3% CO and no H\textsubscript{2}, the calculated NO\textsubscript{X} conversion was 15% while with just 1.75% CO and 1.25% H\textsubscript{2}, 36% was attained. The increased performance can be attributed to the decrease in CO poisoning, via simple competition with H\textsubscript{2} present. With the first two degradation exposures, at 600 and 650\textdegree{}C, the NO\textsubscript{X} conversion decreased to 12 and 9%, respectively. The decrease in the catalyst performance was mostly observed in the trapping period, since there was little released. With the first exposure at 700\textdegree{}C for \(1/2\) hr, the NO\textsubscript{X} conversion increased from 9% at 650\textdegree{}C degradation step to 63%. The NO\textsubscript{X} trapped also increased from 0.043 to 0.139 mmoles. This was coincident with a significant decrease in NO\textsubscript{X} release. Subsequently, there was a decrease in the catalyst performance with the two intermediate 700\textdegree{}C degradation times of 2 and 5 hours. However, again after exposure for 8 and 15 hours, the NO\textsubscript{X} conversion increased. This trend is inconsistent with the pure H\textsubscript{2} or CO data, but can be explained by the high release coincident with CO and fast reduction by H\textsubscript{2}. When the exposure time increased from 5 to 8 hours at 700\textdegree{}C, the NO\textsubscript{X} release in conjunction when only CO was used increased from 0.013 to 0.025 mmoles respectively. A similar trend could also occur when using 1.75% CO but the presence of H\textsubscript{2} in the mixture resulted in fast reduction of the released NO\textsubscript{X}. As a result, an increase in the catalyst performance was observed. With 15 hours exposure at 700\textdegree{}C, the increased performance was coincident with an increase that was observed with CO data with similar exposure time. The overall trends with either H\textsubscript{2}, CO, or mixture of H\textsubscript{2} and CO are overall relatively similar.
Selected data obtained at 300°C with a mixture of CO and H\textsubscript{2} are shown in Figure 5-12. Like the data presented in Figures 5-3 and 5-8, the lean phase was 150 seconds and the regeneration phase was 5 seconds. The conversion and trapped and released amounts are listed in Table 5-1. With the unaged catalyst the calculated conversion was 97%. The NO\textsubscript{X} conversion slightly decreased to 94% after just the first degradation step at 600°C. With higher temperature exposure, little if any change in performance occurred until the last exposure step at 750°C where the conversion decreased to 87%.
As the aging temperature increased, the NO\textsubscript{X} release increased. Interestingly, the amount of NO\textsubscript{X} released during the regeneration, when a mixture of CO and H\textsubscript{2} was used, was always lower than that with either H\textsubscript{2} or CO. Overall, the conversions as a function of thermal degradation temperature with using the mixture of CO and H\textsubscript{2} were always higher than with using either H\textsubscript{2} or CO alone. This might be attributed to a larger release with CO but faster reduction with H\textsubscript{2}.

The data obtained from the experiments carried out at 400°C using the mixture during regeneration are shown in Figure 5-13. The NO\textsubscript{X} conversion performance, trapping and released amounts are also listed in Table 5-1. After exposure to the high temperatures, the observed trends were similar to those with H\textsubscript{2} and CO. But again, with the mixture, the trapping and reduction performance was always better than with either
H₂ or CO alone. Again from the data shown in Figure 5-13 and results listed in Table 5-1, there was an improvement in performance after longer exposure time at 700°C. This supports the idea of a redistribution and/or redispersion of trapping materials, in this case those active at high temperatures.

![Diagram](image)

**Figure 5-13** NOₓ outlet concentrations as a function of thermal degradation obtained when testing the sample at 400°C with mixture of 1.75 % CO and 1.25% H₂ in the regeneration phase

Figure 5-14 compares the NOₓ storage and reduction performance as a function of thermal degradation at 500°C using the mixture of 1.75% CO and 1.25% H₂ under otherwise the same conditions as described in Figures 5-6 and 5-10. The conversions and amounts of NOₓ trapped and released for these experiments are also listed in Table 5-1. Again, the performance with a mixture was better than the performance with either H₂ or CO alone. With the degradation step at 600°C, a small change in performance was observed. However, a big drop in the catalyst performance was observed after the
degradation step at 650°C with the NO\textsubscript{X} conversion decreasing from 57% to 40%. The NO\textsubscript{X} release also increased from 0.070 to 0.086 mmoles. No significant changes were observed with the exposures at 700°C. With the exposure at 750°C, there was another drop in catalyst performance, to 33%.

![Graph showing NO\textsubscript{X} outlet concentrations as a function of thermal degradation obtained when testing the sample at 500°C with mixture of 1.75 % CO and 1.25% H\textsubscript{2} in the regeneration phase.]

**Figure 5-14** NO\textsubscript{X} outlet concentrations as a function of thermal degradation obtained when testing the sample at 500°C with mixture of 1.75 % CO and 1.25% H\textsubscript{2} in the regeneration phase.

### 5.2 Effect of thermal degradation on NO oxidation to NO\textsubscript{2}

The objective of this set of experiments was to evaluate NO to NO\textsubscript{2} oxidation as a function of temperature and thermal degradation. These experiments were carried out under the same lean phase conditions as those used in the cycling experiments, and as described in Table 3-1. The temperature was stepped upward in 25°C increments from 150°C to a temperature where equilibrium limitations were observed. This occurred
between 375 and 425°C. The data listed in Table 5-3 were obtained after a steady value of 330 ppm NO + NO₂ was measured at the outlet. It is clear from Table 5-3 that no significant effect was observed with the 600 and 650°C degradation temperatures. After exposing the sample to 700°C for two hours, the conversions across the whole temperature range dropped. This is inconsistent with the trend observed with the cycling data at 200°C. After the first exposure at 700°C there was an increase in NOₓ conversion, while a decrease in the NO oxidation across the whole temperature range was observed. It therefore seems that the improved cycling performance is not due to increased NO oxidation. With further exposure at 700°C, the NO oxidation performance increased across the entire range. With the 750°C exposure, low temperature NO oxidation slightly increased but decreased above 275°C.

It is important to point out that Pt particle size has an influence NO oxidation [89]. It has been shown that as Pt particle sizes increase on a Pt/Al₂O₃ and a Pt/Ba/Al₂O₃ catalyst, with a coincident decrease in dispersion, the NO oxidation rate increased [90]. Although an increase in NO oxidation was observed with one high temperature treatment, the overall trend discussed in the literature was not observed here. However, the catalyst used in this research is not a model sample, but commercial and likely made differently than that used in literature studies. Overall, NO oxidation decreased as the thermal degradation temperature was increased. But there were no consistent trends with each increase in thermal degradation.
Table 5-3 performance changes as a function of thermal degradation.

<table>
<thead>
<tr>
<th>Test</th>
<th>Temperature (°C)</th>
<th>Unaged Catalyst</th>
<th>Aged at 600°C</th>
<th>Aged at 650°C</th>
<th>Aged at 700°C (2hrs)</th>
<th>Aged at 700°C (8 hrs)</th>
<th>Aged at 750°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO Oxidation (%)</td>
<td>175</td>
<td>4.9</td>
<td>5.5</td>
<td>6.9</td>
<td>3.4</td>
<td>3.9</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>7.7</td>
<td>11.4</td>
<td>10.9</td>
<td>5.3</td>
<td>8.1</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>24.8</td>
<td>26.3</td>
<td>29.5</td>
<td>12.1</td>
<td>18.3</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>47.8</td>
<td>42.7</td>
<td>50.7</td>
<td>24.6</td>
<td>33.4</td>
<td>27.2</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>58.1</td>
<td>53.2</td>
<td>54.3</td>
<td>44.0</td>
<td>48.1</td>
<td>37.5</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>50.7</td>
<td>51.5</td>
<td>53.3</td>
<td>48.8</td>
<td>48.4</td>
<td>50.3</td>
</tr>
<tr>
<td>OSC (mnoles)</td>
<td>200</td>
<td>0.50</td>
<td>0.17</td>
<td>0.061</td>
<td>0.22</td>
<td>0.091</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.63</td>
<td>0.32</td>
<td>0.13</td>
<td>0.30</td>
<td>0.27</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.90</td>
<td>0.55</td>
<td>0.34</td>
<td>0.44</td>
<td>0.45</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1.1</td>
<td>0.74</td>
<td>0.62</td>
<td>0.59</td>
<td>0.70</td>
<td>0.43</td>
</tr>
<tr>
<td>WGS (%CO) conversion</td>
<td>200</td>
<td>10</td>
<td>6.3</td>
<td>0.80</td>
<td>4.3</td>
<td>3.5</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>62.4</td>
<td>58.4</td>
<td>58.2</td>
<td>45.2</td>
<td>44.3</td>
<td>32.2</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>90.9</td>
<td>89.0</td>
<td>88.6</td>
<td>89.6</td>
<td>88.7</td>
<td>86.6</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>81.1</td>
<td>81.3</td>
<td>79.9</td>
<td>80.6</td>
<td>80.4</td>
<td>81.6</td>
</tr>
<tr>
<td>NOx Storage Capacity</td>
<td>200</td>
<td>2.1</td>
<td>2.28</td>
<td>2.0</td>
<td>2.6</td>
<td>2.2</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>2.6</td>
<td>2.5</td>
<td>2.3</td>
<td>2.2</td>
<td>2.1</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.51</td>
<td>0.51</td>
<td>0.51</td>
<td>0.52</td>
<td>0.49</td>
<td>0.32</td>
</tr>
</tbody>
</table>

5.3 Effect of thermal degradation on water-gas-shift reaction (WGS) extent

In this set of experiments, a lean period of 60 seconds and a rich period of 30 seconds were used, with the lean composition containing 10% O₂, 5% CO₂, 5% H₂O and a balance of N₂ and the rich phase containing 1% CO, 5% CO₂, 5% H₂O and a balance of N₂. The cycles were repeated 10 to 15 times to ensure steady performance. The data
shown in Figure 5-15 and results listed in Table 5-3 were obtained and calculated after a steady-state CO and CO₂ value were reached.

Again, the lower thermal degradation temperature steps resulted in negative changes for the low temperature performance. At 200°C, the WGS reaction extent dropped from 10% to near-zero after the 650°C exposure. However, at the higher test temperatures, little change was observed. As a matter of fact, no significant change in the extent of WGS was observed at 400 and 500°C after any of these thermal degradation steps. For 300°C, there is a steady decrease in WGS performance with each increased degradation temperature, dropping from 62.4% for the fresh sample to 32.2% after being aged at 750°C.

![Figure 5-15](image.png)

**Figure 5-15** CO conversion via the WGS reaction as a function of temperature and thermal degradation
However, at 200°C there appears to be an improvement with the 700°C degradation mode, at least it is not nil. This could be, or is likely, related to the “activation” of ceria or some other OSC related component, as the WGS reaction is definitely promoted by such OSC-type components.

5.4 Effect of thermal degradation on NOₓ storage capacity (NSC)

The total NOₓ storage capacity was also evaluated as a function of thermal degradation. The experiment consisted of cleaning the sample at 500°C and then reducing the temperature to the target temperature, and exposing the sample to the same conditions as those of the lean phase in the cycling experiments. The lean phase was ended once a steady value of 330 ppm NO + NO₂ was measured at the outlet rather than at some set time. The data are listed in Table 5-3 and plotted in Figure 5-16.

As shown there is little change in total capacity when trapping at 500°C until the thermal degradation temperature exceeds 700°C. This is not coincident with the cycling data at 500°C. This inconsistency stems from better earlier trapping rates but constant total available sites. As the catalyst was thermally aged, the rates of trapping decreased, especially when aged between 600 and 650°C, but the total number of active trapping sites remained unchanged.

Operating at 350°C, the trapping capacity decreased with high temperature exposure, and the loss in trapping capacity accelerated as the temperature was increased. At 200°C, the capacity actually increased with the 700°C thermal degradation step. This was earlier attributed to redispersion of some trapping component. With further exposure
at 700 and exposure at 750°C, the capacity decreased, following the cycling performance trend.

There are several reasons that could explain the drop in the NO\textsubscript{X} storage capacity as a function of thermal degradation. One is that there is a reaction between the trapping components and the washcoat ingredients. A second possibility is the loss of interface contact between the precious metals and the trapping components because of particle size growth of both. Furthermore, the drop in NSC could be due to agglomeration of just the adsorbent material [51].

**Figure 5-16** Total NO\textsubscript{X} storage capacity as a function of temperature and thermal degradation
5.5 Effect of thermal degradation on oxygen storage capacity (OSC)

The OSC of the catalyst was also calculated at different temperatures before and after thermal degradation. The OSC data are shown in Figure 5-17 and also listed in Tables 5-3 and 5-4. In this set of experiments, 10 to 15 cycles were repeated at the 4 standard test temperatures. A lean period of 60 seconds and a rich period of 30 seconds were used, with the lean composition containing 10% O₂, 5% CO₂ and a balance of N₂ and the rich phase containing 1% CO, 5% CO₂ and a balance of N₂. To remove the effect of the water gas shift reaction on the oxygen storage capacity, water was not used in these experiments.

![Figure 5-17 Oxygen storage capacity measurements as a function of temperature and thermal degradation](image)
The measured OSC at each temperature consistently decreased with each increase in thermal degradation temperature, except again after the 700°C step. With the shorter exposure at 700°C, the measured OSC increased at 200°C, coincident with the increase in NOX performance observed during cycling at 200°C. With longer exposure at 700°C, the measured OSC also increased at 400 and 500°C, which also is consistent with improved cycling performance at 400 and 500°C.

These data indicate that an OSC component becomes “activated” with a 700°C treatment, possibly due to redispersion/redistribution. In either case, these data clearly relate back to the improved NOX performance observed. Ceria for example is a known NOX storage material at low temperature [91] and if it was to become “activated” then this could explain the 200°C cycling data. Exposing the sample to higher temperatures or for longer times at 700°C resulted in decreased OSC.

Table 5-4 Oxygen storage capacities after different aging times at 700°C

<table>
<thead>
<tr>
<th>Test OSC (mmoles)</th>
<th>Temperature (°C)</th>
<th>½ hr</th>
<th>2hrs</th>
<th>5hrs</th>
<th>8 hrs</th>
<th>15 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.11</td>
<td>0.22</td>
<td>0.092</td>
<td>0.091</td>
<td>0.098</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.155</td>
<td>0.30</td>
<td>0.29</td>
<td>0.27</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>0.34</td>
<td>0.44</td>
<td>0.43</td>
<td>0.45</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>0.69</td>
<td>0.59</td>
<td>0.67</td>
<td>0.70</td>
<td>0.45</td>
<td></td>
</tr>
</tbody>
</table>

5.6 Effect of thermal degradation on ammonia formation

Evidence of NH3 formation as by-product over NSR has been widely reported [79], [80],[92]. It should be pointed out that NH3 has been labeled as a hydrogen carrier and a reductant participating in the NOX reduction reaction [75]. Additionally, if the NSR
catalyst is followed by an SCR catalyst [93], the NH\(_3\) produced over the NSR catalyst can used as a reductant source to reduce NO\(_X\) to N\(_2\).

The amounts of NH\(_3\) formed during the cycling experiments were calculated as a function of temperature and thermal degradation exposure and listed in Table 5-5. NH\(_3\) was readily observed at the lowest test temperature and increased slightly with thermal degradation. NH\(_3\) release/formation was found to track the amount of NO\(_X\) trapped as a function of thermal degradation at 200°C. Similarly, the amount formed, or observed at the outlet, during 300°C cycling tests also increased with thermal degradation, although there is an apparent discrepancy after the 700°C thermal degradation mode that may be related to the “activation” of a catalyst component as mentioned above.

### Table 5-5 Ammonia Formation (mmoles) during the cycling experiments

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reducing Agent H(_2)</th>
<th>Reducing Agent CO</th>
<th>Unaged Catalyst</th>
<th>Aged at 600°C</th>
<th>Aged at 650°C</th>
<th>Aged at 700°C (2hrs)</th>
<th>Aged at 700°C (8 hrs)</th>
<th>Aged at 750°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>3</td>
<td>0</td>
<td>0.0785</td>
<td>0.0736</td>
<td>0.0736</td>
<td>0.0959</td>
<td>0.100</td>
<td>0.0942</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>3</td>
<td>0.0016</td>
<td>0</td>
<td>0.0033</td>
<td>0.0057</td>
<td>0.0018</td>
<td>0.0011</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>1.75</td>
<td>0.0194</td>
<td>0.0035</td>
<td>0.0033</td>
<td>0.0525</td>
<td>0.0687</td>
<td>0.0095</td>
</tr>
<tr>
<td>300</td>
<td>3</td>
<td>0</td>
<td>0.010</td>
<td>0.0325</td>
<td>0.0442</td>
<td>0.0129</td>
<td>0.0325</td>
<td>0.0670</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>3</td>
<td>0.011</td>
<td>0.0185</td>
<td>0.0208</td>
<td>0.0112</td>
<td>0.0353</td>
<td>0.0580</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>1.75</td>
<td>0.016</td>
<td>0.0317</td>
<td>0.0196</td>
<td>0.0184</td>
<td>0.0493</td>
<td>0.0727</td>
</tr>
<tr>
<td>400</td>
<td>3</td>
<td>0</td>
<td>0.0004</td>
<td>0.0002</td>
<td>0.0012</td>
<td>0.0004</td>
<td>0.0013</td>
<td>0.0024</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>3</td>
<td>0.0002</td>
<td>0</td>
<td>0.0002</td>
<td>0.0003</td>
<td>0.0005</td>
<td>0.0000</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>1.75</td>
<td>0.0003</td>
<td>0.0001</td>
<td>0.0014</td>
<td>0.0003</td>
<td>0.0001</td>
<td>0.0030</td>
</tr>
<tr>
<td>500</td>
<td>3</td>
<td>0</td>
<td>0.0003</td>
<td>0.0006</td>
<td>0.0014</td>
<td>0.0007</td>
<td>0.0015</td>
<td>0.0031</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>3</td>
<td>0.0004</td>
<td>0.0010</td>
<td>0.0017</td>
<td>0.0012</td>
<td>0.0025</td>
<td>0.0040</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>1.75</td>
<td>0.0008</td>
<td>0.0006</td>
<td>0.0020</td>
<td>0.0017</td>
<td>0.0020</td>
<td>0.0059</td>
</tr>
</tbody>
</table>
At 400°C, during most tests the NH₃ release was again found to track the NOₓ trapped, before and after aging. And again, there is a break in the trend after the 700°C aging, which could be explained by the “activation” of an OSC catalyst component. Crocker and coworkers [94] have observed that the amount of OSC significantly affects NH₃ formation. Overall, with thermal degradation, more NH₃ is formed at the lower operating temperatures and NH₃ release was consistent with NOₓ trapped during cycling data.
Chapter 6  Conclusions

This research project had two main objectives:

1. Evaluating the effect of amount and ratio of H\textsubscript{2} and CO reductants on the trapping and reduction performance of a commercial NSR catalyst.

2. Investigating the effect of thermal degradation on the performance of a commercial NSR catalyst.

Overall, the performance of the catalyst improved with each increase in regeneration-phase H\textsubscript{2} concentration. With CO, the same was true, except at 200°C where increasing the CO concentration beyond 1.5% resulted in decreased catalyst performance, which was attributed to CO poisoning of precious metal sites. With mixtures of CO and H\textsubscript{2} at 200°C, the CO poisoning effect outweighed the positive effect of H\textsubscript{2} use. At 300°C, the calculated conversions using either reductant or the mixtures were comparable, with H\textsubscript{2} resulting in slightly improved performance. At 400°C, overall performance was again comparable, but best with the mixtures of reductants, rather than with just H\textsubscript{2}. Similar trends were observed at 500°C. NH\textsubscript{3} in the outlet was observed at all temperatures, but increased with decreasing temperature. At 200°C, the amount formed was proportional to the amount of H\textsubscript{2} in the inlet, while at 300 and 500°C, mixtures of CO and H\textsubscript{2} resulted in more NH\textsubscript{3} observed than with just H\textsubscript{2}, although the amount of total reductant was maintained.
The performance of the catalyst was also characterized before and after several high-temperature treatments. The characterization included “standard” storage and reduction cycling experiments conducted between 200 and 500°C, evaluating H₂ versus CO and mixtures of H₂ and CO as the reductant source, NOₓ storage capacity measurements, oxygen storage capacity measurements, water-gas-shift and NO oxidation reaction extents. For the cycling experiments, there was a steady drop in NOₓ conversion after each thermal degradation temperature; except when catalyst was heated at 700°C, where there was an increase in NOₓ conversion. For the NOₓ storage capacity at 350 and 500°C, a steady drop was observed with each thermal degradation step. There were also decreases in NOₓ storage capacity at 200°C after aging at 600 and 650°C, but aging at 700°C resulted in an increase in capacity. There wasn’t any significant change in the extent of the water-gas-shift reaction with thermal degradation at high test temperatures whereas a decrease was observed at low temperature. There was a gradual decrease in oxygen storage capacity at test temperatures between 200 and 500°C with each increase in thermal degradation temperature, except again when the sample was degraded at 700°C, where a significant increase was observed. These data indicate that there was redispersion of a trapping material component during the 700°C thermal degradation treatment while the oxygen storage capacity data indicate redispersion of oxygen storage components, therefore we conclude that it is these oxygen storage components that are becoming “activated” as trapping materials at low temperature.
Chapter 7: Recommendations

The purpose of this thesis was to evaluate the effect of regeneration mixture properties and thermal aging on the performance of a NSR catalyst. However, there are still some questions that need to be answered. The following are some recommended future opportunities:

- The NO\textsubscript{X} source in this study was NO. What would occur if NO\textsubscript{2} was the NO\textsubscript{X} source? How would the regeneration characteristics differ with NO\textsubscript{2} used as the NO\textsubscript{X} source?

- Similarly, what would be the effect of an upstream oxidation catalyst on the overall NO\textsubscript{X} reduction to N\textsubscript{2}?

- Would the NH\textsubscript{3} formed be sufficient to feed a downstream SCR catalyst?

- The regeneration mixture used in this study includes CO and H\textsubscript{2}. What would be the effect of adding hydrocarbon to the mixture? Would it affect NO\textsubscript{X} release and reduction?

- The aging procedures used air and 2\% H\textsubscript{2}O. What would occur if the gas mixture was more representative?

- This study suggests redispersion/redistribution of OSC components. However, at the present time there is no trusted method to measure the dispersion of trapping components, OSC components and precious metals on these commercial samples.
What is a suitable physical technique that can measure and investigate this redispersion/redistribution?
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