Application of Environmental Technology Management (ETM) to Automobile Exhaust Emission Reduction

by

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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.
Abstract

Vehicle emissions, arising from incomplete fuel combustion and reactions between \( \text{N}_2 \) and \( \text{O}_2 \) leading to \( \text{NO}_\text{x} \), have detrimental effects on human health and environment quality. Engine exhaust contains a variety of regulated components, such as hydrocarbons, \( \text{CO} \), nitrogen oxides (\( \text{NO}_\text{x} \)), and particulate matter (PM). Government environmental agencies have been continuously establishing regulations for automobile manufacturers to reduce these emissions. Lean-burn engines operate with an excess of oxygen, which makes the reduction of \( \text{NO}_\text{x} \), challenging, with a coincident challenge for diesel engines being PM. Diesel particulate filters have been successfully employed to reduce PM. \( \text{NO}_\text{x} \) storage and reduction (NSR) catalysts and selective catalytic reduction (SCR) catalysts are two promising technologies used to mitigate \( \text{NO}_\text{x} \) emissions. A diesel oxidation catalyst (DOC) is usually placed upstream of these to reduce hydrocarbons and CO emissions and oxidize NO to \( \text{NO}_2 \), which leads to improved performance over these catalysts.

In this study, the performance of DOCs and NSR catalysts, individually and in series, has been investigated as a function of temperature, gas composition, catalyst length, and catalyst configuration. The catalytic oxidation of CO, hydrocarbons, and NO, both individually and in mixtures with \( \text{NO}_2 \), was investigated over a monolith-supported DOC. The data clearly show mutual inhibition effects between these species. Addition of each gas to the inlet gas mixture caused an increase in the light-off temperatures of the other species, mainly due to site adsorption competition. CO was less affected by other species because its light-off temperatures began prior to those of \( \text{NO}_\text{x} \) and other
hydrocarbons, and it is likely the primary surface species poisoning the active sites at low temperature.

Hydrogen production via hydrocarbon steam reforming and water gas shift reactions was also investigated over a DOC during steady-state and cycling conditions (to mimic NSR catalyst operation) along the catalyst length. C₃H₆ and dodecane steam reforming started at 375 and 450°C, respectively, whereas the water gas shift reaction started at 225°C, and proceeded further than hydrocarbon steam reforming in terms of H₂ production. It should be mentioned that H₂ production via the hydrocarbon steam reforming and water gas shift reactions during cycling experiments, was higher than that observed during steady-state experiments. According to temperature programmed oxidation experiments performed after steam reforming, the better performance during cyclic operation is because less coke was deposited compared to that with steady-state experiments.

Experiments were also performed over a NSR catalyst. The evaluations included testing the performance as a function of NOₓ source, NO or NO₂, testing different regeneration protocols, and evaluating different reducing agents (hydrocarbons, H₂, or CO). For NO and NO₂ as the NOₓ source, the trapping and reduction performance was better when NO₂ was used at all operating temperatures except 300°C, likely due to high NO oxidation activity and rapid trapping of NO₂ at 300°C. Numerous reasons were provided to explain the improved performance with NO₂ at other tested temperatures. The foremost reason though, is treating the monolith as an integral reactor. With NO₂ as the NOₓ source, NO₂ can be readily trapped at the very inlet and along the catalyst length, resulting in a higher trapping amount. Along the same concept, the released NOₓ
from the inlet of the catalyst has more residence time and contact with downstream Pt sites, but more importantly more interaction between reductant and stored NOX. In the second set of experiments, different regeneration protocols were used. Different regeneration times, 4, 8 and 16 seconds with 4, 2, and 1% H2 as the reductant amounts, and constant lean times were evaluated. The data clearly show an improvement with longer regeneration times in both NOX trapping and overall reduction performance at all temperatures except 500°C, where the more significant NOX release resulted in an overall decrease in NOX conversion with increasing regeneration time. The improved performance at the lower temperatures is due to more extensive nitrate/nitrite decomposition with longer regeneration times, thus leading to more extensive surface cleaning. The performance of the NSR catalyst was also investigated using hydrocarbons, H2, or CO as reducing agents. H2 was found the best at T ≤ 250°C, where the decreased performance with CO and hydrocarbons was due to Pt site poisoning at 200°C and as a result of slow kinetics at 250°C. CO and hydrocarbons, however, proved to regenerate the catalyst as efficiently as H2 at T ≥ 300°C. Hydrogen production via steam reforming experiments can not explain the improved performance with hydrocarbons, since propylene steam reforming occurred at 375°C, with only a small amount of H2 generated, and dodecane or m-xylene reforming did not occur below 450°C. TPR data show that propylene started to activate as low as 217°C and the complete reduction of NO by propylene was achieved at 287°C. For surface chemisorbed NOX species, propylene was observed to reduce these species at T > 200°C, with high rates by 264°C, with this activity eventually leading to comparable performance with either CO or H2 at similar temperatures during NOX cycling experiments.
The performance of two different hybrid DOC+NSR systems was also investigated. In the first configuration, a DOC and NSR catalyst were placed in series while in the other configuration, the DOC and NSR catalysts were divided into two equal volumes and placed in series (DOC + NSR + DOC + NSR). Overall, the data show an increase in the NO\textsubscript{X} performance with the split configuration at all temperatures tested, with small changes at 200°C due to poisoning effects of Pt and Ba sites by CO and hydrocarbons being significant. The improved performance with the split configuration was related to further NO oxidation occurring over the 2\textsuperscript{nd} DOC, more H\textsubscript{2} formed from steam reforming and WGS reactions, and reduced inhibition of the WGS reaction by hydrocarbons.
Acknowledgements

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I would also like to thank my parents, brothers and sisters, and my best friend Musaed AL-Fadly. They were always supporting me and encouraging me with their best wishes. I am grateful to all my friends who I knew in Waterloo, for being the surrogate family during the many years I stayed there and for their continued moral support there after. My deep appreciation also goes to all my friends in Catalysis Research Groups, and secretaries and technicians in the chemical engineering department.

Finally, I would like to thank Kuwait University, Natural Sciences and Engineering Research Council of Canada Discovery Grant Program, and Auto 21 for financial support, and Johnson Matthey and Umicore for the samples provided.
Dedication

To my beloved parents,

my beloved wife...Manal,

and my lovely son...Mohammed
Table of Contents

Author’s Declaration............................................................................................................. ii
Abstract................................................................................................................................. iii
Acknowledgements............................................................................................................ vii
Table of Contents............................................................................................................... ix
List of Figures....................................................................................................................... xiii
List of Tables......................................................................................................................... xix

Chapter-1: Introduction and Background

1.1 Environmental Technology Management (ETM)......................................................... 1
1.2 Environment...................................................................................................................... 3
1.2.1 Automobile Emissions................................................................................................. 3
1.2.2 Pollutants and their effects........................................................................................... 4
1.3 Management of Automobile Emissions........................................................................... 5
1.3.1 Standards and regulations.......................................................................................... 6
1.4 Technology...................................................................................................................... 7
1.4.1 Diesel Automobile....................................................................................................... 8
1.4.2 Diesel Exhaust Emissions Technologies...................................................................... 8
1.4.2.1 Threeway catalytic (TWC) converter................................................................. 9
1.4.2.2 Selective catalytic reduction (SCR)................................................................. 9
1.4.2.3 Diesel Oxidation Catalyst (DOC)................................................................. 11
1.4.3.4 NSR Catalyst Technology.................................................................................. 11
1.5 Motivation....................................................................................................................... 12
1.6 Objectives....................................................................................................................... 13
1.7 Research Contribution.................................................................................................... 14
1.8 Thesis outline ................................................................................................................ 16
 References........................................................................................................................... 19

Chapter-2: Literature Review

2.1 Diesel oxidation catalyst (DOC)................................................................................... 21
2.1.1 Reactions on a Diesel Oxidation Catalyst.............................................................. 22
2.1.2 Diesel Oxidation Catalyst formulation ........................................25
2.1.3 Hydrocarbon steam reforming ....................................................27
2.2 NO\textsubscript{X} storage and reduction technology ............................29
  2.2.1 NO Oxidation to NO\textsubscript{2} over noble metal component ........30
  2.2.2 Adsorption of NO/NO\textsubscript{2} on the trapping sites ................32
  2.2.3 Reductant evolution ..................................................................36
  2.2.4 Nitrate decomposition and NO\textsubscript{X} release .........................37
  2.2.5 Reduction of NO\textsubscript{X} to N\textsubscript{2} ....................................38
  2.2.6 Spatially Resolved Capillary Inlet Mass Spectrometry (SpaciMS) ...41

References ..........................................................................................44

Chapter-3: Competitive NO, CO and hydrocarbon oxidation reactions over a diesel oxidation catalyst
3.1 Abstract .........................................................................................50
3.2 Introduction ....................................................................................51
3.3 Experimental Methods .................................................................54
3.4 Results and Discussion ................................................................54
  3.4.1 Overall trends ...........................................................................55
  3.4.2 Effect of NO\textsubscript{2}, HCs, and CO on NO oxidation ................63
  3.4.3 Effect of NO, NO\textsubscript{2}, CO and HCs on HC oxidation ............71
  3.4.4 Effect of NO, NO\textsubscript{2}, and Hydrocarbons on CO oxidation ...77
3.5 Conclusion .....................................................................................81
3.6 Acknowledgement ........................................................................81

References ..........................................................................................82

Chapter-4: Hydrogen generation and coke formation over a diesel oxidation catalyst under fuel rich conditions
4.1 Abstract .........................................................................................86
4.2 Introduction ....................................................................................87
4.3 Experimental Methods .................................................................89
4.4 Results and Discussion ................................................................91
  4.4.1 H\textsubscript{2} generation during non-cycling conditions .................91
List of Figures

Figure 1-1: Application of the environmental technology management concept to automobile emissions.................................................................2
Figure 2-1 Overall NOX cycle.................................................................30
Figure 2-2 Effect of Temperature on NO oxidation.......................................31
Figure 2-3 NOX Storage Capacity.............................................................33
Figure 2-4 NOX breakthrough profiles as a function of catalyst length at T = 430°C....42
Figure 2-5 The reactions distribution inside a commercial NSR catalyst at 325°C
   before and after sulfation.................................................................43
Figure 3-1 Outlet concentrations obtained during TPO with 1080 ppm C₃H₆, 200 ppm
   NO, 100 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and balance N₂..................56
Figure 3-2 Outlet C₃H₆ and NOx concentrations obtained at 100°C with 200 ppm
   NO, 100 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and balance N₂ in the
   presence and absence of 1080 ppm C₃H₆............................................57
Figure 3-3 Outlet concentrations obtained during TPO with 3240 ppm CO, 200
   ppm NO, 100 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and balance N₂..........60
Figure 3-4 Outlet concentrations obtained during TPO with either 270 ppm dodecane
   or 405 ppm xylene, 200 ppm NO, 100 ppm NO₂, 10% O₂, 5% CO₂, 5%
   H₂O, and balance N₂.................................................................62
Figure 3-5 NO to NO₂ conversion obtained during TPO with 200 ppm NO, 0, 20, 100,
   or 200 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and balance N₂. Conversion
   is based on NO₂ produced...............................................................64
Figure 3-6 NO to NO₂ conversion obtained during TPO with 1080 ppm C₃H₆, 200 ppm
   NO, 0, 20,100, or 200 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and balance
   N₂. Conversion is based on NO₂ produced...........................................66
Figure 3-7 NO to NO₂ conversion obtained during TPO with 3240 ppm CO, 200 ppm
   NO, 0, 20,100, or 200 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and balance
   N₂. Conversion is based on NO₂ produced..........................................69
Figure 3-8 C₃H₆ conversion obtained during TPO with 1080 ppm C₃H₆, 200 ppm NO,
   0, 20,100, or 200 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and balance N₂.....72
Figure 3-9  C₃H₆ conversion obtained during TPO with 1080 ppm C₃H₆, and either 3240 ppm CO, 270 ppm dodecane, and/or 200 ppm NO, 200 ppm NO₂, and 10% O₂, 5% CO₂, 5% H₂O, and balance N₂. ………………………………………………………74

Figure 3-10 Outlet concentrations obtained during TPO with 3240 ppm CO, 1080 ppm C₃H₆, 200 ppm NO, 100 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and balance N₂………………………………………………………….75

Figure 3-11 Dodecane conversion obtained during TPO with 270 ppm dodecane and either 1080 ppm C₃H₆, and/or 200 ppm NO, 200 ppm NO₂, and 10% O₂, 5% CO₂, 5% H₂O, and balance N₂……………………………………………………….77

Figure 3-12 CO conversion obtained during TPO with 3240 ppm CO, and either 1080 ppm C₃H₆, and/or 200 ppm NO, 200 ppm NO₂, and 10% O₂, 5% CO₂, 5% H₂O, and balance N₂……………………………………………………79

Figure 4.1 H₂ concentrations obtained at different temperatures and lengths of the catalyst during steam reforming experiments. The inlet gas composition was 900 ppm C₃H₆, 5% H₂O, and balance N₂……………… 92

Figure 4.2 Outlet H₂ concentrations obtained at different temperatures and with different hydrocarbon feed mixtures during steam reforming experiments. The inlet gas composition was 900 ppm C₃H₆, 225 ppm C₁₂H₂₆, or 900 ppm C₃H₆ and 225 ppm C₁₂H₂₆, 5% H₂O, and balance N₂…………………93

Figure 4.3 Outlet H₂ concentrations obtained at different temperatures during non-cycling and cycling water gas shift reactions experiments. The inlet gas composition was 2700 ppm CO, 5% H₂O, and balance N₂…………………. 96

Figure 4.4 H₂ concentrations obtained at different temperatures and lengths of the catalyst during cycling steam reforming experiments. The inert phase gas composition was 5% H₂O and balance N₂. The rich phase gas composition was 900 ppm C₃H₆, 5% H₂O, and balance N₂. The inert phase was 60 sec and the rich phase was 10 sec. The front position represents the inlet of sample (~1mm in)…………………………………………………………98

Figure 4.5 Outlet H₂ concentrations obtained at different temperatures and with different hydrocarbon feed mixtures during cycling steam reforming experiments. The inert phase gas composition was 5% H₂O and
balance N₂. The rich phase gas composition was 900 ppm C₃H₆, 225 ppm C₁₂H₂₆, or 900 ppm C₃H₆ and 225 ppm C₁₂H₂₆, 5% H₂O, and balance N₂. The inert phase was 60 sec and the rich phase was 10 sec.

Figure 4.6 Outlet H₂ concentrations obtained during C₃H₆ steam reforming experiments at 450°C. The inlet gas composition was 900 ppm C₃H₆, 5% H₂O, and balance N₂.

Figure 4.7 CO₂ formation obtained during temperature programmed oxidation experiments at 2 and 4 cm from the front of the catalyst. After C₃H₆ steam reforming experiments, the reactor was cooled down to 50°C with only N₂ and then 10% O₂ was added to feed and the reactor was ramped to 500°C at rate of 7°C/min.

Figure 4.8 CO₂ formation obtained during a temperature programmed oxidation experiments at 1, 2 and 4 cm from the front of catalyst. After cycling C₃H₆ steam reforming experiments at 375°C, the reactor was cooled down to 50°C with only N₂ and then 10% O₂ was added to the feed and the reactor was ramped to 500°C at rate of 7°C/min.

Figure 4.9 CO₂ formation data obtained during temperature programmed reduction experiments at 4 cm from the front of catalyst. After non-cyclic C₃H₆ steam reforming experiments during a temperature programmed ramp from 300 to 490°C at 1°C/min, the reactor was cooled down to 50°C with only N₂ and then (A) 5% H₂O was added to the feed, or (B) 1000 ppm H₂ and 5% H₂O were added to feed, and the reactor was ramped to 525°C at a rate of 7°C/min.

Figure 5-1 NOₓ outlet concentrations obtained when testing the sample at 200°C.

Figure 5-2 NOₓ outlet concentrations obtained when testing the sample at 300°C.

Figure 5-3 NOₓ outlet concentrations obtained when testing the sample at 400°C.

Figure 5-4 NOₓ outlet concentrations obtained when testing the sample at 500°C.

Figure 6-1 NOₓ outlet concentrations obtained at 200°C with 1% H₂ and 16 sec, 2% H₂ and 8 sec, and 4% H₂ and 16 sec regeneration phases.

Figure 6-2 NOₓ outlet concentrations obtained at 300°C with 1% H₂ and 16 sec, 2% H₂ and 8 sec, and 4% H₂ and 16 sec regeneration phases.
Figure 6-3  NOX outlet concentrations obtained at 400°C with 1% H2 and 16 sec, 2% H2 and 8 sec, and 4% H2 and 16 sec regeneration phases………………154
Figure 6-4  NOX outlet concentrations obtained at 500°C with 1% H2 and 16 sec, 2% H2 and 8 sec, and 4% H2 and 16 sec regeneration phases………………155
Figure 6-5  NH3 and NOX outlet concentration data obtained at 200°C during different regeneration protocols……………………………………161
Figure 7-1  NOX outlet concentrations obtained at 170°C with 1% H2, 1% CO, or 3333 ppm C3H6…………………………………………………………176
Figure 7-2  NOX outlet concentrations obtained at 250°C with 1% H2, 1% CO, 3333 ppm C3H6, 833 ppm C12H26, or 1250 ppm C8H10………………178
Figure 7-3  NOX outlet concentrations obtained at 200°C with different regeneration times; 5, 10, and 20 sec. (A) 3333 ppm C3H6 and (B) 1% CO…………180
Figure 7-4  NOX outlet concentrations obtained at 250°C with regeneration times; 5, 10, and 20 sec. (A) 3333 ppm C3H6, (B) 1% CO and (C) 1% H2………182
Figure 7-5  NOX outlet concentrations obtained at 300°C with 1% H2, 1% CO, 3333 ppm C3H6, 833 ppm C12H26, or 1250 ppm C8H10………………184
Figure 7-6  H2 concentrations obtained at different temperatures and lengths of the catalyst during steam reforming experiments. The inlet gas composition was 3333 ppm C3H6, 5% H2O, and balance N2…………………………188
Figure 7-7  H2 concentrations obtained at different temperatures and lengths of the catalyst during steam reforming experiments. The inlet gas composition was 833 ppm C12H26, 5% H2O, and balance N2…………………………189
Figure 7-8  H2 concentrations obtained at different temperatures and lengths of the catalyst during steam reforming experiments. The inlet gas composition was 1250 ppm C8H10, 5% H2O, and balance N2…………………………190
Figure 7-9  H2 concentrations obtained at different temperatures and lengths of the catalyst during steam reforming experiments. The inlet gas composition was 3333 ppm C3H6, 833 ppm C12H26, 5% H2O, and balance N2………192
Figure 7-10 NO and C3H6 outlet concentrations obtained during a temperature programmed reduction experiment; the ramp rate was 3.3°C/ min. The inlet gas composition was 1017 ppm C3H6, 257 ppm NO, 5% H2O, …
and balance N₂ .......................................................... 194

Figure 7-11  C₃H₆ outlet concentrations obtained during a temperature programmed reduction experiment; the ramp rate was 2.1°C/ min. The catalyst was first heated to 300°C and saturated with NOₓ using a mixture containing 350 ppm NO, 10% O₂, 5% CO₂, 5% H₂O, and a N₂ balance. The reactor was then cooled to 115°C to start the TPR experiment. The TPR gas composition contained 55 ppm C₃H₆ and a N₂ balance ......................... 196

Figure 8-1  Catalysts configurations used in this study ........................................ 208

Figure 8-2  NOₓ outlet concentrations obtained at 500°C with 1% H₂, 3% CO, and
0.5% C₃H₆ used in the regeneration phase with group 1 configurations ... 209

Figure 8-3  NO and NO₂ outlet concentrations obtained at 500°C with 1% H₂, 3%
CO, and 0.5% C₃H₆ used in the regeneration phase with group 1
configurations .............................................................. 212

Figure 8-4  NOₓ and NH₃ outlet concentrations from the 1st NSR catalyst and 2nd DOC
for configuration B of group 1, obtained at 500°C with 1% H₂, 3% CO, and
0.5% C₃H₆ used in the regeneration phase ............................... 213

Figure 8-5  NO and NO₂ outlet concentrations obtained at 500°C with 1% H₂, 3% CO,
and 0.5% C₃H₆ used in the regeneration phase with group 2
configurations .............................................................. 218

Figure 8-6  CH₄ concentrations obtained at 500°C with (A) 1% H₂, 3% CO and (B) 1%
H₂, 3% CO, and 0.5% C₃H₆ used in the regeneration phase, using a 1 cm
DOC followed by a 2 cm NSR catalyst ................................. 220

Figure 8-7  NO and NO₂ outlet concentrations obtained at 350°C with 1% H₂, 3% CO,
and 0.5% C₃H₆ used in the regeneration phase with group 1
configurations .............................................................. 221

Figure 8-8  NO and NO₂ outlet concentrations obtained at 350°C with 1% H₂, 3% CO,
and 0.5% C₃H₆ used in the regeneration phase with group 2 configurations
..................................................................................... 223

Figure 8-9  NOₓ outlet concentrations obtained at 200°C with 1% H₂, 3% CO, and
0.5% C₃H₆ used in the regeneration phase with group 1 configurations.... 224
Figure 8-10  NO and NO$_2$ outlet concentrations obtained at 200°C with 1% H$_2$, 3% CO, and 0.5% C$_3$H$_6$ used in the regeneration phase with group 1 configurations .................................................................225

Figure 8-11  NO$_X$ outlet concentrations obtained before steady cycle-to-cycle performance was reached at 200°C with 1% H$_2$, 3% CO, and 0.5% C$_3$H$_6$ used in the regeneration phase with group 1 configurations .............226

Figure 8-12  NO$_X$ outlet concentrations obtained before steady cycle-to-cycle performance reached at 200°C with 1% H$_2$ used in the regeneration phase with group 1 configurations ......................................................228
List of Tables

Table 1-1: Automobile Emissions Relative to Total Emission Sources (Kilotones) in 2002 ..........................................................3
Table 1-2: History of automobile legislations, g/KW-hr ...........................................7
Table 1-3: Heavy duty diesel Vs Heavy duty gasoline engine .............................8
Table 2-1: Emission rate of some hydrocarbons from diesel engine exhaust ...........24
Table 3-1 Temperatures (°C) required for 10 and 50% conversion of NO to NO2 ....67
Table 3-2 Temperatures (°C) required for 25, 50, and 90% conversion of hydrocarbon species .........................................................73
Table 3-3 Summary of the temperatures at which the 50% conversion of CO was attained and the increase in temperature to achieve 50% CO conversion with the addition of other reactive species .................................80
Table 5-1 Details of flow conditions used in the experiments .............................121
Table 5-2 Calculated performance characteristics as a function of temperature, NOX source, and lean phase time over a Pt/BaO/Al2O3 catalyst ...........123
Table 6-1 Details of flow conditions used in the experiments ...............................148
Table 6-2 Calculated performance characteristics as a function of temperature, amount of H2, and regeneration time ...................................................150
Table 6-3 Calculated amount of NOX trapped and released (μmoles) at 200°C with and without reductant in the regeneration portion of the cycle ....159
Table 7-1 Details of flow conditions used in the cycling experiments .................174
Table 7-2 Calculated performance characteristics as a function of temperature and reducing agent type. The calculated errors associated with these measurements was less than 1% for trapping conditions and less than 2% for regeneration conditions .........................................................177
Table 7-3 Calculated performance characteristics as a function of reductant type and regeneration time at 250°C ..................................................182
Table 8-1 Calculated performance characteristics as a function of temperature and catalyst configurations, for group 1 in Figure 8.1. The calculated errors
associated with these measurements were less than 1% for trapping conditions and less than 2% for regeneration conditions.

Table 8-2 Outlet reductant amounts as a function of temperature and catalyst configuration for group 1, Figure 8.1.

Table 8-3 Calculated performance characteristics as a function of temperature and catalyst configuration for group 2, as shown in Figure 8.1.

Table 8-4 Outlet reductant amounts as a function of temperature and catalyst configurations for group 2, as shown in Figure 8.1.
Chapter 1: Introduction

1.1 Environmental Technology Management (ETM)

Environmental Technology Management (ETM) is a multidisciplinary science that combines three interrelated fields; environmental science, environmental management, and environmental technology. Environmental science is the field that studies the environment (air, water, and land) and the interaction between the environment and humans [1]. Environmental management is an approach to environmental stewardship which deals with prevention and resolution of environmental problems, establishing limits, and identifying new technologies or policies that are useful [2]. Environmental technology is defined as any technology that reduces risks to humans and environmental ecology, improves process efficiency, and creates products that are environmentally friendly [3]. These disciplines collectively aim to provide a comprehensive understanding of environmental issues for air, water, and land and solutions to those issues.

The focus of the research to be described is a proposed solution to control emissions from automobiles. Figure 1.1 describes an example of application of the ETM concept to motor vehicle emissions. In the rest of this section, automobile emissions and the approaches to manage automobile emissions via stipulating standards and regulations will be discussed. Finally, the feasibility of using different technologies to control these emissions, specifically for diesel engines, will be evaluated.
Figure 1.1 Application of the environmental technology management concept to automobile emissions
1.2 Environment

1.2.1 Automobile Emissions

Automobile emissions are the largest contributor to urban air contaminant emissions and one of the largest sources of greenhouse gases [4,5]. In 2002, about 67.4% of CO, 60% of nitrogen oxides, and 7.1% of particulate matter (PM) emitted came from automobiles, as cited by the Environmental Protection Agency (EPA) with highlights in Table 1.1 [6]. Additionally, automotive CO$_2$ emissions are considered a significant contributor to global warming and thus climate change. Compounding this is the increasing numbers of vehicles on the road and different emissions regulations in different countries.

Table 1.1 Automobile Emissions Relative to Total Emission Sources (Kilotons) in 2002

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>CO</th>
<th>NO$_x$</th>
<th>VOCs</th>
<th>PM</th>
<th>SO$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>On Road Vehicle</td>
<td>62,957</td>
<td>8,133</td>
<td>4,660</td>
<td>14.433</td>
<td>257.6</td>
</tr>
<tr>
<td>Non Road Vehicle</td>
<td>22,414</td>
<td>4,517</td>
<td>2,623.7</td>
<td>301.8</td>
<td>515</td>
</tr>
<tr>
<td>Fires</td>
<td>14,520</td>
<td>16.1</td>
<td>3,036</td>
<td>1,230</td>
<td>102</td>
</tr>
<tr>
<td>Residential Wood Consumption</td>
<td>2,704</td>
<td>36.7</td>
<td>1,222.8</td>
<td>338</td>
<td>5.1</td>
</tr>
<tr>
<td>Industrial Processes</td>
<td>2,414</td>
<td>1,158</td>
<td>1,680</td>
<td>491</td>
<td>1,233.8</td>
</tr>
<tr>
<td>Waste Disposal</td>
<td>2,018</td>
<td>120</td>
<td>464</td>
<td>273.9</td>
<td>26</td>
</tr>
</tbody>
</table>
### Pollutants and Their Effects

As discussed in the previous section, automobile emissions account for a significant portion of some pollutants. Pollutants are typically classified as either primary or secondary. Primary pollutants are substances that are released directly into the atmosphere from their sources. Common examples include SO₂, CO, nitrogen oxides (NOₓ), particulate matter less than 10 μm in diameter (PM-10), and volatile organic compounds (VOCs). Secondary pollutants are not directly emitted from sources, but form in the atmosphere as a result of chemical and photochemical reactions between other emitted molecules. A common example of secondary pollutants is ground level ozone.
In our research, NO\textsubscript{X} is used as a generic term for mononitrogen oxides, NO and NO\textsubscript{2}. NO\textsubscript{X} is one of the major contributors to ground-level ozone, which forms when NO\textsubscript{X} reacts with VOCs in the presence of sunlight.

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

(1-1)

In addition, NO\textsubscript{X} is a major component of smog. Smog is a mixture of poisonous gases (e.g. hydrocarbons, SO\textsubscript{2}, and CO\textsubscript{2}) with ground-level ozone as the main component. NO\textsubscript{X} can also react with atmospheric water to form acid which falls to earth as rain, fog, or dry particles.

These pollutants, whether primary or secondary, have harmful effects on human, plant, and animal life. They can cause breathing problems, dizziness, severe headaches, irritate the respiratory system, and at high concentrations can cause death.

1.3 **Management of Automobile Emissions**

Although the emissions per automobile have decreased over time, due to the large increase in the number of automobiles on the road, the overall emissions are still high. Therefore, it is still essential to manage and control these emissions to minimize the adverse impact to human health and the environment.

Environmental agencies begin the management scheme by evaluating the effect of automobile emissions on human health and the environment. Then, they develop standards and regulations and impose them on automobile manufacturers. Automobile manufacturers then try to find and develop solutions or technologies that meet the
regulatory requirements. The third step in the management scheme is evaluating these technologies and whether they meet the requirements or not. The last step is implementation and subsequently monitoring, which is accomplished in two ways. The first is installing on-board diagnostic (OBD) systems; in some cases these are sensors that can detect emissions levels. The second is emissions test programs established by government agencies, which has been done in many countries such as the US, Canada, and Japan.

1.3.1 Standards and Regulations

Standards and regulations for automobile emissions are set by accounting for the effects of each pollutant on public health and the environment. Due to the increase in the number of automobiles and a recognized need for better air quality, government environmental agencies have been continuously imposing tighter regulations to reduce emissions from vehicle engines. Overall, automobile manufacturers have made remarkable progress in reducing pollutant emissions via advanced engine design and using cleaner fuels and highly developed exhaust aftertreatment technologies. Table 1.2 summarizes the history of heavy-duty, diesel-fueled vehicle emissions legislation in the U.S, Europe, and Canada from 1998 to 2010 [7, 8].
Table 1.2 History of automobile legislations, g/KW-hr

<table>
<thead>
<tr>
<th>United States (US)</th>
<th>Year</th>
<th>HC</th>
<th>NO\textsubscript{X}</th>
<th>CO</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1998</td>
<td>1.75</td>
<td>5.4</td>
<td>20.8</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>2004</td>
<td>0.67</td>
<td>3.35</td>
<td>20.8</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>2007</td>
<td>0.187</td>
<td>1.6</td>
<td>20.8</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>2010</td>
<td>0.187</td>
<td>0.26</td>
<td>20.8</td>
<td>0.013</td>
</tr>
<tr>
<td>Europe</td>
<td>2000 (Euro III)</td>
<td>0.66</td>
<td>5.0</td>
<td>2.1</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>2005 (Euro IV)</td>
<td>0.46</td>
<td>3.5</td>
<td>1.5</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>2008 (Euro V)</td>
<td>0.25</td>
<td>2.0</td>
<td>1.5</td>
<td>0.02</td>
</tr>
<tr>
<td>Canada</td>
<td>1998-2004</td>
<td>1.75</td>
<td>5.4</td>
<td>20.8</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>2005</td>
<td>HC + NO\textsubscript{X} = 1.0</td>
<td>19.3</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2008-2010</td>
<td>0.187</td>
<td>0.26</td>
<td>19.3</td>
<td>0.013</td>
</tr>
</tbody>
</table>

1.4 Technology

In the previous sections, automobile emissions and how these emissions are managed and controlled by environmental agencies were discussed. The ultimate step is finding
suitable pollution control technologies to mitigate these emissions and meet the regulatory requirements.

1.4.1 Diesel Automobile

The interest in diesel engines has recently increased due to their better fuel economy, and associated reduced CO$_2$ emissions, relative to gasoline engines. Switching to diesel powered vehicles could reduce CO$_2$ emissions from the transportation sector by 25% from their current levels [9]. Diesel engines not only emit less CO$_2$, but also less hydrocarbon (HC), CO, and NO$_X$ as shown in Table 1.3 [9].

Table 1.3 Heavy duty diesel vs heavy duty gasoline engine emissions

<table>
<thead>
<tr>
<th>Emissions (g/KW-h)</th>
<th>Diesel Engine</th>
<th>Gasoline Engine</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>0.2</td>
<td>1.08</td>
</tr>
<tr>
<td>CO</td>
<td>2</td>
<td>40.5</td>
</tr>
<tr>
<td>NOx</td>
<td>4.6</td>
<td>5.76</td>
</tr>
<tr>
<td>PM</td>
<td>0.09</td>
<td>-</td>
</tr>
</tbody>
</table>

1.4.2 Diesel Exhaust Emissions Technologies

Despite the fact that the diesel engine is promising from a fuel economy standpoint, further efforts are needed to reduce emissions in order to meet recently imposed, and upcoming, regulations. The following sections will describe some exhaust aftertreatment technologies that could be, and have already been, applied to diesel engines to minimize emissions.
1.4.2.1 Three-Way Catalytic Converter

The three-way catalytic (TWC) converter is used to clean exhaust from most gasoline vehicles. The TWC converter contains precious metals, such as platinum, palladium and rhodium, for chemically converting some pollutants in the exhaust gases, such as CO, unburned hydrocarbons, and NO\textsubscript{X}, into harmless compounds. The basic chemical reactions occurring on the TWC can be described as follows:

\begin{align*}
2 \text{NO}_X & \rightarrow x\text{O}_2 + \text{N}_2 \\
\text{CO} + \frac{1}{2}\text{O}_2 & \rightarrow \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}
\end{align*}

TWC converters have been used in cars since 1980 [10] and have had a significant impact in the reduction of NO\textsubscript{X}, CO and hydrocarbons from engine exhaust. The TWC converter is designed for use in exhaust that is net-free of oxygen, in other words the engine operates with a stoichiometric air to fuel ratio. Diesel engines operate with excess air, therefore there is a significant amount of O\textsubscript{2} in the exhaust. In the literature, there is a consensus that the TWC converter can reduce only a small fraction of lean-burn engine NO\textsubscript{X} emissions due to its design focus on operation where little to no oxygen is present during reaction.

1.4.2.2 Selective Catalytic Reduction (SCR)

Selective catalytic reduction (SCR) is a process where a reductant such as ammonia (NH\textsubscript{3}) or a hydrocarbon is added to the engine’s exhaust gas to reduce NO\textsubscript{X} emissions. Some available vehicle models utilizing SCR technology are the Mercedes-Benz E320
and Vision GL 320. In NH₃-based SCR, NH₃ can either be injected as NH₃ or originate from the decomposition of injected urea. The reductants, NH₃ or hydrocarbons, react selectively with NOₓ to form N₂ and H₂O. NH₃-based SCR can meet the regulations being imposed, however there is currently no catalyst for hydrocarbon-based SCR that has the efficiencies required to meet today’s regulations. NH₃ SCR reactions take place in the presence of a catalyst, which is commonly a Fe or Cu-doped zeolite catalyst.

Several SCR reaction pathways have been suggested. The three primary ones are:

\[
\begin{align*}
4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 & \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \quad \text{(standard reaction)} \tag{1-5} \\
2 \text{NH}_3 + \text{NO}_2 + \text{NO} & \rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O} \quad \text{(fast reaction)} \tag{1-6} \\
8 \text{NH}_3 + 6 \text{NO}_2 & \rightarrow 7 \text{N}_2 + 12 \text{H}_2\text{O} \quad \text{(slow reaction)} \tag{1-7}
\end{align*}
\]

The first reaction pathway is called the "standard reaction" [11] and is considered relatively slow, especially at low temperature. The second is called the "fast reaction" [12] and is considered much faster than the standard SCR reaction, especially at low operating temperature (~200˚C). The third pathway reaction involves the reaction of NH₃ with NO₂ and is slow relative to the others. This reaction tends to occur at temperatures greater than 250°C and when NO₂ exceeds 50% of the total NOₓ (NO+NO₂) [13,14].

Although SCR technology can achieve significant reductions in NOx emissions, it has some associated problems:

- SCR technology would require a distribution network for urea or NH₃. In addition, there are toxicity, storage and refueling problems with these reductants [15].
NH$_3$ slip, and an associated odor [16], can occur and consequently SCR requires a very accurate injection system for urea or NH$_3$ to assure that all the NH$_3$ is consumed.

### 1.4.2.3 Diesel Oxidation Catalyst

Diesel oxidation catalysts (DOCs) are used in most diesel engine exhaust clean-up technologies. DOCs are typically comprised of precious metals dispersed on Al$_2$O$_3$ or zeolite [9]. The DOC is effective for the control of CO, hydrocarbons, and the soluble organic fraction of PM.

As the name implies, DOCs are effective oxidation catalysts, with the common reactions including CO, hydrocarbon and NO oxidation. CO and hydrocarbon emissions are thus reduced. NO oxidation, as will be discussed in greater detail in the literature review section, is also a desired reaction, as several downstream technologies are more efficient with NO$_2$ as the NO$_X$ source, relative to NO.

The incorporation of zeolite into the formulation is a recent development. Zeolites adsorb hydrocarbons at low temperature and release them at about 250°C, where they can then be oxidized by the precious metals [17]. The adsorption at low temperature helps reduce cold start hydrocarbon emissions.

### 1.4.2.4 NSR Catalyst Technology

NO$_X$ storage/reduction (NSR) is a relatively new catalyst technology for NO$_X$ emission abatement from lean-burn engines. NSR catalysts were first placed on both the Dodge
Ram and GM’s Humvee in 2007 are expected to be used more wide-spread in the near future to meet 2007 and 2010 emissions standards in the US, Europe, and Japan. Reduction of NO\textsubscript{X} to N\textsubscript{2} over a NSR catalyst is accomplished in sequential reaction steps [18]. Key reactions include storage of NO\textsubscript{X} by adsorption onto alkali and/or alkaline earth components, such as Ba, in the form of nitrate or nitrite species, and an intermittent addition of reductant to reduce the surface NO\textsubscript{X} species to N\textsubscript{2}. This technology operates in two phases; called lean and rich. The lean phase is the trapping or storage phase and the rich phase is the regeneration or reduction phase. In NSR, one cycle takes approximately ½ to 2 minutes, with 1 to 5 seconds for the rich phase. The lean phase can be considered normal engine operation where the exhaust gas includes CO\textsubscript{2}, H\textsubscript{2}O, O\textsubscript{2}, N\textsubscript{2} and NO\textsubscript{X} species. The NO\textsubscript{X} species react with the alkali or alkaline earth species to form nitrites and nitrates. With time, the storage materials become saturated with NO\textsubscript{X} species. Thus, the rich phase is needed to clean the storage materials from adsorbed NO\textsubscript{X}, thereby beginning a new cycle where the storage species are nitrate-free and are able to adsorb entering NO\textsubscript{X} species again. This rich phase contains many of the same gas species, except there should be some form of reductant, such as fuel, CO, or H\textsubscript{2}, but little or no O\textsubscript{2}. In NSR, the reductants react with surface NO\textsubscript{X} species and convert them to N\textsubscript{2}. These reductants originate in the exhaust via combustion of the extra fuel and air.

1.5 Motivation

Emissions from vehicles have become a societal concern. In many cities, the automobile is the single greatest polluter, as emissions from millions of vehicles on the road add up. In the U.S. for example, 28% of all US greenhouse gases come from the transportation
Despite the fact that new vehicles emit significantly less pollutants compared with older-model vehicles, due to the continuing growth in the number of vehicles and total distance traveled by each vehicle, the total emissions remain high.

In diesel-powered automobiles, the DOC can significantly reduce the amounts of unburned hydrocarbons and CO. However, it is very difficult to dissociate the nitrogen oxides to elemental N\textsubscript{2} and O\textsubscript{2} due to the oxygen present in diesel engine exhaust. Consequently, different catalyst technologies, such as SCR and NSR have been developed to reduce NO\textsubscript{X} to N\textsubscript{2} in lean exhaust.

1.6 Objectives

The aim of this study is to evaluate the effect of operating conditions on, and integration of, the DOC and NSR catalyst on NO\textsubscript{X} emissions. The investigation included effects of temperature, gas composition, and cycling times on the overall conversion efficiencies for key reactants.

The specific objectives as related to DOC research are:

1. Investigate the oxidation of NO, CO, and hydrocarbons individually and in mixtures with NO\textsubscript{2} under oxidizing conditions.

2. Study hydrocarbon steam reforming and water gas shift reactions, quantify the production of H\textsubscript{2}, and probe carbon deposition and regeneration during steady-state and cycling operations.

The specific objectives as related to the NSR catalyst are:
1. Evaluate the effect of NO\textsubscript{X} source (NO or NO\textsubscript{2}) on the overall conversion to N\textsubscript{2}.

2. Investigate the influence of different rich times with same reductant type and amount on the overall reduction to N\textsubscript{2}.

3. Investigate the effect of HC species during the regeneration event on catalyst performance.

**DOC and NSR in series**

The aim of this part of the study is to evaluate performance when both the DOC and NSR catalyst are placed in series, which represents the actual configuration in NSR-equipped diesel automobiles. Two configurations of a DOC and NSR catalyst were compared. In the first configuration, the DOC and NSR catalyst were placed in series. In the second configuration, the DOC and NSR catalysts were divided into two equal volumes and placed in alternating series.

**1.7 Research Contribution**

This research provides unique contributions in developing advanced aftertreatment technologies that mitigate diesel automobile emissions. These include the following highlights:

- Competitive reactions between NO, NO\textsubscript{2}, CO and hydrocarbons are evaluated, leading to a more representative understanding of the mechanisms on a DOC in practice.

- Hydrogen production via the hydrocarbon steam reforming and water gas shift reactions over the DOC during rich conditions is evaluated. This will demonstrate
the amount of hydrogen formed, which would subsequently be used as a reductant to reduce NO\textsubscript{X} species in the downstream NSR catalyst. This also provides insight about any fuel penalty associated with NO\textsubscript{X} traps.

- A systematic and comprehensive understanding of the performance of a NSR catalyst when either NO or NO\textsubscript{2} is used as the feed NO\textsubscript{X} source is provided. The comparison was made between the two when the same amount of NO\textsubscript{X} is trapped so that the effects during the regeneration phase could also be observed.

- The effects of regeneration-phase time, while keeping the total amount of reductant introduced during the regeneration phase the same, is evaluated. Such a study provides guidance for control strategies that could help minimize fuel penalties associated with NSR technology.

- Regenerating the NSR catalyst using hydrocarbons is systemically investigated. This will show at what temperatures WGS and steam reforming reactions become important, and if the direct reaction between the HC and the surface is key, rather than the indirect intermediate route, both of which are still proposed in the literature.

- Integrated systems containing both DOC and NSR catalysts, which represents the actual configuration in NSR-equipped diesel automobiles, is studied. A novel configuration was also evaluated, by alternating DOC and NSR catalysts in series, taking advantage of increased NO oxidation and H\textsubscript{2} evolution through more extensive WGS and steam reforming reactions.
1.8 Thesis Outline

This thesis is divided into nine chapters and it is organized as follows:

**Chapter 1: Introduction and Background**

This chapter provides an introduction and background about automobile emissions and their effect, standards and regulations to manage and control these emissions, and a brief description about some automobile aftertreatment emission reduction technologies. It also provides the motivation for this research, research objectives, contributions, and organization of the thesis.

**Chapter 2: Literature Review**

This chapter presents a detailed background and a review of several relevant previous studies for DOCs and NSR catalysts.

**Chapter 3-4: Diesel Oxidation Catalyst (DOC)**

In Chapter 3, competitive reactions between NO, NO$_2$, CO and different hydrocarbons (C$_3$H$_6$, dodecane, and xylene) are discussed. Hydrogen production via the SR and WGS reactions is extensively discussed in Chapter 4. The main focus is to compare and quantify the amount of hydrogen formed during steady-state and cyclic operation. As a part of this study, coke formation and regeneration was investigated after these experiments to explain the observed differences.
Chapter 5-7: NO\textsubscript{X} Storage and Reduction (NSR) Catalyst

In Chapter 5, the performance of a model NSR catalyst as a function of NO\textsubscript{X} source, NO versus NO\textsubscript{2}, is discussed. The assessment included comparison with constant cycling times and trapping the same amount of NO\textsubscript{X} during the lean phase. In Chapter 6 the effect of regeneration time, while keeping the total amount of reductant introduced during the regeneration phase the same, is evaluated. The evaluation included trapping performance, NO\textsubscript{X} release and formation of NH\textsubscript{3}. In Chapter 7, the regeneration of a NSR catalyst using representative HCs, propylene for short chain, dodecane for long chain and m-xylene for cyclic species, is discussed. Hydrogen and CO were also used for comparison with the HCs. Hydrocarbon steam reforming and temperature programmed reduction (TPR) experiments were also performed to characterize the performance changes observed as a function of temperature.

Chapter 8: DOC and NSR Catalyst in Series

In this chapter, the performance when both the DOC and NSR catalyst are placed in series, which represents the actual configuration in NSR-equipped diesel automobiles, is presented. Two configurations of a DOC and NSR catalyst were compared. In the first configuration, the DOC and NSR catalyst are placed in series, while in the second configuration, the DOC and NSR
catalysts were divided into two equal volumes and were placed in alternating series

Chapter 9:  Conclusions and Recommendations

In this chapter, the overall conclusions from this research and recommendations for future work are listed.

Note: Chapters 3 through 8 have been or will be submitted individually for journal publication. Therefore, each of these chapters is “stand-alone” and includes its own introduction, experimental methodology and reference sections.
References

5. R. D. Griffin, Principles of air quality management, Published by Lewis, 1994, page 324.

Chapter 2: Literature Review

The literature review includes discussion of both diesel oxidation catalyst (DOC) technology and NO\textsubscript{X} storage and reduction catalyst (NSR) technology. The first section will focus on the DOC and highlight the oxidation reactions, competitive reactions, catalyst formulation, and the effect of thermal degradation on DOC performance. In the next section, a detailed review on the five sequential reaction steps in NSR catalysis and a technique by which the chemistry of an NSR catalyst can be axially resolved is presented.

2.1 Diesel Oxidation Catalyst

DOCs were originally used to oxidize CO and hydrocarbons (HCs) into CO\textsubscript{2} and H\textsubscript{2}O and help eliminate odors associated with diesel exhaust. DOCs are now also used with NO\textsubscript{X} and PM control systems. Their role in these systems is as preheating devices for diesel particulate filters (DPFs) and SCR and NSR catalysts [1,2], as well as for NO oxidation. The heat is generated from exothermic HC oxidation reactions, with HC amounts controlled either by directly injecting fuel into the exhaust stream or adjusting the combustion strategy in the engine [1,3,4]. NO oxidation is desired for better low temperature SCR performance (as mentioned in the Introduction, the “fast SCR” reaction requires an equimolar mixture of NO-NO\textsubscript{2} and diesel engine exhaust contains on the order of 5-10\% NO\textsubscript{2}) and also results in more efficient NSR catalyst performance as will be discussed below.
2.1.1 Reactions on a Diesel Oxidation Catalyst

Due to the complicated nature of diesel fuel and combustion, a vast number of species are emitted from the combustion process. For most applications, a DOC is the first catalyst in the aftertreatment system. Key reactions that occur over the DOC include the following [5]:

\[
2C_xH_y + (2x + y/2) O_2 \rightarrow 2xCO_2 + yH_2O \quad (2-1)
\]

\[
CO + \frac{1}{2} O_2 \rightarrow CO_2 \quad (2-2)
\]

\[
NO + \frac{1}{2}O_2 \rightarrow NO_2 \quad (2-3)
\]

\[
SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \quad (2-4)
\]

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad (2-5)
\]

\[
C_nH_m + 2nH_2O \rightarrow (2n + m/2) H_2+nCO_2 \quad (2-6)
\]

In general, DOCs can achieve more than 90% reduction in CO and HC emissions at exhaust temperatures higher than \(~300°C\) [6]. At lower operating temperatures however, as in the case of low-speed driving and engine start-up, the catalytic oxidation of HC and CO remains a significant challenge [7,8]. One solution to overcome the low operating temperature difficulty is incorporating zeolites into the catalyst formulation [9,10]. Zeolites can adsorb and trap HCs at low operating temperatures. Then as the temperature rises, to about 250°C, which is above the light-off temperature (the temperature necessary to initiate the catalytic reaction) for most HCs over Pt [11], HCs desorb and are oxidized to H2O and CO2. Another proposed solution for low temperature HC and CO emissions control is using an electrically heated catalyst to decrease the time required for HC light-
off [12]. Finally, it has also been proposed [13] to take advantage of low temperature exothermic H₂ oxidation, which can occur at room temperature over precious metals. The H₂ can be generated in an on-board device by hydrolysis of water. However, this method is complex and expensive [14].

It is important to note that high HC or CO conversions, at high temperature, can be limited by mass transfer in the catalyst [6]. This is influenced by cell density, pore size, and dispersion of active sites.

There is no single HC exiting the engine, and therefore, there is the possibility of competing reactions. For the sake of simplicity, individual HCs and simple HC mixtures are always studied [2, 10,15-17]. If competing reactions exist, the measured conversions in tests with individual reactant species would always be higher than that in real application. In practice, engine exhaust contains many HC species, which react at different rates [18]. Some HC emission rates, in grams per mile, in diesel exhaust from two vehicles are shown in Table 2.1 [6]. Conversions of CO and HC would not necessarily be comparable with laboratory measured conversions, where pure HC or CO is usually used. Therefore, it is of great importance to study more representative HCs and mixtures of those HCs to have a better understanding of HC oxidation reaction rates and mechanisms.

As a simpler example, CO and H₂ react competitively and affect other reactions, either promoting or suppressing the light-off temperatures. In a recent study [19], self-inhibition of CO on Pt/Al₂O₃ occurred when CO was used, but the addition of H₂ to the mixture caused a reduction in the light-off temperature of CO. In the same study, the authors
found that H₂, without CO, would oxidize at room temperature, but when CO was added H₂ oxidation began only when 50% CO conversion was attained. Similar observations have been reported in other studies [20,21]. Recent evidence suggests that H₂ reduces the light-off temperature of CO by promoting CO desorption from Pt, while CO inhibits the H₂ oxidation due to competitive adsorption [22].

Table 2.1 Emission rates of some hydrocarbons in diesel engine exhaust

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Heavy duty diesel (HD) (g/mile)</th>
<th>Light duty diesel (LD) (g/mile)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total HC</td>
<td>3.65</td>
<td>0.23</td>
</tr>
<tr>
<td>Methane</td>
<td>NA</td>
<td>0.01</td>
</tr>
<tr>
<td>Ethylene</td>
<td>NA</td>
<td>0.04</td>
</tr>
<tr>
<td>Propylene</td>
<td>NA</td>
<td>0.01</td>
</tr>
<tr>
<td>n-decane</td>
<td>0.01</td>
<td>NA</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>0.027</td>
<td>NA</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.024</td>
<td>0.02</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.01</td>
<td>0.006</td>
</tr>
<tr>
<td>Xylene</td>
<td>0.006</td>
<td>0.002</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>NA</td>
<td>0.03</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>NA</td>
<td>0.02</td>
</tr>
</tbody>
</table>

NA= data not available, therefore the sum of the individual amounts listed do not equal the total measured.

Although DOCs do little in terms of reducing total NOₓ emissions, they do oxidize NO to NO₂. The NO₂ formed can be used in the downstream aftertreatment technologies. For example, NO₂ can be used to oxidize soot on particulate filters [1, 23]. Particulate filters,
as the name implies, filter soot. At some point however, the soot builds up and needs to be removed. This is done via oxidation. Oxidation of soot with O\(_2\) occurs at temperatures greater than 500\(^\circ\)C, while with NO\(_2\), oxidation can occur as low as 300\(^\circ\)C [7,24]. Therefore, if the amount of NO\(_2\) is increased by using an upstream DOC, this will lower the required temperature for filter regeneration. SCR catalysts, as mentioned above, perform better with an equimolar mix of NO and NO\(_2\), especially at low operating temperature (~200\(^\circ\)C) [25]. Engine out NO: NO\(_2\) is on the order of 90:10. Therefore, if the amount of NO\(_2\) can be increased upstream of the SCR catalyst, this will result in higher NO\(_X\) reduction efficiency. For NSR catalysts, as will be discussed in further detail below, NO\(_2\) is more readily trapped relative to NO, and NO oxidation is therefore critical for NSR catalyst efficiency.

2.1.2 Diesel Oxidation Catalyst Formulation

DOCs are typically made of a catalyst coating a ceramic or metallic monolithic substrate. Monolith substrates are used as they do not result in a high pressure drop, and provide excellent high temperature and thermal shock resistance [26]. The monolith wall is then coated with a porous, high surface area washcoat such as alumina or zeolite. The precious metals are dispersed on the surface and within the pores of the washcoat [14, 26].

Platinum and palladium are the most active precious metals in the oxidation of CO and HCs from diesel exhaust [27, 28]. In a comparative study, the activities of Pt- and Pd-based DOC catalysts were tested for CO and HC oxidation [6], and both CO and HC emissions over the Pd catalyst were higher than that of Pt. Most literature demonstrates
that Pd activity is less than Pt for the oxidation reactions involved in diesel exhaust [29-31]. Rhodium has also been studied for HC, CO, and NO oxidation [28, 32, 33] but the order of activity was Pt > Pd > Rh [28].

A combination of Pt/Pd has also been investigated [15, 34, 35]. After thermal aging, CO and C$_3$H$_6$ light-off temperatures were always lower when using the Pt/Pd bimetallic catalyst compared to tests with a monometallic Pt or Pd catalyst [15]. The authors attributed the higher activity of the bimetallic catalyst to two reasons. First, when only Pd is used, the chemical state of the Pd will be metallic after thermal aging, and metallic Pd is inactive toward HC oxidation. When using a combination of Pt/Pd, Pd will exist in both metallic and oxide states after thermal aging. The second reason is that Pd stabilizes Pt against sintering. This could be due to oxygen exchange between Pt and Pd at high aging temperatures, keeping Pt in a metallic form, which is more stable [28] or possibly because of strong interactions between PdO and the oxide supports [36]. Similar observations were found when comparing monometallic Pt or Pd and bimetallic Pt/Pd supported on γ-Al$_2$O$_3$ for benzene oxidation [35].

The catalyst support can also have a substantial effect on DOC performance. The main function of the catalyst support is to provide high surface area for good dispersion of the precious metal catalytic sites. Inorganic base metal oxides such as Al$_2$O$_3$, SiO$_2$, TiO$_2$, V$_2$O$_5$, ZrO$_2$, and zeolites have been tested as catalyst supports for DOCs [6, 37]. Al$_2$O$_3$ and zeolite washcoats are the most commonly used in commercial DOCs. Al$_2$O$_3$ is often used due to its high surface area, high porosity, and thermal stability. The increased use of zeolites is due their ability to store HCs at low operating temperatures. Due to their
nanometer diameter pore size, they can selectivity adsorb HCs during engine start up and then desorb them at temperatures where HC oxidation starts [38]. Incorporating zeolites in DOC washcoats has shown success in decreasing HC emissions during cold start up [14, 9, 26].

Cerium dioxide (CeO$_2$) is commonly added to DOC formulations [26, 37]. Ceria has the ability to adsorb oxygen in oxidizing atmospheres, and liberate oxygen in reducing atmospheres:

oxidizing: $\text{Ce}_2\text{O}_3 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CeO}_2 \quad (2-7)$

reducing: $2\text{CeO}_2 + \text{CO} \rightarrow \text{Ce}_2\text{O}_3 + \text{CO}_2 \quad (2-8)$

CeO$_2$ also enhances the water gas shift (WGS) reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$, and steam reforming reaction in a reducing environment to generate H$_2$, which can then act as a reducing agent for NO$_X$ to N$_2$ [26]. CeO$_2$ also stabilizes Pt against sintering [26] by maintaining the dispersion of Pt particles.

**2.1.3 Hydrocarbon Steam Reforming**

Some current diesel automobiles are equipped with a DOC as an upstream catalyst and downstream SCR and/or NSR catalysts. For example, the Dodge Ram, Humvee, and some Toyota models are already equipped with both DOC and NSR catalysts. While the Mercedes-Benz E320 and Vision GL 320 in Europe are equipped with both DOC and SCR catalysts.
For this project, the design assumed is a DOC placed upstream of a NSR catalyst. For NSR catalyst application, as will be discussed in more detail below, the engine operates in two cycles; lean and rich. The lean phase is typically the normal diesel engine operating condition, whereas in the rich phase, the flow composition is similar except no $O_2$ and less $NO_X$ is present, and reductant species are present. $H_2$, the most efficient $NO_X$ reductant as will be shown below, can be produced in this rich phase from HC steam reforming:

$$C_nH_m + 2nH_2O \rightarrow (2n + m/2) H_2 + nCO_2$$ (2-9)

HC steam reforming has been extensively studied over the last several decades. The main interest in this study, however, is HC steam reforming during cyclic operation, and specifically what occurs when cycling between lean and rich atmospheres during NSR catalyst application.

Several studies have investigated HC steam reforming over Pd and Pt. The temperatures investigated in those past studies match the temperature range NSR catalysts operate in and since DOCs contain Pt and Pd supported on either alumina or zeolites, steam reforming is likely to occur. The following is a summary of a few studies that evaluated catalysts with similar components and in temperature ranges of interest.

$C_3H_8$ steam reforming has been investigated over Pd/CeO$_2$/Al$_2$O$_3$ and Pt-Rh/CeO$_2$/Al$_2$O$_3$ catalysts [39, 40]. Steam reforming started at about 350°C. Steam did not need to be added to the inlet gases to initiate steam reforming if oxygen was present since water formed from oxidation of some of the $C_3H_8$. Steam reforming began after the oxygen was
completely consumed. Steam reforming of C\textsubscript{3}H\textsubscript{6} and isopropanol (CH\textsubscript{3}CHOHCH\textsubscript{3}) was also investigated over a powder Pd–Cu/γ-Al\textsubscript{2}O\textsubscript{3} catalyst [41]. Steam reforming of both C\textsubscript{3}H\textsubscript{6} and CH\textsubscript{3}CHOHCH\textsubscript{3} started as low as 327ºC and increased steadily until complete conversion at about 527ºC.

During the reductant-rich phase of NSR catalyst testing, CH\textsubscript{4} has been observed [42], and it is therefore important to also consider CH\textsubscript{4} reforming reactions. Steam reforming of CH\textsubscript{4} was investigated over Pd/Al\textsubscript{2}O\textsubscript{3}, Pd/CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} [43] and Rh/α-Al\textsubscript{2}O\textsubscript{3} catalysts [44]. Again, steam reforming began at 345-400ºC and increased with temperature. The catalyst including CeO\textsubscript{2} showed higher amounts of H\textsubscript{2} formed, indicating CeO\textsubscript{2} has the ability to enhance the steam reforming reaction.

### 2.2 NO\textsubscript{X} Storage and Reduction Technology

The NSR process cycles through two phases; a lean phase and a rich phase. In the lean phase, NO is oxidized to NO\textsubscript{2}. NO\textsubscript{2} is then adsorbed by trapping materials, such as Ba, in the form of Ba(NO\textsubscript{3})\textsubscript{2} and/or Ba(NO\textsubscript{2})\textsubscript{2}. In operation, the lean phase continues until NO\textsubscript{X} starts to slip. At some point after slip is observed, the second phase of the cycle is typically started. In the rich phase, reductants are introduced to reduce the NO\textsubscript{X} species to N\textsubscript{2}.

The entire process takes approximately ½ to 2 minutes. Overall, the reduction of NO\textsubscript{X} to N\textsubscript{2} over an NSR catalyst can be described, as shown in Figure 2.1 [45], with five sequential reaction steps.
2.2.1 NO Oxidation to NO₂ over the Noble Metal Component

The majority of NO\textsubscript{X} emitted is NO, usually around 90\%, with the rest NO\textsubscript{2}. Since NO\textsubscript{2} is trapped more readily than NO, or may even be the required reactant for trapping, NO oxidation is a key step in the process. For this reason, DOCs are typically placed upstream of NSR catalysts, but NO oxidation can also occur on the NSR catalyst. Pt is the most commonly used catalyst component due to its high red-ox activity and results typically show that Pt is better than Pd for NO oxidation [29-31, 46]. Although Pd and Rh have less NO oxidation activity, they are key for NO\textsubscript{X} reduction, thus their addition [47]. It has been demonstrated that Pt particle size affects NO oxidation rates; as the particle size of Pt increases, NO oxidation surprisingly increases, demonstrating structure dependence [48].

\textbf{Figure 2.1} Overall NSR cycle
Figure 2.2 Effect of temperature on NO oxidation. The inlet gas contained 10% O₂, 330 ppm NO, 5% H₂O, 5% CO₂ and a balance of N₂ and the experiment was run with a commercial NSR sample at a space velocity of 30,000 hr⁻¹.

As shown in Figure 2.2 [45], NO oxidation is a function of temperature. At low temperature, the NO oxidation rate increases as the temperature increases and is kinetically limited. The conversion under the conditions of the test described reached its maximum at approximately 350°C and then started to decrease. The decrease at high temperature is due to thermodynamic limitations; the equilibrium conversion was reached.

The rate of NO oxidation has a positive dependency with respect to NO concentration and a negative dependency with respect to the product NO₂ concentration [49]. However,
the NSR catalyst traps NO\textsubscript{2} and therefore may minimize this inhibition when trapping sites are available, but will still result in less NO oxidation once those sites are full. This inhibition is due to the fact that Pt activity toward NO oxidation drops with oxygen chemisorption [50]. The oxygen may not only originate from gas-phase O\textsubscript{2}, but also can come from product NO\textsubscript{2}, and NO\textsubscript{2} is known as a strong oxidizer [51].

### 2.2.2 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 trapping components, which are usually alkali and alkaline earth components, the most typical studied being BaO. Numerous studies [52-54] have suggested that NO\textsubscript{2} is a precursor for adsorption and nitrate formation. However, there is some indication that NO might also be adsorbed by trapping materials in the presence of O\textsubscript{2}, although to a lesser extent and at slower rates [55]. Overall, NO\textsubscript{X} is adsorbed in the form of nitrate and/or nitrite 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} [54] while nitrites and nitrates have been detected when NO + O\textsubscript{2} was introduced at low temperature [56].

The selection of trapping materials is obviously an important factor and several have been tested, such as mixed oxides, perovskites, and inorganic oxides [55]. However, alkali and alkaline earth components show better trapping capacity due to their higher basicity [57]. 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}. For example, 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 [58], however, the amount of NO\textsubscript{2} adsorbed was small; approximately 1% of the NO\textsubscript{X} trapped by Ba [55].
Temperature also impacts NO\textsubscript{X} sorption. As shown in Figure 2.3 [45], sorption increases with temperature until the 300 to 400°C range and then decreases.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.3.png}
\caption{NO\textsubscript{X} storage capacity. The reactant gas was composed of 10\% O\textsubscript{2}, 330 ppm NO, 5\% H\textsubscript{2}O, 5\% CO\textsubscript{2} and a balance of N\textsubscript{2} at a space velocity of 30,000 hr\textsuperscript{-1} using a commercial NSR catalyst.}
\end{figure}

With increasing temperature, the thermal stability of nitrate and/or nitrite species decrease, and therefore, at temperatures greater than ~350°C, typically NO\textsubscript{X} storage capacity decreases [59, 60]. One reason for the increase observed, when the temperature is increased from a relatively low temperature, is increasing NO oxidation. NO conversion to NO\textsubscript{2} typically reaches a maximum at around 350°C, helping to increase storage rates up to this temperature as well. The increase in capacity as the temperature increases, at low test temperatures, is also due to improved regeneration with temperature as will be discussed below. Thus, at low temperatures, the amount of NO\textsubscript{X} 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 NO\textsubscript{X} trapping capacity is the gas composition. A common assumption is that BaO is the easiest to form nitrates, relative to hydroxides or carbonates [48]. The presence of CO\textsubscript{2} in the gas stream results in BaCO\textsubscript{3} formation which is more stable than BaO. This increased stability can hinder nitrate and/or nitrite formation, which in turn will affect the trapping capacity. In one example, with a Pt/K/Al\textsubscript{2}O\textsubscript{3} catalyst the trapping capacity decreased by 45\% when CO\textsubscript{2} was added to the gas mixture [61].

Similarly, the presence of H\textsubscript{2}O can cause decreased trapping capacity by Ba(OH)\textsubscript{2} formation. In the same study described above, the addition of 5\% H\textsubscript{2}O to a dry mixture caused a 16\% loss in trapping capacity [61]. However, when both CO\textsubscript{2} and H\textsubscript{2}O are added, the H\textsubscript{2}O had a positive impact on NO\textsubscript{X} storage capacity, via equilibrium between BaCO\textsubscript{3} and Ba(OH)\textsubscript{2}. The carbonate is more stable than the hydroxide, so additional hydroxide relative to carbonate resulted in better trapping performance.

The presence of O\textsubscript{2} also can influence the trapping capacity via oxidation of NO to NO\textsubscript{2} as well as oxidation of surface NO\textsubscript{X} to nitrates. It has been shown [62] that as O\textsubscript{2} concentration increases, the NO\textsubscript{X} storage capacity increases.

Although the trends and mechanisms of NO\textsubscript{X} storage have been investigated [51,55,63,64], due to the complexity of the catalyst, process and their sensitivity to experimental conditions, there is still debate regarding the mechanisms and the potential reactions involved in multiple catalytic steps [64]. Several mechanisms have been
suggested for NO\textsubscript{X} adsorption. The more accepted are listed below, with Ba used as a representative alkali or alkaline earth components. Hydroxide and carbonates are also present, but the oxide is selected as an example.

- NO\textsubscript{2} reacts with BaO to form nitrate in the absence of O\textsubscript{2} via the disproportionation reaction [65]
  \[
  \text{BaO} + 3\text{NO}_2 \rightarrow \text{Ba(NO}_3\text{)}_2 + \text{NO} \quad (2-10)
  \]
- NO\textsubscript{2} reacts with BaO first and then with BaO\textsubscript{2} to form nitrate [51]
  \[
  \text{BaO} + \text{NO}_2 \rightarrow \text{BaO}_2 + \text{NO}, \quad \text{BaO}_2 + 2\text{NO}_2 \rightarrow \text{Ba(NO}_3\text{)}_2 \quad (2-11)
  \]
- NO\textsubscript{2} reacts with BaO to form nitrate in the presence of O\textsubscript{2}
  \[
  \text{BaO} + 2\text{NO}_2 + \text{O} \rightarrow \text{Ba(NO}_3\text{)}_2 \quad [66] \quad (2-12)
  \]
- NO\textsubscript{2} reacts with BaO to form nitrate and nitrite species [67]
  \[
  2\text{BaO} + 4\text{NO}_2 \rightarrow \text{Ba(NO}_2\text{)}_2 + \text{Ba(NO}_3\text{)}_2 \quad (2-13)
  \]

Several mechanisms have been proposed to explain the performance improvements observed when NO\textsubscript{2} is used instead of NO as the NO\textsubscript{X} source. First, if trapping is a function of NO\textsubscript{2} partial pressure [68], then when NO\textsubscript{2} is used, the very inlet of the catalyst can participate in trapping [48] whereas with NO, oxidation to NO\textsubscript{2} must occur before efficient trapping can be seen. A second possibility invokes the presence of two types of trapping sites. One Ba site type is that near Pt and the other is distant from Pt. NO can only adsorb on the Ba sites which are in close proximity with Pt since it needs to be oxidized to NO\textsubscript{2} prior the adsorption event. While with NO\textsubscript{2}, it can be adsorbed on both Ba site types.
2.2.3 Reductant Evolution

Trapping rates decrease with time as the trapping sites become saturated. Consequently, the catalyst needs to undergo periodic regeneration to remove the adsorbed NO\textsubscript{X}, and hopefully reduce these to N\textsubscript{2}. This can be achieved by introducing reductants and removing the O\textsubscript{2}, 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 [69]. 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 O\textsubscript{2}, thus the stream is reductant rich. The most widely used reductants in NSR catalyst testing are H\textsubscript{2}, CO, and C\textsubscript{3}H\textsubscript{6} [70-77] the former two observed in rich engine exhaust and the last representing hydrocarbon species, also observed. H\textsubscript{2} is superior for NO\textsubscript{X} reduction with NSR catalysts at lower temperatures compared to CO and C\textsubscript{3}H\textsubscript{6}; however, they are all comparable at higher temperature [70-76]. CO can go through the water-gas-shift reaction to produce H\textsubscript{2}, which can act as a reductant as well. It has been extensively demonstrated that the WGS reaction occurs over NSR catalysts [60,78]. But, the CO can poison Pt at lower temperatures (< ~200°C), affecting NO oxidation and NO\textsubscript{X} reduction reactions. For example, in a previous study with both commercial and model NSR catalysts [79], CO was found to decrease performance when present at 200°C, due to Pt poisoning, primarily of the reduction and nitrate decomposition reactions.

Hydrogen can also be obtained from HC steam reforming during regeneration, either over an upstream DOC, as discussed in the previous section, or over the NSR catalyst since it
contains precious metal components as well. Ultimately, the formed H₂ can then act as a reductant to reduce NOₓ species over the NSR catalyst.

Reductants are not only required to reduce the trapped NOₓ, but they are also competitively consumed by oxygen stored on the catalyst surface. Consequently, the amount of reductant needed for regeneration and reduction is also dependent on surface oxygen; the more stored oxygen, the more reductant required.

2.2.4 Nitrate Decomposition and NOₓ Release

Nitrate decomposition and the release of NOₓ from the trapping site occurs due to (1) heat caused by the exothermic reaction between the entering reductant and any surface or residual gas-phase oxygen and (2) a change in gas composition with the switch from the lean to rich environment [48]. In terms of the temperature change, more heat will be generated with more reactant oxygen. Nitrate stability and therefore NOₓ release is a function of temperature and therefore, the associated temperature rise may be enough to decrease the stability of the surface nitrate or nitrite species and result in NOₓ release from the trapping site.

The NOₓ observed in the catalyst outlet gas composition of course originates from NOₓ release, but also lack of reduction of those released species. For reduction to occur, nitrates must first decompose. The NOₓ can then be reduced on the surface, if in contact with a precious metal site, or is released into the gas-phase for re-adsorption onto a precious metal site. What is observed in the outlet gas during the rich phase is a portion of the latter. For example, at lower temperatures, the observed release of NOₓ is strongly dependent on the degree that the catalyst can activate the reductants [48]. 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, and therefore increased amounts released, is the main cause for observed NO\textsubscript{X} release [48].

The absence of NO\textsubscript{X} and O\textsubscript{2} in the regeneration phase leads to a decrease in the stability of nitrate and/or nitrite species. For example, by Liu and Anderson [76] demonstrated 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 become less stable, leading to nitrate and/or nitrite species decomposition and NO\textsubscript{X} release. Via thermodynamic calculations, it has been predicted [80] that there is a direct correlation between the amount of CO\textsubscript{2} and the stability of NO\textsubscript{X} species, with more CO\textsubscript{2} present resulting in more NO\textsubscript{X} released; likely associated with carbonate/nitrate stability. The presence of H\textsubscript{2}O in the gas stream decreased the amount of observed NO\textsubscript{X} release [80, 81], possibly being related to displacement of carbonate groups by hydroxyl groups.

Pt catalyzes the decomposition of nitrate species [76], and therefore another contributing factor to nitrate decomposition and NO\textsubscript{X} release is the proximity of Pt sites to the alkali and alkaline earth components [82].

**2.2.5 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. 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
N₂ over the precious metals. Two main mechanisms have been proposed for reduction of NOₓ to N₂ 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 [73]. The second mechanism [83] proposes that the reductant is activated on the precious metal and reacts directly with NOₓ. Propylene was taken as an example for the reductant source in the scheme presented below.

\[
\begin{align*}
\text{C}_3\text{H}_6 (g) + \text{Pt} & \rightarrow \text{Pt}-\text{C}_3\text{H}_6 & (2-14) \\
\text{Pt-C}_3\text{H}_6 + 2\text{Pt} & \rightarrow 3\text{Pt-CH}_2 & (2-15) \\
\text{Pt-CH}_2 + 3\text{Pt-NO} & \rightarrow 4\text{Pt} + \text{CO}_2 (g) + \text{H}_2\text{O} (g) + 1.5 \text{N}_2 (g) & (2-16)
\end{align*}
\]

Reductant type and amount, temperature, and lean/rich time ratio are known to affect NOₓ reduction.

Abdulhamid et al. [84] did a comparative study between H₂, CO, C₃H₆, and C₃H₈ for reduction of NOₓ over BaO/Al₂O₃ samples containing Pt, Pd, or Rh. The results of this study showed that H₂ and CO were superior for NOₓ reduction in comparison to C₃H₆ and C₃H₈ especially when Pt/BaO/Al₂O₃ was used. Another study compared H₂, CO, and a mixture of H₂ and CO as the reductant source over a Pt/BaO/Al₂O₃ catalyst [85]. The results showed that when mixtures of CO and H₂ were used at low temperature (~147°C), low NOₓ reduction was achieved in comparison with using only H₂. The authors attributed the poor NOₓ reduction when using the mixture to reductant competition for adsorption on Pt sites. With stronger CO bonding, the surface H₂ concentration would be lower in the presence of CO, and if conditions favor reduction with H₂ 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. In a separate study [79] the effect of CO and H\textsubscript{2} mixtures on overall reduction performance was studied. At 200\degree C, the mixture of CO and H\textsubscript{2} was better than using only CO, but using only H\textsubscript{2} always resulted in better performance. At 300\degree C, the trapping and reduction of NO\textsubscript{X} were comparable when either H\textsubscript{2}, CO, or mixtures of the two for were used. At 400 and 500\degree C, mixtures of the two led to slightly improved performance relative to H\textsubscript{2} and CO. The authors found that the lower performance at 200\degree C when CO was present was due to CO poisoning the precious metal sites to not just reduction of released NO\textsubscript{X}, but also toward the catalyzed decomposition of the nitrates.

The amount of reductant of course also has an impact on NO\textsubscript{X} reduction. In one study [79] the performance of the catalyst improved with each incremental increase in H\textsubscript{2} or CO concentration, except at 200\degree C, where the performance decreased with each increase in CO amount due to Pt poisoning. In another study, Bailey et al. [86] demonstrated that increasing the amount of CO during the regeneration phase at T > 300\degree C resulted in improved overall NO\textsubscript{X} reduction under the conditions tested.

NH\textsubscript{3} is a by-product that can be formed during the regeneration phase [75, 87-89]. NH\textsubscript{3} formation has been observed when H\textsubscript{2} was used as a reducing agent in the regeneration period over Pt/Ba-based catalysts [88, 89] as well as with mixtures of H\textsubscript{2} and CO [87],
and pure CO [75]. NH$_3$ can be formed in two ways; directly from reaction of H$_2$, added during regeneration, with NO on the catalyst or with the H$_2$ produced from the WGS reaction when CO and H$_2$O are available in the regeneration mixture [90]. NO can be easily dissociated to atomic nitrogen and oxygen over precious metals at higher temperatures [91]. Subsequently, the N atom would react with dissociated H$_2$ to form NH$_3$. It should also be pointed out that NH$_3$ has been labeled as a hydrogen carrier and a reductant participating in NO$_X$ reduction via SCR reaction chemistry [88]. Cumaranatunge et. al. [92] have demonstrated equivalent reduction efficiency of H$_2$ and NH$_3$ in NSR catalysis, and facile formation of NH$_3$ from a feed of NO and H$_2$ over a Pt/Al$_2$O$_3$ catalyst.

Formation of N$_2$O during the regeneration phase is also common. In a proposed path, during the regeneration phase, the reductant can reduce the Pt site allowing NO to decompose and form N$_2$O via: 2Pt-NO $\rightarrow$ N$_2$O (g) + Pt + Pt-O [94]. Formation of N$_2$O demonstrates incomplete reduction of NO$_X$ species.

### 2.2.6 Spatially Resolved Capillary Inlet Mass Spectrometry (SpaciMS)

A mass spectrometer (MS) can be used to spatially resolve concentration profiles within a reactor and has been used to measure the gas species concentrations at different locations in monolith-supported NSR catalysts. Such a technique has been developed at Oak Ridge National Laboratory and is called spatially-resolved capillary-inlet mass spectrometry (SpaciMS). Choi et al. [94, 95] have investigated NO$_X$ and H$_2$ concentration profiles over a monolith Pt/K/Al$_2$O$_3$ catalyst. As an example, the NO$_X$ concentrations at different axial
positions along the catalyst are shown in Figure 2.4. This initial study showed that the reaction chemistry in NSR catalysts is a function catalyst length, with some parts of the catalyst utilized more than others.

![Figure 2.4](image)

**Figure 2.4** NO\textsubscript{X} breakthrough profiles as a function of catalyst length at T = 430°C. The lean gas composition was 250 ppm NO, 8% O\textsubscript{2}, 5% H\textsubscript{2}O and N\textsubscript{2} balance; and the regeneration gas consisted of 4% CO, 1% O\textsubscript{2}, 5% H\textsubscript{2}O and N\textsubscript{2} balance [94].

In a more recent study [96], SpaciMS was used to investigate the influence of sulfur and temperature on the spatiotemporal distributions of NSR reactions over a commercial NO\textsubscript{X} trap. The authors divided the catalyst into two zones for discussion; namely a NO\textsubscript{X} storage and reduction zone and an oxygen storage capacity (OSC) zone. The NSR zone was upstream, where both NO\textsubscript{X} and oxygen storage occurred, while in the downstream zone only oxygen storage was relevant, as shown in Figure 2.5. At 200°C, it was found that the NSR zone extended to more than half of the catalyst length, while less than half was used to store NO\textsubscript{X} at 325°C. At 325°C, and after sulfur exposure, the catalyst could
be described with three zones, a sulfated zone with no NO\textsubscript{X} or oxygen storage, then an NSR zone, and finally the OSC zone.

**Figure 2.5** The reactions distribution inside a commercial NSR catalyst at 325°C before and after sulfation. 40 ppm SO\textsubscript{2} was added into the feed for 1 hr at 400°C. The lean phase composition was 300 ppm NO, 10% O\textsubscript{2}, 5% H\textsubscript{2}O, 5% CO\textsubscript{2} and N\textsubscript{2} balance; and the regeneration phase composition was 3.4% H\textsubscript{2}, 5% H\textsubscript{2}O, 5% CO\textsubscript{2}, and N\textsubscript{2} balance. The space velocity was 30,000 h\textsuperscript{-1}.

Overall, those three studies showed that using SpaciMS can develop an improved understanding of dynamic spatiotemporal distribution reaction chemistry inside a monolithic NSR catalyst.
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Chapter 3

Competitive NO, CO and hydrocarbon oxidation reactions over a diesel oxidation catalyst

3.1 Abstract

The oxidation of NO, CO, and hydrocarbons individually, and in mixtures with NO\textsubscript{2}, were investigated over a monolith-supported Pt/Al\textsubscript{2}O\textsubscript{3} catalyst under oxidizing conditions. NO\textsubscript{2} was completely reduced by CO and C\textsubscript{3}H\textsubscript{6}, under NO\textsubscript{2} limited conditions, at temperatures as low as 110°C and at temperatures above 140°C with dodecane and m-xylene. NO\textsubscript{2} was then again observed once the extent of oxidation of the other species by oxygen was significant. Under the conditions tested, NO, CO, and hydrocarbon oxidation was inhibited by NO\textsubscript{2} in the feed gas mixture. Hydrocarbons were also found to inhibit the oxidation of NO and other hydrocarbon species due to site adsorption competition. For CO, hydrocarbons did not change the onset of oxidation, but did inhibit the extent after their light off began. At low temperatures, CO was found to initially inhibit NO oxidation, but at higher temperatures, once CO oxidation was significant, CO promoted NO conversion to NO\textsubscript{2}. The observed inhibition effects of the different gases on hydrocarbon oxidation were not additive, indicating one species would cause inhibition, but once its inhibition ended, another species could still then cause inhibition. The combined effect of C\textsubscript{3}H\textsubscript{6}, NO and NO\textsubscript{2} on CO conversion was found to be additive unlike that observed for C\textsubscript{3}H\textsubscript{6}. This is because CO oxidation started prior C\textsubscript{3}H\textsubscript{6}. 
3.2 Introduction

Relative to today’s gasoline engine, which uses a stoichiometric amount of fuel and air for combustion, the diesel engine and lean-burn gasoline engines have better fuel economy, and emit less CO₂. However, NOₓ emissions, and particulate matter (PM) for diesel engines, remain an issue. An oxidation catalyst, called a diesel oxidation catalyst (DOC) in diesel engine exhaust aftertreatment systems, is commonly used to reduce CO and hydrocarbon exhaust emissions. Pt and Pd are the most frequently used metals [1, 2] in DOC formulations, with Pd added for some activity, but also to stabilize the Pt [1-6].

In general, DOCs can achieve more than 90% reduction in CO and HC emissions at exhaust temperatures higher than ~300°C [6]. At low operating temperatures however, as in the case of low-speed driving and engine start-up conditions, the catalytic oxidation of HC and CO remains a significant challenge [7, 8]. One solution to overcome the low operating temperature difficulty is incorporating zeolites into the catalyst formulation [9, 10]. Zeolites can adsorb and trap HCs at low operating temperatures. Then as the temperature rises, to about 250°C, which is above the light-off temperature (the temperature necessary to initiate the catalytic reaction) for most HCs over Pt [11], HCs desorb and are oxidized to H₂O and CO₂.

DOCs are now also used with NOₓ and PM control systems. Their role in these systems is as a preheating device for the diesel particulate filters (DPFs), selective catalytic reduction (SCR) and NOₓ storage and reduction (NSR) catalysts [12, 13], as well as for NO oxidation. The heat is generated from exothermic HC oxidation reactions, with HC amounts controlled either by directly injecting fuel into the exhaust stream or adjusting the combustion strategy in the engine [12, 14, 15]. Although DOCs have little
effect on reducing NO\textsubscript{X} emissions, they do oxidize NO to NO\textsubscript{2}. NO\textsubscript{2} is a key reactant for SCR, NSR and DPF aftertreatment technologies. For example, NO\textsubscript{2} can be used to oxidize soot on DPFs at lower temperatures than O\textsubscript{2} [7, 12, 16, 17]. In SCR, ammonia is used as a reducing agent and it has been shown that SCR catalysts perform better with an equimolar mix of NO and NO\textsubscript{2}, especially at low operating temperature [18-20]. Furthermore, NO\textsubscript{2} is more readily trapped on NSR catalysts, relative to NO, and NO oxidation is therefore critical for low temperature NSR catalyst efficiency [21-24].

Although an increased amount of NO\textsubscript{2} is beneficial for the downstream SCR, NSR, and DPF catalysts, previous studies show that NO\textsubscript{2} can inhibit both NO and HC oxidation over Pt/Al\textsubscript{2}O\textsubscript{3} catalysts. Mulla et al. [25] studied NO oxidation kinetics over a Pt/Al\textsubscript{2}O\textsubscript{3} catalyst and found the rate is first order with respect to both NO and O\textsubscript{2} concentrations, but negative first order with respect to NO\textsubscript{2} concentration. The inhibition effect was attributed to the strong oxidizing character of NO\textsubscript{2}, where on the Pt it dissociates to NO and elemental oxygen, the latter causing the inhibition. Further work has shown [26] that adsorbed oxygen can react with NO resulting in the restoration of the activity, but when Pt oxides formed as a result of NO\textsubscript{2} dissociation (forming elemental oxygen), the catalyst did not regain its initial oxidation activity. Other literature has attributed inhibition by NO\textsubscript{2} to its high sticking coefficient on Pt [25, 27].

In a recent study [28], C\textsubscript{3}H\textsubscript{6} inhibition of NO oxidation was shown over a model Pt-Pd/Al\textsubscript{2}O\textsubscript{3} catalyst. The apparent decrease in NO oxidation was due the preferential consumption of product NO\textsubscript{2} as an oxidant for C\textsubscript{3}H\textsubscript{6} oxidation. In the same study, it was found that the addition of NO\textsubscript{2} inhibits C\textsubscript{3}H\textsubscript{6} oxidation, after the onset of light-off, due to the decomposition of NO\textsubscript{2} to NO, which then competed with C\textsubscript{3}H\textsubscript{6} for adsorption sites
[29]. Although inhibition of hydrocarbon oxidation by NO has been studied, there is little evidence of similar inhibition by NO\textsubscript{2} [25-27, 30].

Numerous studies have addressed the influence of hydrocarbons and CO on NO oxidation. In one study, the interaction of CO, NO\textsubscript{2} and NO in the presence of excess O\textsubscript{2} was studied over Pd/SiO\textsubscript{2} catalysts [31]. The authors found that CO was effective in reducing NO\textsubscript{2} at low temperature (below 180°C), but above 200°C reduction stopped because CO was consumed via oxidation by O\textsubscript{2}. Additionally, the interaction between C\textsubscript{3}H\textsubscript{6}, NO and O\textsubscript{2} was also studied over a Pt supported on zeolite catalyst [32], where it was shown that O\textsubscript{2} promotes the reduction of NO by C\textsubscript{3}H\textsubscript{6} between 200 and 300°C, by facilitating the activation of C\textsubscript{3}H\textsubscript{6}. In the same study, NO\textsubscript{2} was found to selectively react with C\textsubscript{3}H\textsubscript{6}, being reduced primarily to NO, although N\textsubscript{2}O formation was also observed. Moreover, NO oxidation light-off is inhibited by hydrocarbons and CO over DOCs [33], which the authors attributed to competitive adsorption between NO, CO and hydrocarbons on oxidation sites. Several similar observations have also been reported [34-38].

The effect of hydrocarbon and/or CO addition on the oxidation of CO and hydrocarbons has also been investigated [39-41]. In these studies, the addition of a second HC species typically resulted in reaction inhibition relative to individual HC oxidation performance. In terms of CO effects, the oxidation of benzene, toluene and hexane individually and in the presence of a mixture of CO and isooctane over supported Pt, Pd, and Rh catalysts has been characterized [42]. The authors observed that inclusion of CO in the mixture considerably inhibited the oxidation of all the hydrocarbons. Such
inhibition was attributed to competitive adsorption between the hydrocarbons and CO for catalytic sites.

Diesel exhaust contains a variety of reactive species, with key regulated species including CO, hydrocarbons and NO. DOCs are used to oxidize all of these. Based on the above discussion, it is likely that each of these influences the catalyst’s performance toward the other species. In the present study, reactions involving NO, NO$_2$, CO and different hydrocarbons (C$_3$H$_6$, dodecane, and xylene), all during lean conditions, were investigated to study the extent of inhibition between the species.

### 3.3 Experimental Methods

The monolith-supported sample was supplied by Umicore. The sample contains 95 g/ft$^3$ Pt supported on Al$_2$O$_3$. The sample was cut to 0.9” diameter with a length of 2.4” from a monolith block that had a cell density of 400 cpsi. The sample was placed into a horizontal quartz tube, which was placed inside a Lindberg Minimite temperature-controlled furnace. To ensure that no gas slipped around the sample, the catalyst was wrapped with 3M insulation material to seal the catalyst in the quartz tube. For temperature measurements, two thermocouples were used; one just inside the inlet face and one just inside the outlet face of the catalyst.

The gases and gas mixtures were supplied by Praxair and were metered with Bronkhorst mass flow controllers. Water was introduced using a Bronkhorst CEM system downstream, after the dry gas mixture had been heated. In experiments using dodecane and m-xylene, the hydrocarbons were again metered with a Bronkhorst CEM system and introduced after the wet gas mixture had been heated to $>170^\circ$C to avoid condensation.
Experiments were performed between 100 and 400°C with a space velocity, at standard conditions, of 25,000 hr\(^{-1}\). The outlet CO, CO\(_2\), NO, NO\(_2\), N\(_2\)O, H\(_2\)O, C\(_3\)H\(_6\), C\(_{12}\)H\(_{26}\) and C\(_{8}\)H\(_{10}\) gas concentrations were measured using a MKS MultiGas 2030 FT-IR analyzer.

In experiments investigating the effect of NO\(_2\) concentration on NO oxidation activity in the absence of both hydrocarbons and CO, the catalyst was heated from 150°C to 400°C at a rate of ~3.5°C/min in a mixture containing 200 ppm NO, 0, 20, 100 or 200 ppm NO\(_2\), 10% O\(_2\), 5% H\(_2\)O, 5% CO\(_2\), and balance N\(_2\). In the second set of experiments, where hydrocarbons and CO were used, the catalyst was heated from 100°C to 350°C at a rate of ~5°C/min. The gas concentrations used were 1080 ppm C\(_3\)H\(_6\), 270 ppm dodecane, 405 ppm xylene, 3240 ppm CO, 200 ppm NO, 0, 20, 100 or 200 ppm NO\(_2\), 10% O\(_2\), 5% H\(_2\)O, 5% CO\(_2\), and balance N\(_2\). Relatively high concentrations of CO and HC species were used due to lower flow limitations of the dodecane, and all others were kept on the same C\(_1\) basis.

3.4. Results and Discussion

This discussion is divided into four sub-sections, based on different trends observed in Figure 3.1. In section 3.1, discussion of the overall trends when NO, NO\(_2\), O\(_2\), hydrocarbons and CO are present in the inlet feed, is presented. In section 3.2, the effect of NO\(_2\), hydrocarbons, and/or CO on NO to NO\(_2\) conversion specifically, which takes place when most of the reductant species have been consumed, will be discussed, and is described in Figure 3.1 as part B. In sections 3.3 and 3.4, the effect of NO, NO\(_2\), hydrocarbons, and/or CO on the oxidation of hydrocarbons and CO will be discussed,
which occurs in the temperature regime covered in the section labeled as “A” in Figure 3.1.

Figure 3.1 Outlet concentrations obtained during TPO with 1080 ppm C₃H₆, 200 ppm NO, 100 ppm NO₂, 10 % O₂, 5% CO₂, 5% H₂O, and balance N₂.

3.4.1 Overall trends

The effect of temperature on the various key gas species concentrations, with 200 ppm NO, 100 ppm NO₂, 1080 ppm C₃H₆, and 10% O₂ in the feed stream, is shown in Figure 3.1. NO₂ was not detected in the outlet stream below ~190°C, though 100 ppm was in the feed stream. The NO₂ is preferentially reduced by C₃H₆ in the presence of O₂ via selective catalytic reduction chemistry, even at low operating temperatures (~110°C was the starting temperature). The NO outlet concentration increased by approximately
83 ppm from its initial value (200 ppm) at the experiment onset. The increase in the NO concentration is due to incomplete NO\textsubscript{2} reduction.

**Figure 3.2** Outlet concentrations obtained at 100°C in the presence and absence of 1080 ppm C\textsubscript{3}H\textsubscript{6}, 200 ppm NO, 100 ppm NO\textsubscript{2}, 10 % O\textsubscript{2}, 5% CO\textsubscript{2}, 5% H\textsubscript{2}O, and balance N\textsubscript{2}.

To further investigate the reduction of NO\textsubscript{2} by C\textsubscript{3}H\textsubscript{6} below 200°C, an extra experiment was carried out at 100°C with 200 ppm NO, 100 ppm NO\textsubscript{2}, 10% O\textsubscript{2}, and in the presence and absence of C\textsubscript{3}H\textsubscript{6}, with the data shown in Figure 3.2. At the beginning of the experiment, NO, NO\textsubscript{2} and O\textsubscript{2} were introduced and both NO and NO\textsubscript{2} were detected, at their nominal inlet values. When C\textsubscript{3}H\textsubscript{6} was introduced, the NO\textsubscript{2} concentration immediately decreased, reaching zero, and the NO concentration increased, again by
about ~83 ppm. When C$_3$H$_6$ was shut off, the NO$_2$ concentration increased and re-achieved its inlet value and NO decreased to its inlet value. According to Figures 3.1 and 2, 83% of NO$_2$ was converted to NO via reduction of NO$_2$ by C$_3$H$_6$ while the rest of NO$_2$ was reduced to N$_2$.

C$_3$H$_6$ and NO concentrations steadily decreased from 110 to ~160-170°C, after which, the decrease in both C$_3$H$_6$ and NO concentrations accelerated. Complete C$_3$H$_6$ conversion was reached by ~202°C. NO reached a minimum value (10 ppm) at 205°C and then slowly increased as temperature increased. NO$_2$ was observed at 192°C and reached a maximum at 275°C. The formation of N$_2$O and CO, presumably as a product of incomplete NO reduction and C$_3$H$_6$ oxidation, or the selective reduction between the two, was detected at approximately ~150°C. The maximum outlet CO detected was 17 ppm at 190°C and then decreased to zero by 197°C. N$_2$O formation reached a maximum value of 82 ppm at 198°C, and then slowly decreased and reached zero by 310°C. The N$_2$O data show that C$_3$H$_6$ is still reducing some NO and/or NO$_2$ at temperatures higher than when complete C$_3$H$_6$ conversion was observed.

Hydrocarbon SCR, or in this case the interaction between NO-C$_3$H$_6$-O$_2$, has been extensively investigated in the literature. In a previous study investigating the interactions of C$_3$H$_6$-NO-O$_2$ over Pt-based catalysts, at T < 250°C, high NO reduction efficiency was observed and the authors attributed this activity to O$_2$ facilitating the activation of C$_3$H$_6$, forming oxidized hydrocarbon intermediates on catalytic sites [43]. These intermediates are believed to preferentially react with adsorbed NO, forming N$_2$ and/or N$_2$O. However, at T > 250°C, NO reduction decreased due to combustion of C$_3$H$_6$ by O$_2$ becoming competitive/dominant [44]. NO$_2$-C$_3$H$_6$-O$_2$ interactions have also been
studied [23, 28, 34, 35, 45, 46]. Most agree that SCR of NO\textsubscript{2} is faster than NO [45, 46], especially over un-promoted oxides, such as Al\textsubscript{2}O\textsubscript{3}. Burch et al. reported that NO\textsubscript{2} is more reactive than NO, with NO\textsubscript{2} reacting rapidly with the surface of the catalyst to form ad-NO\textsubscript{X} species (surface adsorbed NO\textsubscript{X} species), including organo-nitro, organo-nitrite species, and hydroxynitropropane, considered intermediates in the reaction. The observations from Figures 3.1 and 3.2 are seemingly consistent with those previously made, in terms of NO\textsubscript{2} reduction by C\textsubscript{3}H\textsubscript{6} being more favored compared to that with NO. Although the data cannot explicitly be used to show whether it is NO or NO\textsubscript{2} participating in the SCR reaction, no NO\textsubscript{2} is observed until the higher temperatures. According to the data shown in Figure 3.1, NO\textsubscript{2} is easily reduced, at least to NO at lower temperatures. And as will be shown below, NO oxidation occurs at temperatures lower than 150°C over this catalyst (> 60% conversion at 150°C). These results therefore suggest that NO\textsubscript{2} is selectively and preferentially consumed by C\textsubscript{3}H\textsubscript{6} at low operating temperatures, either to primarily NO at lower temperatures and then to N\textsubscript{2}O and N\textsubscript{2} with increasing temperature.

Similar experiments were performed but with 3240 ppm CO instead of C\textsubscript{3}H\textsubscript{6}. The outlet concentration of CO and NO\textsubscript{X} species are shown in Figure 3.3, along with the equilibrium NO\textsubscript{2} levels for reference. Overall, trends were similar as those with C\textsubscript{3}H\textsubscript{6} are observed with CO. Again, no NO\textsubscript{2} was detected at the onset of the experiment and not below 168°C. The NO concentration increased by only 65 ppm compared with 83 ppm with C\textsubscript{3}H\textsubscript{6}. A steep decrease in the NO concentration was observed starting at 170°C and reached a minimum value at 195°C, then NO slowly increased as the temperature increased. A sharp drop in the CO concentration was observed starting at 164°C, and
reached 0 ppm by 176°C (C₃H₆ reached zero at 201°C). NO₂ was observed starting at 168°C, at which point 40% of the CO was consumed, and is lower by 24°C compared to that with C₃H₆. The maximum NO₂ amount was attained at 215°C. The N₂O amounts were very small, indicating that CO suppressed the N₂O formation pathway compared with C₃H₆.

![Outlet concentrations obtained during TPO with 3240 ppm CO, 200 ppm NO, 100 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and balance N₂.](image)

**Figure 3.3** Outlet concentrations obtained during TPO with 3240 ppm CO, 200 ppm NO, 100 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and balance N₂.

In a previous study with aged DOCs [32], the effect of hydrocarbons and CO on NO oxidation and NO₂ reduction was investigated. Like the data shown in Figures 3.1-3, the authors showed that both hydrocarbons and CO can completely reduce NO₂ to NO at low temperature, until around 250°C in their study, and then the NO was oxidized back to NO₂. Studies involving CO-NO-O₂ have shown similar trends [28, 31, 47].
The effects of dodecane and m-xylene were also investigated, with NO, NO\textsubscript{2}, N\textsubscript{2}O and the hydrocarbon concentrations shown in Figure 3.4. Unlike with CO and C\textsubscript{3}H\textsubscript{6}, NO\textsubscript{2} was observed at the onset of the experiment, i.e. at 110°C. This shows that neither dodecane nor xylene are as strong as the CO and C\textsubscript{3}H\textsubscript{6} in reducing NO\textsubscript{2} to NO or N\textsubscript{2}. The summation of NO\textsubscript{2} and NO at 110°C was equal to the inlet value of NO\textsubscript{X}. The likely reason for the lower activity of dodecane and xylene at 110°C is related to the nature of hydrocarbon chains. First, long chain and cyclic hydrocarbons can partially block access of NO\textsubscript{2} to active sites, resulting in lower reduction activity. Also, their reactivity is lower in the sense that they are not activated at such low temperature. However, as the temperature increases, the activity of both dodecane and xylene to reduce NO\textsubscript{2} improved. With m-xylene, NO\textsubscript{2} was completely reduced by 145°C and by 165°C with dodecane. NO\textsubscript{2} was then again observed at 190°C with m-xylene, and reached a maximum value at about 295°C. With dodecane, NO\textsubscript{2} was observed starting at 170°C, and reached a plateau again at 295°C. NO\textsubscript{2} being observed at low dodecane conversion demonstrates that m-xylene is more reactive toward NO\textsubscript{2} reduction, which will be discussed further in section 3.3. No CO was observed in these two cases, indicating complete combustion once these hydrocarbons were activated. The combined data also show that NO reduction is coincident with reductant oxidation, suggesting that reduction is tied to the reductant activation as the limiting step at low temperature.

It should be noted that due to the presence of various types of hydrocarbons, CO, NO\textsubscript{X} and excess O\textsubscript{2} in diesel exhaust, SCR chemistry over a DOC is inevitable. Figures 3.1 to 3.4 show this overall trend. With CO and C\textsubscript{3}H\textsubscript{6}, NO\textsubscript{2} is preferentially being reduced by either CO or C\textsubscript{3}H\textsubscript{6} to NO and N\textsubscript{2}. With larger hydrocarbons (dodecane and
xylene) reduction is still observed, but to a lesser extent. Once the temperature is high enough to oxidize most of the incoming CO and hydrocarbons, NO oxidation to NO$_2$ is observed. N$_2$O formation was very low when CO was used as a reductant, ~ 5 ppm, while more than 80 ppm was detected when hydrocarbons were used. Hydrocarbons require an intermediate to reduce NO$_2$ to NO and N$_2$, facilitating the formation of N$_2$O, as will be discussed below.

![Image](image.png)

**Figure 3.4** Outlet concentrations obtained during TPO with either 270 ppm dodecane or 405 ppm m-xylene, 200 ppm NO, 100 ppm NO$_2$, 10% O$_2$, 5% CO$_2$, 5% H$_2$O, and balance N$_2$.

The interactions between HCs-NO$_X$-O$_2$ and CO-NO$_X$-O$_2$ over Pt/Al$_2$O$_3$-based catalysts have been widely discussed [23, 28, 31, 34, 35, 45-50]. Burch et al. [50] suggested the following NO$_X$ reduction mechanism. CO and hydrocarbons first reduce
some Pt-O sites to metallic sites and subsequently NO dissociates on these reduced Pt sites, leading to N₂O formation at lower temperature and N₂ at higher temperature. Other research has provided an alternate explanation, with the path mentioned above possibly still occurring. For example, (1) NO oxidizes to NO₂ and subsequently reacts with the hydrocarbon over Pt [51-53], and (2) formation of an oxidized hydrocarbon or isocyanate as an intermediate [54-56]. The latter mechanism could explain the trend observed in our data, where reduction activity increased as the extent of NO oxidation to NO₂ increased or once inlet NO₂ increased. It has also been proposed that the ad-species originating from decomposition of CO and hydrocarbons could facilitate the decomposition of NO [57], which the data here also follow, since the activation of the reductant is critical for reduction to begin.

3.4.2 Effect of NO₂, hydrocarbons, and CO on NO oxidation

The NO oxidation conversion calculated and plotted is based on NO₂ made, not NO consumed. For the data after Figure 3.5, these calculations were made when most of the reductants have been consumed as illustrated in Figure 3.1, part B. Figure 3.5 shows data obtained during NO oxidation tests as a function of temperature, where 200 ppm NO were added with various NO₂ concentrations. A maximum conversion was reached between 240 and 270°C for all NO₂ concentrations. Below 240°C, the conversions increased as a function of temperature because the reaction is kinetically limited. At high temperature, the NO conversion to NO₂ is limited by thermodynamic equilibrium [58, 59]. The data clearly show that the conversion decreases with increasing concentrations of NO₂ in the feed, consistent with previous studies [25, 26, 60, 61]. The reason for the significant inhibition by NO₂ is the reduced activity of Pt when
substantially covered with chemisorbed oxygen species or if in a more fully oxidized state, and more extensive oxide formation or oxygen coverage is evident when Pt is exposed to NO\textsubscript{2} compared to O\textsubscript{2} [26, 61, 62]. For example, previous work has shown that with O\textsubscript{2}, Pt [111] can have up to a 2/3 monolayer coverage by oxygen, whereas with NO\textsubscript{2} the coverage is 3/4 monolayer [62].

![Figure 3.5](image)

**Figure 3.5**  NO to NO\textsubscript{2} conversion obtained during TPO with 200 ppm NO, 0, 20, 100, and 200 ppm NO\textsubscript{2}, 10 % O\textsubscript{2}, 5% CO\textsubscript{2}, 5% H\textsubscript{2}O, and balance N\textsubscript{2}.

Olsson and Fridell [61] reported that NO\textsubscript{2} can readily oxidize Pt supported on Al\textsubscript{2}O\textsubscript{3} and smaller Pt particles were more quickly oxidized, indicating larger particles are ultimately better for NO oxidation. Furthermore, previous experimental work has shown that there can be a slow decrease in oxidation kinetics with time-on-stream, which was specifically
attributed to oxidation of Pt particles by NO\textsubscript{2} with time [26]. The data presented here are all consistent with these previous studies; NO\textsubscript{2} inhibits NO oxidation through formation of Pt oxides or oxygen coverage of the Pt sites.

The results of the effect of C\textsubscript{3}H\textsubscript{6} addition, combined with NO\textsubscript{2}, on NO oxidation are shown in Figure 3.6. The conditions are otherwise the same as those in Figure 3.5. The NO conversion to NO\textsubscript{2}, in terms of outlet NO\textsubscript{2} concentration, was zero at T ≤ 180°C for all NO\textsubscript{2} concentrations. This is not to say that NO oxidation did not occur, but that if it did, the NO\textsubscript{2} formed was immediately reduced via reaction with the C\textsubscript{3}H\textsubscript{6} [28]. Evolution of NO\textsubscript{2} was observed at ~185°C with 0 ppm NO\textsubscript{2} while at 190, 195 and 200°C with 20, 100 and 200 ppm NO\textsubscript{2}, respectively. Once NO oxidation was evident, there was decreased overall NO conversion with increasing inlet NO\textsubscript{2} amount. At T < 215°C, the negative impact of NO\textsubscript{2} was obvious and at higher temperatures less evident. This is due facile hydrocarbon oxidation at the elevated temperature, resulting in easy consumption of the oxygen associated with any Pt oxides and therefore a relative abundance of active metal sites. Thus, the hydrocarbon is able to reduce the negative impact of NO\textsubscript{2} that arises from NO\textsubscript{2} oxidizing the Pt. Also, at the higher temperatures, thermodynamic limitations become more significant, limiting kinetic effects.

However, in comparing the results in Figures 3.5 and 3.6, it is apparent that C\textsubscript{3}H\textsubscript{6} has an overall detrimental effect on NO to NO\textsubscript{2} conversion. At T ≤ 180°C, no NO\textsubscript{2} was observed due to the reduction of any formed NO\textsubscript{2} by C\textsubscript{3}H\textsubscript{6}, as discussed above. At T ≥ 180°C, NO oxidation started, which is associated with the onset of C\textsubscript{3}H\textsubscript{6} oxidation, discussed below, and therefore NO can adsorb and react on the active Pt sites. However, even at higher temperatures, the overall NO oxidation conversions are less than those
observed in the absence of C$_3$H$_6$. This is consistent with previous research that has shown hydrocarbons inhibit NO oxidation. At high temperature, site competition has been proposed to explain hydrocarbon inhibition of NO oxidation [29], with some impact of NO$_2$ being consumed by the hydrocarbon observed as well [28, 32]. Also contributing is competition between NO and C$_3$H$_6$ for surface oxygen.

![Figure 3.6](image)

**Figure 3.6** NO to NO$_2$ conversion obtained during TPO with 1080 ppm C$_3$H$_6$, 200 ppm NO, 0, 20,100, and 200 ppm NO$_2$, 10 % O$_2$, 5% CO$_2$, 5% H$_2$O, and balance N$_2$.

Experiments with dodecane or m-xylene were also performed and data are shown in Table 3.1. Overall there was a decrease in the NO conversion to NO$_2$, similar to that of C$_3$H$_6$. In terms of the effect of NO$_2$ concentration, the temperature changes to achieve the
same NO to NO₂ conversions were on the order of 1 to 5°C, indicating insignificant NO₂ inhibition with the larger hydrocarbon species being present.

**Table 3.1** Temperatures (°C) required for 10 and 50% conversion of NO to NO₂

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<th>NO</th>
<th>NO + 20 ppm NO₂</th>
<th>NO + 100 ppm NO₂</th>
<th>NO + 200 ppm NO₂</th>
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<td>Dodecane</td>
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<tr>
<td>Xylene</td>
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<td>229</td>
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<tr>
<td>C₃H₆ + CO</td>
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<td>227</td>
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<tr>
<td>C₃H₆ + Dodecane</td>
<td>241</td>
<td>247</td>
<td>258</td>
<td>272</td>
</tr>
</tbody>
</table>

These results suggest that NO oxidation inhibition by the larger hydrocarbons is dominant relative to that of NO₂. The temperature differences to attain similar conversions are smaller than those observed with C₃H₆. As will be shown later (Figures 3.9 and 3.11), the light-off of dodecane is faster once oxidation begins (the temperature range from the onset to complete oxidation is narrower), relative to C₃H₆. This is in part due to the exothermicity of the reactions, with dodecane oxidation resulting in more heat.
released. And although the same C1 basis was used, the larger hydrocarbon has more H compared with C₃H₆, therefore the larger hydrocarbons can consume more surface oxygen and, thereby again limit the negative effect of the NO₂.

The effect of mixtures of hydrocarbons and NO₂ on NO oxidation was also studied and summary data are listed in Table 3.1. With a mixture of C₃H₆ and dodecane, NO conversion to NO₂ was significantly decreased. For example, with only C₃H₆, 10 and 50% conversion of NO to NO₂, with 200 ppm NO₂ also added, was achieved at 204 and 225°C, respectively, while the same conversions were achieved with a mixture of C₃H₆ and dodecane at 220 and 272°C respectively. The maximum conversion in the presence of both hydrocarbons did not exceed 58%, which was reached at 275°C. In terms of NO₂ addition, there were decreases in the overall NO conversions to NO₂ with each increase in the amount of NO₂. The decreased performance with addition of dodecane to C₃H₆ is due to additional competitive adsorption between NO and C₃H₆, dodecane, and NO₂ for active sites. The effect of the addition of NO₂ to the mixed hydrocarbon system on the T₅₀ values is more pronounced than when added to mixtures with just the individual species, while the T₁₀ changes were similar. This is due to the decreased overall conversion nearing the 50% conversion and therefore exaggerating the effect relative to the simpler mixtures.

NO oxidation conversion as a function of NO₂ concentration and temperature, in the presence of 3240 ppm CO is shown in Figure 3.7. At low temperature, in the absence of CO, there was appreciable NO conversion at 150°C (Figure 3.5). But, in the presence of CO, no NO₂ was observed at 150°C with or without NO₂ added. Again, this is due to
the inlet and any formed NO$_2$ being reduced by CO. However, at T > 170°C where NO$_2$ was observed, the addition of CO promoted NO conversion to NO$_2$.

In terms of increasing NO$_2$, it is clear that catalyst performance decreased monotonically with each increase in NO$_2$ concentration at T < 190°C. Beyond that, NO conversion to NO$_2$ was relatively independent of NO$_2$ amount, for the same reasons discussed above; surface oxygen consumption by the reductant species and increased local temperatures from the exothermic CO oxidation reaction. NO oxidation to NO$_2$ reached > 90% conversions at the 190°C test point with all NO$_2$ concentrations, which is much higher than that observed in the presence of the individual hydrocarbons, or mixture of

Figure 3.7  NO to NO$_2$ conversion obtained during TPO with 3240 ppm CO, 200 ppm NO, 0, 20,100, and 200 ppm NO$_2$, 10 % O$_2$, 5% CO$_2$, 5% H$_2$O, and balance N$_2$. 
hydrocarbons, and is also higher than the conversions observed in the absence of hydrocarbons and CO (Figure 3.5). Between 190 and 220°C, there were no changes observed in the NO conversion to NO₂ and at higher temperatures the conversions decreased with increasing temperature. One contributing factor to the higher NO₂ amounts made with CO compared to that with hydrocarbons is the absence of H, which could react with NO₂ resulting in NO. Another possibility is that since CO lit-off at a lower temperature than the hydrocarbons, as shown by comparing Figures 3.1, 3.3 and 3.4 for example, there is less reduction by CO as it’s oxidation is likely limited to the very front portion of the catalyst. Consequently, hydrocarbons can reduce more NO or NO₂ to N₂ or N₂O. As shown in Figures 3.1, 3.3 and 3.4, significantly more N₂O formed with hydrocarbons, in the range of 82 to 121 ppm, compared with approximately ~ 6 ppm with CO. Therefore, since reduction of NOₓ continues at higher temperatures with hydrocarbons relative to CO, less NO₂ formation would be observed with hydrocarbons compared with CO, which was observed.

Similar experiments were also performed but with a mixture of CO and C₃H₆. Summary results are also listed in Table 3.1. Overall, there was a decrease in NO conversion with increasing NO₂ amount in the feed stream. The NO conversions with a mixture of C₃H₆ and CO were lower than that with either just C₃H₆ or CO. The more significant inhibition on NO oxidation with the mixture of CO and C₃H₆ is surprising based on the data in Figure 3.7, where CO was shown to promote NO oxidation at temperatures above 180°C. However, CO inhibits C₃H₆ oxidation (with O₂), shifting the 50% conversation by 15°C when CO was added to the C₃H₆-containing feed, as will be shown below. This therefore extends the temperature range where C₃H₆ is reacting with
NOX, either in reducing it to N2, reducing any NO2 made to NO, or in simple site competition. Otherwise, the effect of NO2 is similar to that observed with just CO or C3H6.

3.4.3 Effect of NO, NO2, CO and hydrocarbons on hydrocarbon oxidation

The effect of 200 ppm NO and different concentrations of NO2 on the conversion of 1080 ppm C3H6 is shown in Figure 3.8. With the addition of 200 ppm NO and increasing amounts of NO2, the light-off and complete conversions of C3H6 occurred at higher temperatures. For example, with the addition of 200 ppm NO and 200 ppm NO2, the 50 and 90% C3H6 conversions were achieved at 198 and 203°C compared with 161 and 165°C without NOX added. These data clearly show inhibition by NO, NO2, or total NOX on C3H6 conversion.

Further experiments were performed to investigate whether the inhibition in C3H6 conversion was due to NO, NO2, or total NOX (NO+NO2). In one set of experiments, 300 and 400 ppm NO were used with 1080 ppm C3H6. While, in another set of experiments, a mixture of NO and NO2 was used, with the same total NOX used with NO alone (i.e total NOx was 300 or 400 ppm). The 50% C3H6 conversions with NO only as inlet NOX were 189 and 196°C with 300 and 400 ppm NO, respectively, while they were 192 and 198°C with 300 and 400 ppm of a mixture of both NO and NO2 as inlet NOX, respectively. The 50% C3H6 conversions were very close, the differences in order of 3°C, with temperature error analysis in C3H6 oxidation being +/- 1°C. Although attempts were made to more clearly determine whether it is NO, NO2, or total NOX inhibiting C3H6 conversion, these data indicate it is simply the total NOX amount.
Figure 3.8  \( \text{C}_3\text{H}_6 \) conversion obtained during TPO with 1080 ppm \( \text{C}_3\text{H}_6 \), 200 ppm NO, 0, 20, 100, and 200 ppm NO\(_2\), 10 % O\(_2\), 5% CO\(_2\), 5% H\(_2\)O, and balance N\(_2\).

Dodecane and m-xylene conversions were also evaluated and data are listed in Table 3.2. In the absence of NO and NO\(_2\), 25 and 90% dodecane conversions were attained at 131 and 136°C, respectively, while with m-xylene they were achieved at 161 and 165°C, respectively. Previous literature has shown that the ease of alkane oxidation increases with increasing chain length, [64, 65]. Conversely, the ease of alkene oxidation decreases with increasing hydrocarbon chain length from ethylene to hexene [64], but is less dependent at chain lengths for 7 < \( n \) < 10 [65]. A general consensus is that light alkenes are more reactive than light alkanes, while heavier alkanes are more reactive than heavier alkenes [65]. Additionally, it has been shown that \( \text{C}_6\text{-C}_9 \) aromatics behave similarly to alkenes (\( \text{C}_2\text{-C}_6 \)) in terms of oxidation [64], which coincides with the data.
listed in Table 3.2, where C₃H₆ and m-xylene light off were similar. With the addition of 200 ppm NO and with 0, 20, 100, and 200 ppm NO₂, the conversions of both dodecane and m-xylene were shifted to higher temperatures. The reason for the lower hydrocarbon conversions is due to competition between NO and NO₂ and hydrocarbons for the same adsorption sites. This is consistent with previous literature [28] regarding the effect of NO on higher hydrocarbon oxidation, where evidence suggests that under oxidizing conditions, a Pt-based catalyst showed inhibition by NO.

Table 3.2 Temperatures (°C) required for 25, 50, and 90% conversion of hydrocarbon species

<table>
<thead>
<tr>
<th>Feed Gas</th>
<th>No</th>
<th>NOX</th>
<th>NO</th>
<th>NO + 20 ppm NO₂</th>
<th>NO + 100 ppm NO₂</th>
<th>NO + 200 ppm NO₂</th>
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<tr>
<td></td>
<td>25% HC Conversion (T₂₅)</td>
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<tr>
<td>Dodecane</td>
<td>131</td>
<td>162</td>
<td>163</td>
<td>166</td>
<td>171</td>
<td></td>
</tr>
<tr>
<td>Xylene</td>
<td>156</td>
<td>166</td>
<td>169</td>
<td>173</td>
<td>184</td>
<td></td>
</tr>
<tr>
<td>C₃H₆</td>
<td>157</td>
<td>175</td>
<td>178</td>
<td>185</td>
<td>191</td>
<td></td>
</tr>
<tr>
<td>C₃H₆ + CO</td>
<td>174</td>
<td>208</td>
<td>209</td>
<td>215</td>
<td>223</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50% HC Conversion (T₅₀)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dodecane</td>
<td>133</td>
<td>163</td>
<td>164</td>
<td>167</td>
<td>172</td>
<td></td>
</tr>
<tr>
<td>Xylene</td>
<td>161</td>
<td>175</td>
<td>176</td>
<td>181</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>C₃H₆</td>
<td>161</td>
<td>182</td>
<td>185</td>
<td>192</td>
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</tr>
<tr>
<td>C₃H₆ + CO</td>
<td>176</td>
<td>211</td>
<td>212</td>
<td>218</td>
<td>226</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90% HC Conversion (T₉₀)</td>
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<td></td>
</tr>
<tr>
<td>Dodecane</td>
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<td>165</td>
<td>167</td>
<td>170</td>
<td>174</td>
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<td>Xylene</td>
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<td>182</td>
<td>187</td>
<td>195</td>
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</tr>
<tr>
<td>C₃H₆</td>
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<td>189</td>
<td>196</td>
<td>203</td>
<td></td>
</tr>
<tr>
<td>C₃H₆ + CO</td>
<td>179</td>
<td>215</td>
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<td>222</td>
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</tbody>
</table>

Figures 3.9 - 11 compare the overall effect of individual species and a mixture of NO, NO₂, CO, C₃H₆, or dodecane on the C₃H₆ and dodecane conversions. As shown in Figure 3.9, with the addition of only dodecane, there was an insignificant shift in C₃H₆.
conversion, the 50% conversion temperature shifted by 3°C. The lack of significant effect is due to surface coverages at the onset of the experiment. The C\textsubscript{3}H\textsubscript{6} initially covers the surface, blocking dodecane adsorption, as also shown in Figure 3.9 where dodecane begins oxidizing after C\textsubscript{3}H\textsubscript{6}. Addition of CO to the C\textsubscript{3}H\textsubscript{6}-containing feed shifted the 50% C\textsubscript{3}H\textsubscript{6} conversion temperature by 15°C. This coincides with literature evidence, where CO inhibition has been attributed to CO adsorbing more strongly than the hydrocarbons and consequently occupying Pt sites [42, 66].

![Figure 3.9](image)

**Figure 3.9** C\textsubscript{3}H\textsubscript{6} conversion obtained during TPO with 1080 ppm C\textsubscript{3}H\textsubscript{6}, and either 3240 ppm CO, 270 ppm dodecane, and/or 200 ppm NO, 200 ppm NO\textsubscript{2}, and 10% O\textsubscript{2}, 5% CO\textsubscript{2}, 5% H\textsubscript{2}O, and balance N\textsubscript{2}.

With NO, or a mixture of NO and NO\textsubscript{2}, the 50% conversion temperature was shifted to significantly higher temperatures, on the order of 20 to 40°C under our test conditions. The increase in 50% C\textsubscript{3}H\textsubscript{6} conversion temperature was 53°C with a mixture
of dodecane and NO\textsubscript{X} whereas it increased 65°C with a mixture of CO and NO\textsubscript{X}. As with only CO the shift was 15°C, with only dodecane it was negligible and with the NO/NO\textsubscript{2} mixture it was 37°C, this shift in 50\% C\textsubscript{3}H\textsubscript{6} oxidation temperature in the mixture of CO and NO\textsubscript{X} or dodecane and NO\textsubscript{X} demonstrated that the combined effect is not additive; the increased temperature is beyond that of the sum of the individual inhibitions.

**Figure 3.10** Outlet concentrations obtained during TPO with 3240 ppm CO, 1080 ppm C\textsubscript{3}H\textsubscript{6}, 200 ppm NO, 100 ppm NO\textsubscript{2}, 10 \% O\textsubscript{2}, 5\% CO\textsubscript{2}, 5\% H\textsubscript{2}O, and balance N\textsubscript{2}.

To further explain the combined effect with a mixture of CO, C\textsubscript{3}H\textsubscript{6}, and NO/NO\textsubscript{2}, the species concentration vs. temperature was plotted and data are shown in Figure 3.10. A mixture of 200 ppm NO and 100 ppm NO\textsubscript{2} were used. As shown, the CO concentration gradually decreased and no change was observed for both NO and C\textsubscript{3}H\textsubscript{6} concentrations.
up to 178°C, as shown in left of the shaded area, indicating that CO adsorbs more strongly on Pt and shifts both C$_3$H$_6$ and NO oxidation to higher temperature. Subsequently, when C$_3$H$_6$ oxidation started, after CO oxidation had begun, NO can co-adsorb and compete with C$_3$H$_6$ on Pt sites, causing the observed extra shift in C$_3$H$_6$ conversion.

It could be expected that the addition of CO to a mixture of hydrocarbons can reduce the hydrocarbon light-off temperatures due to the exotherm originating from CO oxidation. This however was not observed. Thus, an exotherm does not explain the observations in this study and the inhibition effects, instead of promoting effects, are relevant to the results obtained.

The dodecane data are shown in Figure 3.11. In the presence of only NO, the temperature required for 50% conversion was shifted by 31°C and with the addition of C$_3$H$_6$, the 50% dodecane conversion shifted by 36°C. So although dodecane had little influence on C$_3$H$_6$ conversion, C$_3$H$_6$ had a negative impact on dodecane conversion as discussed above. The reason is that the C$_3$H$_6$ covers the surface preferentially at low temperature relative to the dodecane. With a mixture of NO and NO$_2$, the temperature for 50% conversion of dodecane was increased by 40°C, and with inclusion of C$_3$H$_6$ to a mixture of NO and NO$_2$ the 50% conversion increased by 86°C, compared to the experiment with only dodecane. Again, the combined effect of the mixtures is more than additive.
Figure 3.11 Dodecane conversion obtained during TPO with 270 ppm dodecane and either 1080 ppm C\textsubscript{3}H\textsubscript{6}, and/or 200 ppm NO, 200 ppm NO\textsubscript{2}, and 10 % O\textsubscript{2}, 5% CO\textsubscript{2}, 5% H\textsubscript{2}O, and balance N\textsubscript{2}.

3.4.4 Effect of NO, NO\textsubscript{2}, and hydrocarbons on CO oxidation

The CO conversion data in the presence and absence of the other components are shown in Figure 3.12. Note: the associated error in the temperature was calculated was 2.3°C for CO conversions. With only CO, 50% conversion was achieved at 145°C and 90% at 153°C. In the presence of 200 ppm NO, the 50% CO conversion temperature increased by 17°C. The addition of 100 and 200 ppm NO\textsubscript{2}, with 200 ppm NO, shifted the 50% conversions to 170 and 177°C, respectively, showing CO oxidation inhibition by NO\textsubscript{X}, again likely through competitive adsorption with CO on the Pt sites [29, 47]. Adding C\textsubscript{3}H\textsubscript{6} in with CO shifted the 50% conversion temperature to 172°C. Adding C\textsubscript{3}H\textsubscript{6}
to the mixtures of 200 ppm NO and NO₂, the 50% CO conversion temperatures increased to 187, 200, and 208°C with 0, 100, and 200 ppm NO₂ respectively. Although above it was pointed out that at low temperature CO preferentially adsorbs to the active sites relative to the C₃H₆, comparing the data in Figure 3.12 with those in Table 3.2, it is obvious that both C₃H₆ and CO result in mutual inhibition. An important observation is that the CO light-off curves are less steep in the presence of C₃H₆ and the NO/NO₂ mixture compared to those in the presence of only NO/NO₂. Furthermore, the inhibition by C₃H₆ and NO/NO₂ on CO oxidation, as shown in Figure 3.10, was minimal at low temperature (and as shown in the shaded area of Figure 3.12), however, as the temperature increased inhibition became apparent, i.e. the slope of the oxidation extent decreased relative to the absence of the other components. This is due to CO poisoning decreasing once oxidation began, freeing sites for both C₃H₆ and NO adsorption, resulting in the inhibition effect. This is consistent with the conclusions made by Voltz who investigated the effect of NO and C₃H₆ on CO oxidation over a Pt/Al₂O₃ catalyst [29] and inhibition by both NO and C₃H₆ was attributed to competitive adsorption on catalytic sites. These data indicate that CO adsorbs more strongly on Pt sites at lower temperature than either C₃H₆ and NO do, and therefore CO was inhibiting both NO and C₃H₆ oxidation. As shown in Figure 3.10, there was no change in the NO and C₃H₆ concentrations up to 178°C, while the CO concentration gradually decreased, as shown in the shaded area. Also as highlighted in the shaded area of Figure 3.12 the onset of CO light-off was not affected by NOₓ and C₃H₆, further suggesting that CO oxidation inhibition, by C₃H₆ and NOₓ, occurs only after CO oxidation begins.
Figure 3.12 CO conversion obtained during TPO with 3240 ppm CO, and either 1080 ppm C\textsubscript{3}H\textsubscript{6}, and/or 200 ppm NO, 200 ppm NO\textsubscript{2}, and 10 % O\textsubscript{2}, 5% CO\textsubscript{2}, 5% H\textsubscript{2}O, and balance N\textsubscript{2}.

Beyond 178°C, the NO concentration progressively decreased indicating enough sites are free of CO for it to adsorb and begin oxidation. The two circles in Figure 3.12 highlight the start and end of an inflection, the first being where C\textsubscript{3}H\textsubscript{6} oxidation begins (~185°C), or where C\textsubscript{3}H\textsubscript{6} can adsorb to Pt sites and compete with both CO and NO. At 213°C, there was a sharp decrease in CO concentration, as observed in Figure 3.10, and at this point the inflection ends as observed in Figure 3.12. Subsequently, steep decreases in both NO and C\textsubscript{3}H\textsubscript{6} concentrations were observed. Inflections in the C\textsubscript{3}H\textsubscript{6} oxidation curves (Figure 3.9) were not observed with a mixture of CO and NO and NO\textsubscript{2}. This is because C\textsubscript{3}H\textsubscript{6} adsorbs and oxidizes after CO.
Table 3.3 Summary of the temperatures at which the 50% conversion of CO was attained and the increase in temperature to achieve 50% CO conversion with the addition of other reactive species.

<table>
<thead>
<tr>
<th>Gases</th>
<th>Temperature (°C) at 50% CO conversion</th>
<th>Increase in temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>145</td>
<td>-</td>
</tr>
<tr>
<td>NO</td>
<td>162</td>
<td>17</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>172</td>
<td>27</td>
</tr>
<tr>
<td>C₃H₆ + NO</td>
<td>187</td>
<td>42</td>
</tr>
<tr>
<td>NO + 100 ppm NO₂</td>
<td>170</td>
<td>25</td>
</tr>
<tr>
<td>NO + 100 ppm NO₂ + C₃H₆</td>
<td>200</td>
<td>55</td>
</tr>
<tr>
<td>NO + 200 ppm NO₂</td>
<td>177</td>
<td>32</td>
</tr>
<tr>
<td>NO + 200 ppm NO₂ + C₃H₆</td>
<td>208</td>
<td>63</td>
</tr>
</tbody>
</table>

Table 3.3 summarizes the temperatures at which the 50% CO conversions were attained and the increase in 50% CO conversion temperatures with the addition of other reactive components. The 50% CO conversion temperature was shifted by 17°C with only NO, whereas it was shifted 27°C with only C₃H₆. With a mixture of both NO and C₃H₆, the 50% conversion of CO was shifted by 42°C, indicating the combined effect of NO and C₃H₆ is additive in this case. Also, the 50% CO conversion temperature increased 25°C with a mixture of 200 ppm NO and 100 ppm NO₂ and 55°C when C₃H₆ was added to a mixture of 200 ppm NO and 100 ppm NO₂. The 50% conversion of CO was increased by 30°C when C₃H₆ was added to a mixture of 200 ppm NO and 100 ppm NO₂, which is similar to the increase in temperature caused by only C₃H₆ (27°C). This again shows that the combined inhibition of C₃H₆ and NO/NO₂ on CO conversion is additive. It should be also mentioned that the effect of CO on C₃H₆, as shown in Figure 3.9, is far from additive. This additive effect on CO oxidation is due to the preferential low
temperature adsorption of CO on the active Pt sites, thus the effect on the onset of CO oxidation is absent and NO and C₃H₆ only adsorb once CO oxidation began.

3.5 Conclusions

The effect of reactant exhaust gas species on the oxidation of NO, hydrocarbons, and CO was investigated over a Pt/Al₂O₃ catalyst in the presence of excess O₂. CO and C₃H₆ were found to reduce NO₂ at temperatures as low as 110°C whereas higher hydrocarbons (dodecane and xylene) reduced NO₂ at temperatures above 140°C, indicating the reduction ability is related to the activation of the reductant species. Once oxidation of the CO or hydrocarbon species with oxygen began, NO₂ was observed in the outlet stream. The addition of NO₂ to the feed stream inhibited the oxidation of NO, CO, and hydrocarbons. Hydrocarbons were also found to inhibit NO oxidation, as well as the oxidation of other hydrocarbon species (i.e. C₃H₆ inhibited dodecane oxidation and vice versa) due to competition for adsorption sites. The influence of these species on hydrocarbon oxidation was not additive. CO was found to initially hinder the oxidation of NO to NO₂, but as the temperature increased, and CO oxidation via O₂ was favored, CO promoted NO conversion to NO₂. The onset of CO oxidation was not affected, but the extent of oxidation after was inhibited. The combined effect of C₃H₆ and NO and NO₂ on CO conversion was additive since C₃H₆ oxidation occurred after CO oxidation.

3.6 Acknowledgements

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Chapter 4

Hydrogen generation and coke formation over a diesel oxidation catalyst under fuel rich conditions

4.1 Abstract

Hydrogen production via hydrocarbon steam reforming and water gas shift reactions was investigated over a monolith-supported Pt-based diesel oxidation catalyst. The evaluation included comparison between constantly rich gas composition conditions and cycling between rich gas conditions and an inert stream. Analysis was performed along the catalyst length at temperatures ranging from 200 to 500°C. During the constant inlet composition experiments, \( \text{C}_3\text{H}_6 \) steam reforming started at 375°C, while dodecane steam reforming began at 450°C, and resulted in less hydrogen produced. With a mixture of \( \text{C}_3\text{H}_6 \) and dodecane, hydrogen production originated solely from \( \text{C}_3\text{H}_6 \) steam reforming and, under otherwise identical conditions, was less than that observed with only \( \text{C}_3\text{H}_6 \), but higher than that with only dodecane. Hydrogen production from the water gas shift reaction was higher than that observed with hydrocarbon steam reforming, and started at 225°C. During cycling experiments, hydrogen production via hydrocarbon steam reforming was higher than that observed during the constant inlet composition experiments. This improvement was observed at all temperatures. Temperature programmed oxidation experiments performed after steam reforming indicate coke formed on the catalyst surface during steam reforming, and that the coke deposits were primarily toward the upstream portion of the catalyst. The data also show that the reason for better performance during cyclic operation is that less coke was deposited compared to that during non-cyclic experiments.
4.2 Introduction

Diesel oxidation catalysts (DOC) are used in a variety of lean-burn engine aftertreatment systems. They are typically installed upstream of selective catalytic reduction (SCR) and NO\textsubscript{X} storage/reduction (NSR) catalysts. Their function in such systems is to oxidize engine-out NO to NO\textsubscript{2}, as NO\textsubscript{2} is trapped more readily than NO on NSR catalysts [1-2] and a 1:1 NO:NO\textsubscript{2} ratio promotes the “fast” SCR reaction over SCR catalysts [3]. DOCs are also installed upstream of diesel particulate filters, again to oxidize NO to NO\textsubscript{2}. NO\textsubscript{2} is more reactive towards soot than O\textsubscript{2}, lowering the soot oxidation temperature by approximately 200°C [4]. Literature evidence shows that the temperature range in which DOCs operate overlaps the temperature range in which steam reforming reactions are possible. Both water and hydrocarbons are present in diesel exhaust, providing reforming reactant species. And since DOCs contain Pt and Pd supported on either alumina or zeolites, steam reforming reactions are likely, especially during the reductant-rich phase of a NSR cycle.

Hydrogen can be produced via numerous catalytic methods, including catalytic partial oxidation, autothermal reforming, or steam reforming of hydrocarbons, alcohols, and biomass [5-9]. Hydrocarbon steam reforming is typically the preferred process for industrial-scale hydrogen production, because it does not require oxygen, operates at relatively low temperature, and maintains a higher product H\textsubscript{2}/CO ratio than that of autothermal reforming and catalytic partial oxidation [10]. The CO produced during steam reforming can also be used in the water gas shift (WGS) reaction to drive the production of extra hydrogen.
Several studies have shown that the metal type [11-13] as well as the support type can influence the extent of steam reforming. Alumina is a typical support in catalysts, but tends to induce coke formation during steam reforming due to its surface acidity [14], with coke formation a primary steam reforming deactivation process [15-16]. However, the presence of precious metals, zirconium, or other alkaline components in the catalyst formulation can minimize coke formation [17] or facilitate its removal [18]. Hydrocarbon steam reforming over Pd and Pt has been extensively investigated. Previous results relevant to the current study include C₃H₆ steam reforming over Pd/CeO₂/Al₂O₃ and Pt-Rh/CeO₂/Al₂O₃ catalysts [19-20], with the reaction starting at about 350°C. Steam reforming of C₃H₆ and isopropanol was also investigated over a powder Pd–Cu/γ-Al₂O₃ catalyst [21], with both reactions starting at 327°C and increasing steadily until complete conversion was attained, which under the conditions of the test, was at 527°C.

For NSR catalysts, hydrogen has repeatedly been reported to be better than other reductant species (CO and hydrocarbons) in reducing surface NOₓ species to N₂ [22-26]. Therefore, if the amount of hydrogen can be increased via steam reforming or WGS in the upstream DOC during the regeneration phase, which is reductant-rich relative to oxygen, the NOₓ conversion to N₂ over the downstream NSR catalyst could be improved. The main interest in this study, is comparing and quantifying the amount of hydrogen formed during steady-state and cyclic operation over a diesel oxidation catalyst. Coke formation and regeneration was also investigated after these experiments to explain the observed differences.
4.3 Experimental Methods

In this study, a commercial monolith diesel oxidation catalyst supplied by Umicore AG was used. The sample contains 95 g/ft$^3$ Pt supported on Al$_2$O$_3$. The monolith block that the sample was removed from had a cell density of 400 cpsi. The sample was 2.3 cm in diameter with a length of 6 cm. The sample was wrapped in 3M insulation material and placed into a horizontal quartz tube reactor, which was in turn placed inside a Lindberg Minomite temperature-controlled furnace. The matting was used to seal the gap between the catalyst and reactor wall. Two K-type thermocouples were placed at the radial centres of the catalyst; one at the inlet face and one at outlet edge of the catalyst. A third was placed ~ 2.5 cm upstream of the sample. During the experiments, the monolith remained nearly isothermal, with only ~2°C temperature differences observed between the inlet and outlet face.

All gases except balance N$_2$ were supplied by Praxair. The N$_2$ was produced using an On-Site nitrogen generator system. Bronkhorst mass flow controllers were used to meter gases to the reactor system. The dry gas mixture was then heated to > 120°C and water was then introduced using a Bronkhorst CEM system. In experiments that included dodecane or m-xylene, they were also metered with a Bronkhorst CEM system and introduced downstream of the water injection location, closer to the reactor, thereby eliminating any reactions with the steel tubing walls. Small quartz tubes, 3 mm OD and 2 mm ID, were placed in the front portion of the furnace and before the catalyst to help in heat transfer and limit fully developed flow.

In the constant gas composition steam reforming and WGS experiments, 5% H$_2$O, 0.27% hydrocarbon on a C1 basis or 0.27% CO and a balance of N$_2$ were used. In cycling
experiments, 60 s inert and 10 s reductant-containing phases were used (labeled rich below, matching that of an NSR cycle). In the inert phase, 5% H\textsubscript{2}O and a balance of N\textsubscript{2} were used while in the rich phase, 5% H\textsubscript{2}O, 0.27% CO or hydrocarbon on a C\textsubscript{i} basis, and a balance of N\textsubscript{2} were used. In cycling experiments, the rich and inert gas mixtures were made in separate manifolds. A fourway, fast-acting solenoid valve was used to switch between the two. Experiments were also performed to investigate coke formation during cycling and non-cycling experiments. C\textsubscript{3}H\textsubscript{6} steam reforming experiments were performed between 300 and 500°C, which typically took about 3 hours in total to complete, or at one temperature depending on the experiment. Upon completion of a steam reforming experiment, the reactor was cooled to 50°C in N\textsubscript{2} and then 10% O\textsubscript{2} was added to the feed and the reactor was ramped to 500°C at rate of 7°C/min. Catalyst regeneration from deposited coke by O\textsubscript{2}, H\textsubscript{2}O, H\textsubscript{2}, and a mixture of H\textsubscript{2}O and H\textsubscript{2} after C\textsubscript{3}H\textsubscript{6} steam reforming experiments were evaluated, using the same TPO protocol, but substituting in the other regeneration species for the O\textsubscript{2}.

Experiments were performed with a 25,000 h\textsuperscript{-1} space velocity at standard conditions. The gas compositions were measured using a MKS MultiGas 2030 FTIR analyzer. Spatially resolved capillary-inlet mass spectrometry (SpaciMS) was also used to measure H\textsubscript{2}, H\textsubscript{2}O and hydrocarbons along a radially-centred monolith channel. In these studies, He was added and used as a tracer for calibration purposes. To resolve the gas concentrations spatially, a silica capillary, connected to the sampling end of a capillary from a Hiden Analytical mass spectrometer, was placed within one of the radially-centred catalyst channels. The capillary dimensions were 0.3 mm I.D. and 0.43 mm O.D. Gases
were collected at different positions by moving the silica capillary tip to different positions within the channel.

4.4 Results and Discussion

4.4.1 H₂ generation during non-cyclic conditions

Hydrogen generation via steam reforming was investigated between 300 and 500°C. In the steam reforming experiments, C₃H₆, C₁₂H₂₆, m-C₈H₁₀ and mixtures of these were selected to represent different hydrocarbon species in diesel exhaust. In this series of experiments, 5% H₂O, 0.27% hydrocarbon on a C1 basis, and a balance of N₂ were used. Also in these experiments, spatially resolved capillary-inlet mass spectrometry (SpaciMS) was used to quantify the amounts of the species and study their axial concentration distribution. In m-C₈H₁₀ steam reforming experiments, no hydrogen was detected in the outlet stream at temperatures as high as 500°C and therefore data associated with m- C₈H₁₀ are not shown.

Figure 4.1 shows the amount of hydrogen formed at different catalyst positions during the C₃H₆ steam reforming experiments. Note, the position labeled zero is just inside the inlet face of the catalyst (really about 1 mm). C₃H₆ steam reforming began at 375°C, though to a very small extent. As the temperature was increased stepwise to 500°C, hydrogen formation monotonically increased. It is also clear from Figure 4.1 that hydrogen production increased as a function of catalyst length. In a recent study [27], C₃H₆ steam reforming was investigated over a model Pt/BaO/Al₂O₃ NSR catalyst. Hydrogen formation started at a similar temperature (375°C), but to a higher extent than that observed in this study due to the presence of Ba. Alkaline materials are known to
suppress the acidity of the alumina support [28] and thus to reduce coke formation, which leads to higher hydrogen formation.

![Graph showing hydrogen concentration vs. catalyst position at different temperatures](image)

**Figure 4.1** H₂ concentrations obtained at different temperatures and lengths of the catalyst during steam reforming experiments. The inlet gas composition was 900 ppm C₃H₆, 5% H₂O, and balance N₂.

Hydrogen generation via dodecane steam reforming was also investigated and the outlet hydrogen concentration data are shown in Figure 4.2. Below 450°C, no steam reforming occurred and beyond that hydrogen production was observed, starting at a higher temperature than that observed with C₃H₆, and increased at 475 and 500°C. Also, the amount of hydrogen formed at 500°C with dodecane was 10, 100, and 209 ppm at 0, 3, and 6 cm from the catalyst face, respectively, whereas the amount of H₂ formed with
C₃H₆ at the same temperatures and locations were 15, 210, and 488 ppm, or about 2 times more by the outlet with C₃H₆. These results demonstrate that the extent of steam reforming over a diesel oxidation catalyst depends on the type of hydrocarbon used. In previous studies [13, 29-32], alkane steam reforming was investigated over Pt, Pd, Rh, Ru, and Pt/Rh catalysts. According to these studies, alkane steam reforming occurs at higher temperatures than those observed with alkenes, consistent with our data, although different hydrocarbon chain lengths were used in the present study.

![Outlet H₂ concentrations obtained at different temperatures and with different hydrocarbon feed mixtures during steam reforming experiments.](chart.png)

**Figure 4.2** Outlet H₂ concentrations obtained at different temperatures and with different hydrocarbon feed mixtures during steam reforming experiments. The inlet gas composition was 900 ppm C₃H₆, 225 ppm C₁₂H₂₆, or 900 ppm C₃H₆ and 225 ppm C₁₂H₂₆, 5% H₂O, and balance N₂.
Similar experiments were also carried out with a mixture of C\textsubscript{3}H\textsubscript{6} and dodecane. The quantified outlet hydrogen amounts are shown in Figure 4.2. During these experiments, no change in the dodecane amount was observed, indicating that dodecane steam reforming did not occur. The C\textsubscript{3}H\textsubscript{6} amount monotonically decreased as a function of temperature and catalyst length (data not shown); consequently, the hydrogen measured during these experiments originated exclusively from C\textsubscript{3}H\textsubscript{6} steam reforming. It should be noted that hydrogen production started at 400°C, slightly higher than that observed with only C\textsubscript{3}H\textsubscript{6} (375°C). This decreased hydrogen production in the presence vs. absence of dodecane was observed at all temperatures tested. For example, at 500°C and in the absence of dodecane, the outlet hydrogen measured was 488 ppm while in the presence of dodecane it was 285 ppm. These results demonstrate that there was mutual inhibition between C\textsubscript{3}H\textsubscript{6} and dodecane, resulting in lower hydrogen production. Maillet et al. [34] investigated hydrocarbon steam reforming over Rh, Pt and Pd supported on Al\textsubscript{2}O\textsubscript{3} catalysts. The authors divided the steam reforming process into three main steps. The first step involves dissociative adsorption of the hydrocarbon on the metal sites, the second includes dissociative adsorption of water on the support, and finally, OH groups from the support migrate to the metal particles to react with a CH\textsubscript{x} fragment originating from the dissociative adsorption to yield CO\textsubscript{2} and H\textsubscript{2}. This mechanism explains the mutual inhibition between dodecane and propylene observed. C\textsubscript{3}H\textsubscript{6} adsorbs strongly on the Pt sites, relative to dodecane, possibly dissociating to a CH\textsubscript{x} fragment and blocking access of dodecane to the Pt. Adsorption on the support is less selective, and some of the dodecane adsorbs on the catalyst support, which in turn inhibits water dissociation, or inhibits migration of OH groups to the metal site, ultimately inhibiting the reaction.
between OH groups and the CHx fragment. TPD of adsorbed dodecane (data not shown) further supports that dodecane is adsorbed on the catalyst surface, as it was observed desorbing up to ~400°C.

Hydrogen production via the water gas shift (WGS) reaction was also investigated, between 200 and 500°C. In this series of experiments, 5% H₂O, 2700 ppm CO, and a balance of N₂ were used. The results are shown in Figure 4.3, along with equilibrium H₂ concentrations for the conditions tested. It is clear that the WGS reaction started at a lower temperature (~225°C) than steam reforming for the hydrocarbons tested. SpaciMS data show that hydrogen concentrations increased as a function of catalyst length and temperature, although the rate of increase slowed at higher temperature with the approach to equilibrium. The amount of hydrogen formed by the outlet via the WGS reaction at 500°C was 3.5 times higher than that observed with C₃H₆ steam reforming and 6 times higher than that observed with dodecane steam reforming. In the WGS reaction, for every mole of CO reacted, 1 mole of hydrogen will form and therefore at 500°C approximately 60% of the CO was consumed in the formation of hydrogen. No methanation was observed, and CO conversion was only associated with H₂ and CO₂ production. This finding is in contrast to previous studies [35, 36], where methane formation started at temperatures > 375°C with a Pt/CeO₂ catalyst during WGS experiments. However, methanation depends on numerous factors such as inlet gas composition, metal loading, and the inclusion of promoters such as alkali and cerium oxide components. In the previous studies [35,36], significantly larger amounts of both CO and H₂O were used in the feed mixtures (e.g. 11.4% CO and 45.7% H₂O) coincident with including H₂, while in this study CO and H₂O concentrations were 0.27% and 10%,
respectively, with no H₂ added. Furthermore, in the present study the catalyst does not contain cerium oxides or other promoters while in the previous studies, the catalyst included cerium oxide, and as stated by the authors, this would provide extra adsorption sites for water rather than CO blocking all surface sites. Therefore, using an excess amount of CO and H₂O with a catalyst containing cerium oxide would lead to high C/H ratios at the catalyst surface, driving the reactions toward methanation.

![Graph](image.png)

**Figure 4.3** Outlet H₂ concentrations obtained at different temperatures during non-cycling and cycling water gas shift reactions experiments. The inlet gas composition was 2700 ppm CO, 5% H₂O, and balance N₂.
4.4.2 H₂ generation during cycling conditions

Hydrogen production via the steam reforming and WGS reactions during cycling experiments was also investigated at different temperatures. Steam reforming is typically carried out under steady-state inlet conditions, however, for diesel aftertreatment NSR applications, the feed is cycled between those of normal engine exhaust and those of the rich phase, where significant steam reforming is possible. In the “inert” phase, which lasted 60 seconds, 5% H₂O and a balance of N₂ were used, while in the rich phase, which lasted 10 seconds, 5% H₂O, 0.27% CO or hydrocarbon on a C1 basis, and a balance of N₂ were used. An inert phase rather than a true lean phase was used to better understand the phenomena occurring along the catalyst during the rich phase. In both steam reforming and WGS experiments, SPACiMS was used to quantify gas-phase concentrations and study their axial distribution at three different catalyst positions. In the plotted data, the front position is at the inlet of the sample (~1mm in).

Propylene steam reforming during cycling was performed between 300 and 500°C. The measured amounts of hydrogen produced are shown in Figure 4.4. C₃H₆ steam reforming again started at 375°C, the same as that for the non-cyclic experiments. The hydrogen formed increased as a function of catalyst length and temperature. Two primary differences were observed in these experiments when compared with non-cyclic C₃H₆ steam reforming. The first is that a significantly higher amount of hydrogen formed at the front of the catalyst during cycling compared with non-cyclic experiments, where the maximum amounts of hydrogen with all temperatures tested did not exceed 15 ppm. For example, at 500°C, the hydrogen production at the front of catalyst during cycling experiment was ~10 times higher than that observed under steady inlet conditions.
Another observation is that the amounts of hydrogen formed at the middle and outlet positions in the catalyst during cycling were also higher, but to a lesser extent, being about 2 times higher than that observed during steady-state experiments. These differences are likely due to more coke being deposited along the catalyst during non-cyclic tests, especially at the upstream portion, which will be discussed in the following section.

**Figure 4.4** H$_2$ concentrations obtained at different temperatures and lengths of the catalyst during cycling steam reforming experiments. The inert phase gas composition was 5% H$_2$O and balance N$_2$. The rich phase gas composition was 900 ppm C$_3$H$_6$, 5% H$_2$O, and balance N$_2$. The inert phase was 60 sec and the rich phase was 10 sec. The front position represents the inlet of sample (~1mm in).
Similar experiments were carried out, but with dodecane, and the H\textsubscript{2} generation results shown in Figure 4.5. Again, dodecane steam reforming started at 450°C and the hydrogen amount progressively increased with catalyst length. Although there were differences in the amounts of hydrogen formed during cycling and non-cycling experiments, they were not as significant as those observed with C\textsubscript{3}H\textsubscript{6}. For example, at 500°C, the hydrogen formed in the middle and outlet of the catalyst was 100 ppm and 210 ppm during non-cycling experiments, while 130 and 300 ppm were formed during cycling experiments. Again, however, more significant differences were observed at the front of the catalyst, where again the hydrogen amount was higher with cycling experiments. The smaller differences between dodecane cycling and non-cycling steam reforming experiments compared with those observed with C\textsubscript{3}H\textsubscript{6} is related to the hydrocarbons type, where C\textsubscript{3}H\textsubscript{6} is activated faster and more easily than dodecane, and therefore steam reforming and associated coke formation occur at lower temperatures. The positive effect of cycling is less evident for dodecane due to the higher temperatures required for the onset of reaction, and at these higher temperatures, as will be shown below, coke can be reacted from the surface.

Hydrogen production with a mixture of C\textsubscript{3}H\textsubscript{6} and dodecane was also investigated and the quantified amounts of hydrogen are shown in Figure 4.5. The conditions are otherwise similar to those experiments with either C\textsubscript{3}H\textsubscript{6} or dodecane. Again, no change in the dodecane amount was observed while the C\textsubscript{3}H\textsubscript{6} concentration steadily decreased along the length and with increasing temperature. This indicates that the hydrogen formed was again solely due to C\textsubscript{3}H\textsubscript{6} steam reforming. The hydrogen amounts formed were also again lower than those observed in the absence of dodecane.
Figure 4.5 Outlet H₂ concentrations obtained at different temperatures and with different hydrocarbon feed mixtures during cycling steam reforming experiments. The inert phase gas composition was 5% H₂O and balance N₂. The rich phase gas composition was 900 ppm C₃H₆, 225 ppm C₁₂H₂₆, or 900 ppm C₃H₆ and 225 ppm C₁₂H₂₆, 5% H₂O, and balance N₂. The inert phase was 60 sec and the rich phase was 10 sec.

The reason as stated earlier is because of the mutual inhibition between C₃H₆ and dodecane. It should also be pointed out that hydrogen production was observed at 375°C, which is 25°C lower than those observed during non-cyclic experiments (Figure 4.2). This suggests that dodecane inhibition was mitigated by the cycling conditions, likely by desorption from the surface during the inert phase. Additionally, the amount of hydrogen formed during cycling experiments was about twice the amount formed during non-
cycling experiments. The lower coke build-up on the catalyst during the 10 s rich phase of the cycle followed by the inert phase, as will be shown in the next section, explains the higher hydrogen production and lower temperature during cycling.

The extent of hydrogen formed via the WGS reaction during cycling was also investigated at different temperatures and different catalyst positions. The hydrogen formed during the 10 sec rich phase was measured and the results are shown in Figure 4.3. Again, hydrogen production started at 225°C and the hydrogen amount increased as a function of catalyst position and temperature. In previous studies [37, 38], the WGS reaction was investigated during cyclic operation over a commercial NSR catalyst. The extent of the WGS reaction was 10% at 200°C and 81% at 500°C, which is higher than those observed in this study. The higher WGS reaction extent in the previous studies is due to the presence of excess O₂ (10%) in the lean phase, thereby removing any residual CO adsorbed during the previous rich phase, and the presence of Ce and alkali and/or alkaline earth elements (e.g Ba), which are known to enhance the WGS reaction [39-41] and suppress coke formation [31, 32]. During cycling experiments with the DOC in this study, the trends were relatively similar to those observed during the non-cycling WGS experiments, except at the front of catalyst, where a higher amount of hydrogen was observed with cycling. Compared with hydrocarbon steam reforming during cycling, the hydrogen formed during cycling for the WGS reaction was still higher along all catalyst positions and all temperatures. Takahashi et al. [42] studied C₃H₆ steam reforming and WGS reactions over a NSR catalyst between 200 and 400°C under cycling conditions. They also showed that the amount of H₂ formed during the WGS reaction was higher than that formed during C₃H₆ steam reforming, consistent with our data. But, it should be
mentioned that the amount of H₂ formed via the C₃H₆ steam reforming and WGS reactions was higher than those observed in our experiments and attained at lower temperatures. In Takahashi’s study, 7% O₂ was used in the lean phase and the catalyst contained alkali and alkaline earth elements (Ba and K) and ceria-zirconia-based oxygen storage components. Therefore, during the rich pulse, the stored or residual oxygen would lead to combustion of some CO and C₃H₆, possibly resulting in a temperature increase within the catalyst bed. Thus, the measured temperatures for hydrogen production in the previous study would be lower than those observed in our study and hence might explain the observed differences. Another contributing factor is that the O₂ in the lean phase removes coke deposited during the previous rich phase, or adsorbed CO, which should not affect the reaction onset temperature, but will the amounts of H₂ or conversions observed.

4.4.3 Coke formation during steady-state and cycling experiments

As discussed above, there were no significant differences in outlet hydrogen formed for the WGS reaction between cycling and non-cycling conditions. However, hydrogen generation was higher during steam reforming under cycling conditions compared to that observed under constant inlet feed steam reforming conditions. To determine if coke formation is the reason for this latter difference, coke formation during steam reforming experiments was investigated. Ethylene was observed during catalyst outlet measurements, and since ethylene is considered a coke precursor during steam reforming, coke formation is likely. And although coke formation is a product of complete hydrocarbon decomposition, CO is the standard reforming product, and at the reforming temperatures, CO is not considered a catalyst poison, while coke deposition
does lead to deactivation because it reduces the effective surface area [43]. It is likely that the amount of coke deposited on the catalyst during non-cyclic steam reforming experiments was ultimately higher than that during the cycling steam reforming experiments. Further evidence includes the time-resolved H₂ concentration profiles, with an example shown in Figure 4.6, where the H₂ measured by mass spectrometry dropped over time during the non-cyclic C₃H₆ steam reforming experiment. C₃H₆ steam reforming was selected for these tests.

![Graph](image)

**Figure 4.6** Outlet H₂ concentrations obtained during C₃H₆ steam reforming experiments at 450°C. The inlet gas composition was 900 ppm C₃H₆, 5% H₂O, and balance N₂.
In the first set of experiments, non-cyclic C\textsubscript{3}H\textsubscript{6} steam reforming experiments were performed between 300 and 500°C under conditions identical to those in Figure 4.1. Upon completion of the steam reforming experiments at 500°C, the reactor was cooled to 50°C in N\textsubscript{2} and then 10% O\textsubscript{2} was added to the inlet gas feed and the reactor was ramped to 500°C at 7°C/min. The capillary for SpaciMS readings was placed at two locations; 2 and 4 cm from the inlet face, to investigate the amount of coke deposited during the test (two experiments were performed, with measurements taken at 2 cm during the first and 4 cm during the second). The amount of evolved CO\textsubscript{2} during these TPO experiments was measured and the results are shown in Figure 4.7; no CO was observed. The amounts of C deposited on the catalyst were quantified based on the CO\textsubscript{2} evolved and were 394 and 395 µmoles upstream of 2 and 4 cm, respectively. As shown, oxygen begins to remove the coke from the catalyst as low as 190°C. Coke removal reached a maximum at 230°C and coke was completely removed by 250°C. Such data suggest that during normal NSR cycling, less inhibition would be observed, at least above 230°C, from coke build-up because O\textsubscript{2} will be available during the lean phase to remove any built-up coke from the previous rich phase of the cycle.

The data shown in Figure 4.7 also show that the amount of formed CO\textsubscript{2} is quite similar at the 2 and 4 cm positions, indicating that the deposited coke was only in the front 2 cm of the catalyst. Based on the data shown in Figure 4.1, reaction is still occurring downstream, and is a combination of steam reforming and WGS, with the WGS originating from CO formed during steam reforming. The constantly higher hydrocarbon concentrations at the front of the catalyst lead to larger coke deposits there, and a drop in formation down the length as the hydrocarbon is consumed.
Figure 4.7 CO₂ formation obtained during temperature programmed oxidation experiments at 2 and 4 cm from the front of the catalyst. After C₃H₆ steam reforming experiments, the reactor was cooled down to 50°C with only N₂ and then 10% O₂ was added to feed and the reactor was ramped to 500°C at rate of 7°C/min.

Furthermore, hydrogen is known to suppress coke formation during steam reforming [44], and thus the product hydrogen leads to decreasing amounts of coke observed down the length of catalyst. With the test ending at 500°C, these effects are even more pronounced due to the higher reaction rates and therefore more reaction at the inlet.

To isolate the effect of the temperature and further investigate coke deposition along the catalyst length, non-cyclic C₃H₆ steam reforming experiments were performed.
at 450°C and for different reaction times; 4, 60 and 180 min. The reactor was subsequently cooled to 50°C in N₂, 10% O₂ was then added, and the reactor was ramped to 500°C at 7°C/min. The capillary for SpaciMS was placed at 4 cm from the catalyst front. As expected, coke formation increased as the reaction time increased. These results indicate that coke deposition builds as a function of reaction time, at least to 180 min, which is consistent with the data shown in Figure 4.6. The formed CO₂ during TPO was measured to quantify the amount of C on the catalyst surface. The amounts of C deposited on catalyst surface were 269, 422, and 887 µmoles at 4, 60 and 180 min, respectively. CO₂ measurements during TPO after non-cyclic C₃H₆ steam reforming experiments performed at 450°C for 180 minutes were obtained at two different locations; 2 and 4 cm. The amounts of C deposited on catalyst surface were 354 and 887 µmoles at 2 and 4 cm, respectively. The amount of coke at 4 cm was almost 2.5 times that at 2 cm. Due to the integral nature of the monolith, coke will be deposited first at the front of the catalyst and further verifies that coke deposition was spread along the catalyst length with this longer reaction time.

Similar experiments were also performed after the cycling C₃H₆ steam reforming experiments, run at 375°C and under conditions otherwise identical to those described for Figure 4.4. During cycling experiments, no CO₂ was observed evolving during the inert phase, up to ~500°C. After the cycling experiment, the reactor was cooled to 50°C and then ramped at 7°C/min to 500°C with 10% O₂ and balance N₂. The capillary was placed at three different locations (thus steam reforming was repeated at 375°C three times); 1, 2, and 4 cm from the catalyst front. The detected CO₂ during TPO was measured and the results are shown in Figure 4.8.
Figure 4.8 CO₂ formation obtained during a temperature programmed oxidation experiments at 1, 2 and 4 cm from the front of catalyst. After cycling C₃H₆ steam reforming experiments at 375°C, the reactor was cooled down to 50°C with only N₂ and then 10% O₂ was added to the feed and the reactor was ramped to 500°C at rate of 7°C/min.

At 1 cm, the maximum amount of CO₂ measured was about 12 ppm whereas 19 and 20 ppm were detected at 2 and 4 cm, and the amounts of C deposited on the catalyst surface were 31, 91 and 102 µmoles at 1, 2 and 4 cm, respectively. Again, these data demonstrate that coke deposition occurred more at the front portion with small reaction times, here over the front 2 cm of the catalyst during the 10 sec of C₃H₆ steam reforming. Coke deposition was also primarily observed in the front 2 cm with longer times in the
non-cyclic runs mentioned above, but in those experiments the temperature was higher, resulting in increased rates at the front as well. For the sake of a more direct comparison, cycling and non-cycling C3H6 steam reforming experiments were performed at 400°C. The non-cyclic experiment was held for 50 min, and three 10 sec rich cycles for the cycling experiment. This admittedly leads to significantly less exposure during the cycling experiments, but based on the TPO data presented above, any built-up coke could be oxidized at these temperatures in any case. The reactor was cooled to 50°C and then ramped at 7°C/min to 500°C with 10% O2 and balance N2. The capillary was placed 4 cm from the catalyst front. The C amount was measured during TPO after 50 min was 385 µmoles, while 137 µmoles was measured after the 10 sec cycling experiment. It is apparent that significantly less total carbon was deposited during the briefer cycling experiments, although definitely non-linear with respect to time, which ultimately leads to the increased H2 production observed.

4.4.4 Regenerating the catalyst from deposited coke

Numerous regeneration methods have been proposed in the literature to remove coke deposited on catalysts. Oxygen, H2O, CO2, and H2 are the most commonly used gases for removing coke [45]. In this study, catalyst regeneration from deposited coke by O2, H2O, H2, and a mixture of H2O and H2 was investigated after non-cyclic C3H6 steam reforming experiments. Although the TPO data show coke removal at relatively low temperatures, it is necessary to determine if the other gas components play a critical role in coke removal as well, in order to understand and model such phenomena. The steam reforming conditions prior to the regeneration tests are similar to those described in
In all of these experiments, the mass spectrometer capillary was placed at 4 cm from the catalyst front. In one experiment, C\textsubscript{3}H\textsubscript{6} steam reforming was performed during a temperature programmed ramp from 300 to 490°C at a rate of 1°C/min. Subsequently, the reactor was cooled in N\textsubscript{2} to 50°C. The reactor was then ramped up at a rate of 7°C/min to 525°C with a feed containing 5% H\textsubscript{2}O and the balance N\textsubscript{2}. The CO\textsubscript{2} measured during the ramp is shown in Figure 4.9.

**Figure 4.9** CO\textsubscript{2} formation data obtained during temperature programmed reduction experiments at 4 cm from the front of catalyst. After non-cyclic C\textsubscript{3}H\textsubscript{6} steam reforming experiments during a temperature programmed ramp from 300 to 490°C at 1°C/min, the reactor was cooled down to 50°C with only N\textsubscript{2} and then (A) 5% H\textsubscript{2}O was added to the feed, or (B) 1000 ppm H\textsubscript{2} and 5% H\textsubscript{2}O were added to feed, and the reactor was ramped to 525°C at a rate of 7°C/min.
Water began to remove coke at 495°C and the catalyst was completely “cleaned” at 525°C. Similar experiments were also performed, but the regeneration mixture during the temperature ramp portion of the experiment contained 1000 ppm H₂ and 5% H₂O (a H₂ value similar to those observed during steam reforming experiments). No CH₄ or CO was detected in the product stream. The CO₂ was observed at the same temperature when regenerating with only H₂O, as shown in Figure 4.9. This indicates the 1000 ppm of H₂ had little, if any, impact on regeneration although it suppresses coke formation [44]. Further experiments were also carried out to investigate the ability of just H₂ to remove coke.

C₃H₆ steam reforming was carried out at 400°C, to eliminate the effect of H₂O on coke removal, since H₂O begins to react with the coke at ~495°C as was shown in Figure 4.9. C₃H₆ was turned off after 50 min of steam reforming and then 500 ppm of H₂ was introduced for 20 min. If the H₂ was able to remove the deposited coke, CH₄ should be detected in the outlet stream via the following reaction: C + 2H₂ → CH₄. However, no CH₄ was observed in the outlet stream. One possible reason is that the formed CH₄ could be reformed in the presence of H₂O to H₂ and CO or CO₂ via the following reactions:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2; \\
\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2.
\]

But, neither CO nor CO₂ was observed in the outlet stream, indicating that CH₄ steam reforming also did not occur. To verify that the coke was not removed from the catalyst, the reactor was cooled to 50°C in N₂, 10% O₂ was then added, and the reactor was ramped to 500°C at 7°C/min. CO₂ was detected in the outlet stream (data not shown).
peaking at 75 ppm at about 225°C, indicating that the H₂ did not clean the catalyst from deposited coke in the presence of H₂O. As further evidence for the lack of H₂ reaction with surface coke, a TPR experiment was performed after C₃H₆ steam reforming during a temperature ramp from 300 to 480°C. The reactor was cooled afterwards in N₂ to 50°C and then ramped at 7°C/min to 525°C with a feed containing 1000 ppm H₂ and a balance N₂. No CH₄, CO, or CO₂ were detected in the outlet stream, again indicating that H₂ did not remove the deposited coke from the catalyst. The reactor was subsequently cooled in N₂ to 50°C and then 10% O₂ was introduced and the reactor was ramped to 500°C at 7°C/min. Again, CO₂ was detected in the outlet stream. Overall, these data demonstrate that H₂ does not react with deposited coke on this DOC at temperatures as high as 525°C. H₂ could be able to regenerate the catalyst at T > 525°C, but this was not investigated to avoid catalyst aging. Furthermore, these data support previous conclusions regarding the effect of H₂ in suppressing coke formation, such that as H₂ is produced via steam reforming, less coke forms, consistent with the observed axial gradient in surface C along the length of catalyst.

4.5 Conclusions

Hydrocarbon steam reforming and water gas shift reactions were investigated as a function of catalyst length and temperature over a monolith supported diesel oxidation catalyst. Hydrogen production was measured during both cycling and non-cycling (constant steam reforming and water gas shift reaction conditions) experiments using spatially resolved capillary-inlet mass spectrometry (SpaciMS). The data demonstrate that hydrogen production with C₃H₆ steam reforming started at 375°C, while dodecane steam reforming occurred at 450°C and with less hydrogen produced. When C₃H₆ and
dodecane were present together, mutual inhibition was observed and the hydrogen formed only originated from C$_3$H$_6$ steam reforming. The amount of hydrogen formed via the WGS reaction was higher, and started at a lower temperature (~225°C) than that observed with hydrocarbon steam reforming. The amount of hydrogen formed during cycling hydrocarbon steam reforming experiments was consistently higher than that obtained from the non-cycling experiments. Coke deposition was investigated during both types of experiments and the results show that higher amounts of coke were deposited during the non-cycling experiments, compared to cycling experiments, providing the reason for the observed differences in hydrogen formed. Coke deposition was found to start at the front of the catalyst and spread downstream as the reaction time increased.

4.6 Acknowledgments

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References

Chapter 5

Investigating the Effect of NO Versus NO₂ on the Performance of a Model NOₓ Storage/Reduction Catalyst *

5.1 Abstract

The effects of using NO or NO₂ as the NOₓ source on the performance of a NOₓ storage/reduction catalyst were investigated from 200 to 500°C. The evaluation included comparison with constant cycling times and trapping the same amount of NOₓ during the lean phase. With NO₂ as the NOₓ source, better trapping and reduction performance was attained in comparison to NO, at all operating temperatures except 300°C. This exception, under the conditions tested, was likely due to high NO oxidation activity and rapid trapping of NO₂, although it is expected that extending the trapping time would lead to consistent differences. Several reasons for the observed improvements at 200, 400 and 500°C with NO₂ relative to NO are discussed. One that can explain the data, for both trapping and release improvement, is treating the monolith as an integral reactor. With NO₂, more NOₓ is trapped at the very inlet of the catalyst, whereas with NO, the maximum in trapping during cycling occurs slightly downstream. Thus more of the catalyst can be used for trapping with NO₂ as the NOₓ source. The decreased release during catalyst regeneration is similarly explained; with more being released at the very inlet, there is more residence time and therefore contact with downstream Pt sites, but more importantly more interaction between reductant and stored NOₓ. NH₃ and N₂O measurements support this conclusion.

* See the permission from Springer Science+Business Media in appendix A
5.2 Introduction

Concern over fluctuating fuel prices and depleting fuel reserves has led to increased interest in more fuel-efficient engines, such as lean-burn gasoline and diesel engines. However, the excess oxygen present in lean-burn engine exhaust significantly decreases the reduction of NO\textsubscript{X} to N\textsubscript{2} over today’s three way catalytic converter (TWC), which was designed to operate efficiently in stoichiometric-burn, near-zero oxygen, engine exhaust. An alternative, emerging catalyst technology for NO\textsubscript{X} clean-up from lean-burn engine exhaust is NO\textsubscript{X} storage and reduction (NSR). NSR catalysts are typically composed of a high surface area substrate such as γ-alumina, alkali and alkaline metal earth components that trap NO\textsubscript{X} in the form of nitrites and nitrates, and precious metals such as Pt, Pd, and Rh for the redox reactions [1-4]. This technology operates in two modes: lean and rich. In the lean mode, which is where the engine normally operates, NO is oxidized to NO\textsubscript{2} over precious metal sites and the NO and/or NO\textsubscript{2} is then stored on the trapping material as a nitrate and/or nitrite [4-8]. When some portion of these trapping materials becomes saturated, the engine exhaust is switched to a reductant-rich mode where reductants such as H\textsubscript{2}, CO, and HC are introduced to induce the reduction of the stored NO\textsubscript{X} to N\textsubscript{2} [9-11].

Although the trends and mechanisms of NO\textsubscript{X} storage, release, and reduction have been investigated [12-15], due to the complexity of the catalyst, process and their sensitivity to experimental conditions, there is still debate regarding the mechanisms and the potential reactions involved in the multiple catalytic steps [15]. However, there is consensus in the literature that improved NO oxidation to NO\textsubscript{2} results in improved NSR catalyst performance. Previous work [16] has demonstrated that over a wide range of
operating temperatures, NO can not be adsorbed over barium aluminates and barium stannate, even in the presence of $O_2$, whereas $NO_2$ is readily absorbed. In a study that investigated the storage of NO and $NO_2$ over a Pt-containing commercial NSR catalyst [17], no storage occurred when NO was used as the NO$_X$ source below 150°C, while significant storage was observed when $NO_2$ was used. However, at 380°C with a Pt/Rh/Ba/Al$_2$O$_3$ sample [18], no significant difference was observed in storage capacity when either NO or $NO_2$ was used. This improvement with NO at higher temperature is likely attributed to one, or all of, three reasons. First, NO oxidation activity in this higher temperature range is significant [19-21]. Second, $NO_2$ is known to inhibit the NO oxidation reaction [22], and with $NO_2$ being trapped more rapidly as the temperature is increased, at least until approximately 300 to 400°C [13,23], less is present to inhibit the reaction, thus allowing even more NO oxidation. Finally, thermodynamic equilibrium between NO and $NO_2$ within this temperature range [18] imposes a constraint on the $NO_2$ concentration, which is easily achieved over a typical NSR catalyst [19]. Therefore at downstream positions, the same amounts of NO and $NO_2$ are present, resulting in similar performance no matter the NO$_X$ source. The interaction of NO, NO/O$_2$, and NO$_2$ mixtures was also investigated at even higher temperature, 500°C, over Pt-Ba/Al$_2$O$_3$, Ba/Al$_2$O$_3$, and Pt/Al$_2$O$_3$ [7]. The trapping efficiency followed the order NO < NO + O$_2$ < $NO_2$. Similar findings were also observed over a commercial NSR catalyst at 400°C [24]. These results indicate that it must be more than just NO oxidation efficiency that dictates performance, otherwise there would be a consistently decreasing difference as the temperature is increased. Overall, NSR catalysts are more efficient with $NO_2$ as the NO$_X$ source, or $NO_2$ may even be a necessary intermediate for NO$_X$ storage.
Several mechanisms have been proposed for NO\textsubscript{X} storage when either NO or NO\textsubscript{2} is present in the inlet gas feed. Previous work has proposed that nitrites and nitrates can form, either individually [7,12,13,18,25-27], or both form simultaneously via \( \text{2BaO} + 4\text{NO}_2 \rightarrow \text{Ba(NO}_3)_2 + \text{Ba(NO}_2)_2 \) [15,18]. NO\textsubscript{X} release mechanisms have also been investigated, with the research indicating that nitrate species decompose releasing NO or NO\textsubscript{2} [7,13,18].

There are several reasons that might explain the performance improvements observed when NO\textsubscript{2} is used instead of NO as the NO\textsubscript{X} source. First, if trapping is a function of NO\textsubscript{2} partial pressure [6], then when NO\textsubscript{2} is used, the very inlet of the catalyst can participate in trapping whereas with NO, oxidation to NO\textsubscript{2} must occur before efficient trapping is realized. A second possibility involves the presence of multiple types of trapping sites [28-30]. As an example, if one Ba site type is near Pt and another is distant from Pt, NO might only adsorb on the Ba sites which are in close proximity with Pt since it needs to be oxidized to NO\textsubscript{2} prior the adsorption event. While with NO\textsubscript{2}, it can be adsorbed on both Ba site types.

Although NO\textsubscript{2} improves NSR catalyst efficiency, increasing NO\textsubscript{2} amounts to the NSR catalyst or within the NSR catalyst requires the addition of more oxidation catalyst. Diesel oxidation catalysts have been added upstream of NSR catalysts to provide higher inlet NO\textsubscript{2}, as well as for other functions. These are currently precious metal-based catalysts. To improve NO oxidation within the NSR catalyst, more precious metal can also be added. These obviously come at a cost and therefore it is important to understand the effects of NO\textsubscript{2} and optimize the amount of NO\textsubscript{2} in the inlet. In the present work, we have investigated the performance of a model NSR catalyst as a function of NO\textsubscript{X} source.
at operating temperatures between 200 and 500ºC. Although there are studies that have investigated the influence of NO versus NO₂, as shown above, the NOₓ trapping, release, and reduction characteristics as well as N₂O and NH₃ formation when the two are used has not been systematically investigated. Furthermore, a comparison was made between the two when the same amount of NOₓ is trapped so that the effects during the regeneration phase could be observed.

5.3 Experimental Methods

The model Pt/BaO/Al₂O₃ sample used in this study was supplied by Johnson Matthey in monolithic form. The model sample contains 2.0 g/in³ Al₂O₃, 1.45% Pt and 20% BaO relative to the Al₂O₃. The sample was removed from a monolith block that had a cell density of 300 cpsi. The sample used was 0.83” in diameter with a length of 3”. The sample was inserted into a horizontal quartz tube reactor, which was placed inside a Lindberg temperature-controlled furnace. The catalyst was wrapped with 3M matting material to cover the gap between the catalyst and the wall of the reactor to ensure that no gas slipped around the sample. 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. A third was placed ~ 1” upstream of the sample.

The gases and gas mixtures were supplied by Praxair and were metered with Bronkhorst mass flow controllers. A four-way, fast-acting solenoid valve was used to switch between the lean and rich mixtures, which were made in separate manifolds. After the dry gas mixture had been heated to >120ºC, water was introduced downstream of this valve. Table 5.1 lists the gas compositions used in the cycling experiments. The gas mixture then passed through a high-capacity furnace, achieving the target test
temperature prior to entering the furnace holding the sample. This set-up minimized any artificial axial and radial temperature gradients during the experiments.

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/conditioned with a gas 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 25,000 hr⁻¹. The gases exiting the reactor were maintained at >190°C to avoid condensation and NH₃ hold-up. The gas compositions were measured using a MKS MultiGas 2030 FT-IR analyzer at approximately a 2 Hz collection rate. CO, CO₂, NO, NO₂, N₂O, NH₃, and H₂O concentrations were measured.

**Table 5.1** Details of flow conditions used in the experiments

<table>
<thead>
<tr>
<th>Flow Conditions</th>
<th>Trapping (lean) phase</th>
<th>Regeneration (rich) phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space velocity</td>
<td>25,000 hr⁻¹</td>
<td>25,000 hr⁻¹</td>
</tr>
<tr>
<td>Concentrations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂ or NO</td>
<td>330 ppm</td>
<td>0</td>
</tr>
<tr>
<td>O₂</td>
<td>10%</td>
<td>0</td>
</tr>
<tr>
<td>CO₂</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>H₂O</td>
<td>5%</td>
<td>3%</td>
</tr>
<tr>
<td>H₂</td>
<td>0</td>
<td>Balance</td>
</tr>
<tr>
<td>N₂</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

**5.4 Results**

**5.4.1 Effect of inlet NO versus NO₂, with identical cycling times**

The outlet NOₓ concentrations when either NO or NO₂ was used as the NOₓ source at 200°C are shown in Figure 5.1. For this set of experiments, the lean, or
trapping, time was 40 seconds, the rich, or regeneration, time was 4 seconds and 3% H₂ was used as the reductant in the regeneration phase. The conversions and amounts of NOₓ trapped and released for these experiments are listed in Table 5.2. All reported values and plotted data were obtained after steady cycle-to-cycle performance was observed. The data plotted in Figure 5.1 show that the trapping performance for both cases, when either NO or NO₂ was used, is similar during the first 11 seconds of the lean phase. Beyond the first 11 seconds, however, differences in the outlet concentrations were observed. The outlet NOₓ concentrations at the end of the lean phase were 63 and 178 ppm with NO₂ and NO, respectively, and the amounts of NOₓ trapped were 101 and 85 µmoles. The amounts released as unreduced NO or NO₂ during the rich period were relatively small, but slightly more was actually released with NO as the feed NOₓ source although less NO was trapped in the prior lean phase. This is somewhat surprising since the same amount of reductant was added in both cases.

![Figure 5.1](image)

**Figure 5.1** NOₓ outlet concentrations obtained when testing the sample at 200°C.
Similar experiments were carried out at 300, 400 and 500°C, with data shown in Figures 5.2–4. At 300°C, 100 seconds of storage and 4 seconds of regeneration were used for cycling. A summary of the results for all temperatures is also listed in Table 5.2.

**Table 5.2** Calculated performance characteristics as a function of temperature, NO\(_X\) source, and lean phase time over a Pt/BaO/Al\(_2\)O\(_3\) catalyst

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>NO(_X) source</th>
<th>Time (sec) Lean</th>
<th>Rich</th>
<th>NO(_X) Trapped (µmoles)</th>
<th>NO(_X) Released (µmoles)</th>
<th>NO(_X) Conversion (%)</th>
<th>N(_2)O Released (µmoles)</th>
<th>NH(_3) Released (µmoles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>NO</td>
<td>40</td>
<td>4</td>
<td>85</td>
<td>3.5</td>
<td>73</td>
<td>5.2</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>NO(_2)</td>
<td>40</td>
<td>4</td>
<td>101</td>
<td>1.5</td>
<td>90</td>
<td>4.1</td>
<td>50.5</td>
</tr>
<tr>
<td></td>
<td>NO(_2)</td>
<td>35</td>
<td>4</td>
<td>92</td>
<td>1.3</td>
<td>94</td>
<td>3.5</td>
<td>45.6</td>
</tr>
<tr>
<td></td>
<td>NO(_2)</td>
<td>30</td>
<td>4</td>
<td>80</td>
<td>0.9</td>
<td>95</td>
<td>3.4</td>
<td>39.6</td>
</tr>
<tr>
<td>300</td>
<td>NO</td>
<td>100</td>
<td>4</td>
<td>264</td>
<td>1.8</td>
<td>94</td>
<td>0.57</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>NO(_2)</td>
<td>100</td>
<td>4</td>
<td>268</td>
<td>1.6</td>
<td>96</td>
<td>0.55</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>NO(_2)</td>
<td>95</td>
<td>4</td>
<td>256</td>
<td>1.6</td>
<td>96</td>
<td>0.51</td>
<td>73</td>
</tr>
<tr>
<td>400</td>
<td>NO</td>
<td>120</td>
<td>4</td>
<td>278</td>
<td>8</td>
<td>81</td>
<td>0.27</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>NO(_2)</td>
<td>120</td>
<td>4</td>
<td>312</td>
<td>6.4</td>
<td>92</td>
<td>0.07</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>NO(_2)</td>
<td>100</td>
<td>4</td>
<td>277</td>
<td>3</td>
<td>98</td>
<td>0.01</td>
<td>24</td>
</tr>
<tr>
<td>500</td>
<td>NO</td>
<td>80</td>
<td>4</td>
<td>163</td>
<td>31</td>
<td>59</td>
<td>0.26</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>NO(_2)</td>
<td>80</td>
<td>4</td>
<td>189</td>
<td>23</td>
<td>75</td>
<td>0.19</td>
<td>26.5</td>
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<tr>
<td></td>
<td>NO(_2)</td>
<td>62</td>
<td>4</td>
<td>162</td>
<td>19</td>
<td>83</td>
<td>0.11</td>
<td>24</td>
</tr>
</tbody>
</table>

At 300°C, with NO\(_2\), the calculated NO\(_X\) conversion was 96%, while with NO, it was 94%. It is apparent from Figure 5.2 that the differences in the breakthrough profiles are less than those observed at 200°C, but with some difference in trapping performance.
noted after 34 seconds into the lean phase. However, even at end of the 100-second lean phase, the difference in the breakthrough was only about 10 ppm. The amounts trapped were 268 and 264 μmoles with NO₂ and NO, respectively, and the amounts released were 1.8 μmoles with NO to 1.6 μmoles with NO₂. Overall, using either NO₂ or NO at 300°C led to similar performance for these cycling conditions.

![Figure 5.2 NOX outlet concentrations obtained when testing the sample at 300°C](image)

The outlet NOX concentration data obtained at 400°C are shown in Figure 5.3. For this set of experiments, the trapping time was 120 seconds and the regeneration time was 4 seconds. With NO as the NOX source, the calculated NOX conversion was 81%, while with NO₂ the NOX conversion was 92%. The NOX released decreased from 8 μmoles
with NO to 6.4 μmoles with NO₂, while the trapping performance increased from 278 to 312 μmoles.

**Figure 5.3** NOₓ outlet concentrations obtained when testing the sample at 400°C.

The data obtained at 500°C are shown in Figure 5.4. The cycle time was 80 seconds for storage and 4 seconds for regeneration. The NOₓ trapped with NO₂ as the NOₓ source was 189 μmoles and 23 μmoles were released during the regeneration phase. When NO was used, 163 μmoles were trapped and 31 μmoles released. From the data shown in Figure 5.4, the NOₓ breakthrough was similar for the first 38 seconds of the lean phase and beyond that, differences were observed. At the end of lean phase, the difference in the concentrations exiting the reactor was about 63 ppm.
Figure 5.4 NO\textsubscript{X} outlet concentrations obtained when testing the sample at 500°C.

5.4.2 Effect of inlet NO versus NO\textsubscript{2} with the same amount trapped

In this set of experiments, the catalyst performance when trapping the same, or similar, amount of NO\textsubscript{X}, using either NO or NO\textsubscript{2}, was monitored. The same reductant amounts during the regeneration phase were delivered, resulting in a constant surface NO\textsubscript{X} species-to-reductant amount in the cycles. The conversions and amounts of NO\textsubscript{X} trapped and released for these experiments are also listed in Table 5.2. In this case, although listed for completeness and to demonstrate the more dramatic effects, the conversions are not directly comparable since the lean times for the experiments differ. For example, at 200°C, when a similar amount is trapped with NO and NO\textsubscript{2}, the lean-phase times were 40 seconds and 30 or 35, respectively. The amount of NO\textsubscript{X} in during 30
seconds is 75% of that in over 40 seconds, and thus when calculating the conversion, the basis or inlet amount is not the same. At 200°C, with NO as the NO\textsubscript{X} source, the NO\textsubscript{X} trapped was 85 μmoles. To achieve a similar trapped amount of NO\textsubscript{X} with NO\textsubscript{2} as NO\textsubscript{X} source, the lean phase was decreased to 30 and 35 seconds. For these two times, the NO\textsubscript{X} trapped was 80 and 92 μmoles, respectively. For all three experiments, 3% H\textsubscript{2} was used in the 4-second regeneration phase. One would think that since a similar amount of NO\textsubscript{X} was trapped with both NO and NO\textsubscript{2} for these experiments, and the same amount of reductant was introduced during the regeneration phase, a similar amount of release might be expected. This was not the case at 200, 400 and 500°C. For the four experiments run at 200°C, the NO\textsubscript{X} released was 3.5 μmoles with NO (85 μmoles trapped) and 1.5, 1.3 and 0.8 μmoles with NO\textsubscript{2} (101, 92 and 80 μmoles trapped). At 300°C, performance was comparable with the same cycling times, therefore extra experiments were not run. At 400°C, the lean time was reduced to 100 seconds when testing with NO\textsubscript{2} so that a similar amount was trapped as that with NO for 120 seconds. When NO was used in the lean phase, the NO\textsubscript{X} trapped was 278 μmoles and the NO\textsubscript{X} released was 8 μmoles, while with NO\textsubscript{2}, the NO\textsubscript{X} trapped was 277 μmoles and the NO\textsubscript{X} released was 3 μmoles. At 500°C, when NO was used, 163 μmoles were trapped and 31 μmoles released and with NO\textsubscript{2}, the lean phase was shortened to 62 seconds resulting in 162 μmoles of NO\textsubscript{X} trapped and 19 μmoles released. The above results demonstrate that the use of NO\textsubscript{2} as the NO\textsubscript{X} source is not merely better for trapping, but also less release occurred.
5.5 Discussion

In comparing the results obtained at 200 and 500°C when testing with either NO or NO₂, similar trapping profiles were observed at the onset of the trapping phase. Low initial NOₓ out values indicate that active trapping sites were regenerated during the prior rich phase. It has been suggested that there are sites with different relative activities and the more active sites for Pt/Ba/Al₂O₃ samples are associated with the outermost layers of Ba particles or are in close proximity to the precious metal sites [28-30]. If the reduction equation is assumed as follows; \( \text{Ba(NO}_3\text{)}_2 + 5\text{H}_2 \rightarrow \text{N}_2 + \text{BaO} + 5\text{H}_2\text{O} \), for 2 moles of NOₓ trapped, 5 moles of H₂ are required for reduction to N₂. At 200°C, the amount of NOₓ that enters the reactor during a 40-second lean phase is 0.11 mmoles, so the H₂ required to reduce all of the entering NOₓ to N₂ if it all were trapped is 0.28 mmoles. Therefore, 3% H₂, or 1.01 mmoles input during the 4 seconds of rich, is in large excess. Since the catalyst does not contain any oxygen storage components, such as ceria, this amount will be in excess even if including that needed to consume the very small amount of oxygen stored on the catalyst surface. Hence, excess reductant was delivered during the regeneration phase and therefore similar cleaning might be expected with either NO or NO₂. However, except at 300°C, the data demonstrate that trapping is significantly more efficient if NO₂ is the NOₓ source. Such improvements in overall performance have been repeatedly observed when comparing NO₂ to NO [7,12,13,15,31-34]. In this study, the differences between the two are especially apparent at the temperature extremes. There are several possible reasons for this trend in trapping.

First, monolith-supported catalysts are integral devices, and introducing NO₂ can increase use of sites at the very inlet of the catalyst if trapping depends on NO₂, or is
enhanced via NO$_2$. With NO, NO$_2$ becomes available via NO oxidation, and therefore the NO$_2$ concentration will be relatively low at the very inlet, but increase downstream, meaning that for some distance within the sample, the amount of NO$_2$ will be significantly less than when introducing NO$_2$ as the NO$_X$ source. For example, applying previously derived NO oxidation kinetics [22], demonstrates that at steady-state conditions, in other words after the Ba is saturated and no trapping occurs, the conversions of NO to NO$_2$ at 200°C and at positions 0", 1", 2" and 3" from the inlet are 0, 11, 16 and 21%, respectively. This build-up in NO$_2$ would result in higher nitrate concentrations downstream of the inlet, which has indeed been observed [35]. Note that with trapping, NO$_2$ would be adsorbed from the gas phase, resulting in higher local NO oxidation rates compared to the absence of trapping. Also, using NO$_2$ as the NO$_X$ source can result in good trapping performance even in the absence of oxygen in the inlet feed [31]. Thus activation of the O$_2$ molecule is not required with NO$_2$, possibly helping reaction at low temperature. Another possible contribution is from different trapping sites having different adsorption affinities for NO$_2$ and NO. Multiple Ba sites or adsorbing types have been proposed [28-30]. In one example, there are two Ba site types, one proximal to Pt sites and the other further away. With such a scheme, only the sites close to Pt might participate in trapping when NO is the inlet NO$_X$ source, as the Pt would oxidize the NO to NO$_2$, which would then “spill-over” to an adjacent Ba site. Otherwise, the NO$_2$ would have to desorb from the precious metal site and re-adsorb to Ba downstream, but as described above, the overall NO oxidation rate is fairly limited at the lower temperatures. NO$_2$ can be adsorbed on both types of Ba sites, the one proximal to Pt and the one far away from Pt via direct nitrite formation, or via the disproportionation
mechanism to nitrates. This of course increases the available amount of trapping sites when NO$_2$ is introduced, therefore increased trapping will occur and overall higher NO$_X$ reduction performance would be expected. Again, however, this would contribute to more being trapped at upstream sites as well as throughout the catalyst. Another possibility, along the same concept, is that nitrate species and not nitrite species are always, or at least preferentially, formed when NO$_2$ was used, while a mixture of the two species are formed with NO. The thermal stability of nitrate species is higher than nitrite species [4,7], and therefore they are less likely to decompose during the lean phase (via an adsorption/desorption like equilibrium) leading to more NO$_X$ trapped. Most evidence, however, suggests that at temperatures below 300°C, a mixture of nitrites and nitrates form when NO is used, but at higher temperatures, although a mixture may initially form, the nitrites are quickly oxidized to nitrates and have therefore not been observed [6,7]. This is therefore unlikely to significantly influence higher temperature performance and therefore cannot explain the differences observed at 400 and 500°C.

At 300°C, the trapping performance of the catalyst appears only slightly dependent on the NO$_X$ source under the conditions of these tests. NO oxidation initially increases with temperature [36] and most NSR catalyst types attain their maximum oxidation activity between 300 and 400°C, resulting in high NO$_2$ amounts, thus leading to more favorable trapping and comparable performance. Again, using previously derived kinetics [22], at 300°C and in the absence of trapping, 50% NO conversion is predicted. However, the generated NO$_2$ over a NSR catalyst can be immediately trapped, leading to maintained, higher overall NO oxidation rates due to lesser NO$_2$ product inhibition, especially in this 300 to 400°C range. Additionally, in this temperature range, some
thermodynamic equilibrium between NO and NO₂ is being established [18], with a calculated maximum 87% conversion allowed at 300°C, indicating the kinetics are still responsible for the lower conversion. Even so, based on the data shown in Figure 5.2, it is expected that with longer lean time, more difference would be observed, with NO₂ still resulting in improved NOₓ trapping at 300°C. At 400 and 500°C, more significant differences were observed. It should also be noted that NO₂ was observed in the outlet gas composition at 400 and 500°C, with NO and NO₂ as the NOₓ source, indicating it is not an absence of NO₂ limiting trapping at these high temperatures.

At all temperatures, with NO₂ used, there was also noticeable improvement in the regeneration phase, i.e. less unreduced NO and NO₂ was released. This is based on the data obtained from the experiments where the same amount of NOₓ was trapped during the prior lean phase, presented in Table 5.2, resulting in a constant reductant-to-trapped NOₓ ratio for comparison purposes. A likely reason that explains this trend as well, is the integral nature of the NSR catalyst system. As mentioned above, if NO₂ is introduced as the NOₓ source, more sites at the front of the catalyst will participate in trapping. Trapping with NO will be limited at the very inlet due to low NO₂ partial pressures, until the extent of NO oxidation is significant enough. Therefore, upon switching from the lean to rich phase, in the case of NO₂, more NOₓ is released at the very front of the catalyst giving it more chance to be reduced by downstream Pt sites before exiting the monolith. While with NO, more is released slightly further downstream, and has less time spent in the monolith or chance to contact the reducing Pt sites. This is compounded by the local reductant-to-NOₓ ratio as will be discussed below.
Another impact, still in conjunction with the integral reactor explanation, is the oxygen stored on the catalyst surface affecting the amount of reductant available for NO\textsubscript{X} reduction. Previous research [37,38] has shown that reductant can be used up in reducing the stored oxygen on the catalyst and hence influences the amount of reductant available for regeneration and reduction of NO\textsubscript{X}. With NO\textsubscript{2}, more NO\textsubscript{X} is trapped at the very inlet and upon switching from lean to rich, the reductant will simultaneously be depleted to reduce both oxygen and NO\textsubscript{X} stored on the catalyst. Although competitive, this still results in the opportunity for reductant to be consumed in the reduction of NO\textsubscript{X}. However, when NO is used, more is trapped slightly downstream and the incoming reductant is first used to deplete the oxygen stored at the very inlet, thereby delaying reductant delivery to downstream Pt and Ba sites where the higher concentrations of stored, or released, NO\textsubscript{X} species are. This will likely play an increasing role as the nitrate decomposition reaction becomes more significant, i.e. with increasing temperature. Also, with the catalyst studied in these experiments, although present, little OSC was measured due to the absence of standard OSC components. Therefore, the effect described may be minor with this system, but more significant with commercial formulations that contain ceria and other OSC components.

Further evidence supporting the increased reduction being related to where the NO\textsubscript{X} was trapped is the formation of N\textsubscript{2}O and NH\textsubscript{3} byproducts during the regeneration event. As shown in Table 5.2, the formation of N\textsubscript{2}O was always higher when NO was used. With more NO\textsubscript{X} trapped at the front of the catalyst when NO\textsubscript{2} is used, during regeneration there is more opportunity for complete reduction downstream, leading to decreased selectivity toward N\textsubscript{2}O formation, where N\textsubscript{2}O can be considered an incomplete
reduction product. While with NO, the distribution of trapped NO\textsubscript{X} is shifted downstream, and there is therefore less chance for released NO\textsubscript{X} to be completely reduced. This is again related to residence time, since for any NO\textsubscript{X} released further upstream, there is more chance for reduction at downstream sites, but can also be related to the reductant-to-NO\textsubscript{X} ratio. As the reductant enters, it is consumed by surface oxygen and in reducing the nitrites and nitrates. Therefore, reductant delivery to downstream active sites lags the lean/rich gas transition, and as time increases, or the lean/rich transition front distance into the catalyst increases, this lag increases as well. With NO\textsubscript{2} as the NO\textsubscript{X} source, more was trapped at the very upstream Ba sites, and a relatively higher reductant-to-NO\textsubscript{X} ratio is achieved, leading to more complete reduction overall. As a matter of fact, NH\textsubscript{3} formation was always higher when NO\textsubscript{2} was used instead of NO (Table 5.2). NH\textsubscript{3} is formed from the trapped nitrite/nitrate species and the H\textsubscript{2} input during regeneration and leads to selective catalytic reduction of NO\textsubscript{X} over the NSR catalyst [39,40]. Following the same concept discussed above, if NO\textsubscript{2} is trapped at the very inlet of the catalyst, more NH\textsubscript{3} can be formed due to longer residence time of the released NO\textsubscript{X} in the channel with the reductant, as well as a higher reductant-to-NO\textsubscript{X} ratio, a key parameter in NH\textsubscript{3} formation on NSR catalysts [41]. Furthermore, with NO\textsubscript{2} leading to more upstream trapping, NH\textsubscript{3} that does form will have less trapped NO\textsubscript{X} downstream to react with, contributing to the greater amounts observed with NO\textsubscript{2} as the feed. In the case of NO, the NO\textsubscript{X} is trapped slightly downstream relative to the NO\textsubscript{2} case, and therefore less NH\textsubscript{3} is formed, due to the decreased reductant-to-NO\textsubscript{X} ratio and decreased residence time. It should be noted that the amount of N\textsubscript{2}O, overall, decreased with increasing temperature, while NH\textsubscript{3} did not show a consistent trend. Typically, observed NH\textsubscript{3}
decreases with increasing temperature, but this was not the case when comparing the data at 400 and 500°C. But, different lean times were used and less NOX was trapped at 500°C, and with the same amount of reductant added, more NH3 was therefore formed at 500°C. With the trapped NOX being different between the temperatures, a direct correlation of NH3 as a function of temperature cannot be made.

Other than the axial distribution of trapped NOX explaining the trends, another possibility is the nature of the stored NOX during the lean phase. Several complex compounds, (e.g., barium aluminates) could be present, which may have different NO and NO2 dependencies on trapping [18]. Similarly, the decomposition trends of the nitrates or surface NOX compounds formed might be different. However, these types of sites are typically formed via high temperature treatments [42], which were not done with this sample, making this an unlikely path.

There are other factors that can contribute to the observed trends differentiating NO and NO2, but these have different extents of significance in different temperature ranges, and therefore do not explain the consistently observed trends ranging from 200 to 500°C. These possible contributing factors are discussed here. The possibility of nitrates forming at sites near and far from the precious metal sites when using NO2 was discussed in conjunction with the trapping results. Previous studies [7,33,43] have also addressed the influence of Pt on the thermal stability and decomposition of nitrate and/or nitrite species. If with NO, more NOX is trapped at Ba sites that are near Pt, then there may be higher release associated with NO as the inlet NOX source as Pt could induce the decomposition of the Ba nitrite/nitrate during the regeneration phase. With a catalyzed release, or simply higher than that compared to sites that are not necessarily near Pt, more
will escape unreduced. Along the same concept, nitrates are more thermally stable than nitrites. More nitrates form with NO₂ introduced as compared to NO, which at low temperatures is trapped as a nitrite or nitrite/nitrate pair [5,6,15,44]. Therefore at low temperature, nitrite decomposition could lead to a higher amount of unreduced NOₓ, while the nitrates formed with NO₂ as the inlet NOₓ source would lead to less. This however, just as with the trends in trapping, does not explain the differences observed at higher temperatures, as above 300°C, nitrites are rapidly oxidized to nitrates during the lean phase [4,7,19]. Another possibility is that NO is released as the decomposition product when NO is used and NO₂ is released when NO₂ is used, for example from Ba(NO₃)₂ decomposition, which is more prevalent with NO₂ as the NOₓ source. In the absence of gas-phase O₂, NO₂ still has some affinity for downstream adsorption, whether it be on Pt or Ba [14]. Therefore, if NO₂ can indeed stick to downstream sites during the regeneration phase, it will have more opportunity for reduction as the reductant propagates along the catalyst length. Again, however, this should only be expected at low temperature where nitrites might still exist with the switch to the regeneration phase.

A last consideration was the associated temperature rise with the switch from the trapping to regeneration phase. This is caused by reaction of the entering reductant with surface oxygen species, nitrate reduction and possibly mixing phenomena between the two phases. Measured temperature rises at the very inlet and outlet of the sample were on the order of 5°C during all tests. These are significantly smaller than those observed with commercial sample [37], due to the lack of a purposefully added oxygen storage component, such as ceria, in the sample used in this study. This small temperature increase, and it being observed at both the front and back of the sample, suggests that
temperature change is not a significant factor for the trends seen. Furthermore, previous work with Pt/Ba/Al$_2$O$_3$ model samples at 350°C has also indicated that with little or no temperature rise at the onset of regeneration, regeneration is associated with a surface-catalyzed reaction, as mentioned above, and not via thermal decomposition of nitrate species [45]. Again, however, at higher temperatures thermal decomposition of the nitrates is expected and therefore this effect distinguishing NO from NO$_2$ less significant.

Overall, of the possibilities proposed, only the integral nature of the NSR catalyst can explain the observations at all temperatures and amounts of NO$_X$ trapped used in this study. The different surface species and their relative rates of decomposition can contribute to the observations at low temperature, but not to the differences still observed at 400 and 500°C. At low temperature, NO$_2$ is readily trapped at the very inlet, while NO is oxidized and then trapped. At higher temperature, NO$_2$ will decompose to establish NO/NO$_2$ equilibrium, but this still leaves higher NO$_2$ amounts at the very inlet. Therefore, with NO, there is a distribution of trapped NO$_X$ as a function of axial position along the catalyst length during cycling that has a maximum, rather than a monotonic decrease with NO$_2$ as the NO$_X$ source. This leads to the better performance consistently observed with NO$_2$ as the NO$_X$ source and when upstream oxidation catalysts are used.

5.6 Conclusions

In this study, the performance of a model monolith-supported NSR catalyst when using NO or NO$_2$ as the inlet NO$_X$ source at temperatures between 200 and 500°C was investigated. The evaluation was based on two different types of experiments; one with the same lean cycle times and the other with same amount of NO$_X$ trapped. The results clearly demonstrated that performance was better when using NO$_2$ at all operating
temperatures. At 300°C, similar performance between the two was observed, due to high NO oxidation activity, rapid trapping of formed NO\textsubscript{2} and therefore no inhibition effect on NO oxidation, but differences were becoming apparent at the end of the lean phase.

The improved performance with NO\textsubscript{2} relative to NO at the other temperatures can be explained by NO\textsubscript{2} being more reactive towards trapping than NO, or even being an intermediate in the trapping process. This NO\textsubscript{2} dependency leads to more NO\textsubscript{X} trapped at the catalyst inlet when NO\textsubscript{2} was used, while with NO there was less since oxidation to NO\textsubscript{2} prior to trapping is required or leads to more appreciable trapping. A distribution of stored NO\textsubscript{X} along the length of catalyst forms, where with NO\textsubscript{2} it monotonically decreases and with NO there is a maximum downstream of the very inlet. Thus more NO\textsubscript{X} is stored with NO\textsubscript{2} as the NO\textsubscript{X} source since the very front of the catalyst can be used and there are no NO\textsubscript{2}/reactant concentration limitations. Also, less released NO\textsubscript{X} during regeneration was observed when NO\textsubscript{2} was used. Again, if with NO\textsubscript{2} more is trapped at the very inlet, upon switching from lean to rich, the reductant is used to simultaneously reduce both surface oxygen and stored NO\textsubscript{X}. While in the case of NO, the reductant will be consumed first to deplete the surface oxygen and lesser quantities of stored NO\textsubscript{X} at the catalyst inlet, resulting in less reductant available to reduce NO\textsubscript{X} at downstream positions where it is being released in higher concentrations. Analysis of byproduct N\textsubscript{2}O and NH\textsubscript{3} formation during the regeneration phase support this conclusion, as more N\textsubscript{2}O was observed with NO as the inlet NO\textsubscript{X} source, and more NH\textsubscript{3} with NO\textsubscript{2}. Possible contributions to improved performance with NO\textsubscript{2} at lower temperatures were also discussed, and included nitrate versus nitrite stability and trapping at sites near or far from the Pt sites.
5.7 Acknowledgment

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Chapter 6

Effects of Different Regeneration Timing Protocols on the Performance of a Model NO\textsubscript{X} Storage/Reduction Catalyst *

6.1 Abstract

The effects of different regeneration times, but with a constant total amount of reductant delivered, were investigated over a model NO\textsubscript{X} storage and reduction (NSR) catalyst. The different regeneration times were 4, 8 and 16 seconds with 4, 2, and 1% H\textsubscript{2} as the reductant amounts, respectively. The lean time was kept the same during these experiments, resulting in a constant inlet NO\textsubscript{X}-to-reductant amount in the cycles. Overall, the results show clear improvements with longer regeneration times in both NO\textsubscript{X} trapping and overall reduction performance at all temperatures except 500°C. At 500°C, there was still an increase in trapping performance with longer regeneration time, but a more significant increased NO\textsubscript{X} release coincident with a small increase in the trapping performance resulted in an overall decrease in NO\textsubscript{X} conversion with increasing regeneration time. The data demonstrate that the different concentrations of H\textsubscript{2} did not lead to different regeneration extents, but that the main factor for the improved performance was the regeneration time itself. With longer regeneration times, more nitrate/nitrite decomposition occurred, thereby leading to more extensive surface cleaning.

* See the permission from Elsevier in appendix A
6.2 Introduction

With growing concern and public awareness about the environmental, ecological and health impacts of air pollution and global warming, environmental agencies have been setting increasingly stringent regulations to mitigate and control vehicle emissions. This is made more difficult by a coincident demand for higher fuel economy. One solution is a shift from stoichiometric burn engines, such as today’s standard gasoline engine, to lean-burn gasoline or diesel engines. Such a transition could result in a reduction in both fuel consumption and CO₂ emissions. A significant challenge that still remains is NOₓ emissions. NOₓ storage and reduction (NSR) catalysis is one of the currently accepted and implemented technologies for lean-burn engine NOₓ emissions control. NSR catalysts are typically composed of precious metals such as Pt, Pd, and Rh for the redox reactions, alkali and alkaline metal earth components that trap NOₓ in the form of nitrites and nitrates, all supported on a high surface area substrate such as γ-alumina [1-4]. This technology cycles through two phases; a lean and a rich phase. In the lean phase NO is oxidized to NO₂ on the precious metal sites and then NO₂ is adsorbed by the trapping materials, such as Ba in the form of Ba(NO₃)₂ and/or Ba(NO₂)₂ [5-7]. In operation, the lean phase continues until some level of NOₓ slips past the catalyst. At this stage, the rich phase of the cycle is started, where reductants such as CO, H₂, and hydrocarbons are introduced to reduce the surface NOₓ species to N₂ thereby regenerating the trapping sites for the next lean phase, with reduction occurring also via participation of the precious metals sites [8-10].

Numerous studies have investigated regeneration phenomena, including the effect of reductant type, reductant amount, and different lean and rich times [10-16]. In terms of
reductant type [11], the reduction efficiencies of H$_2$, CO, C$_3$H$_6$ and C$_3$H$_8$ at different temperatures were investigated over a Pt/BaO/Al$_2$O$_3$ model catalyst. The results showed that H$_2$ was a superior reductant at low temperatures (T≤250°C), while at high temperatures H$_2$ and CO were similar and showed higher reduction efficiency than C$_3$H$_6$. C$_3$H$_8$ was inefficient at all temperatures tested. Similar observations were also reported over a commercial NSR catalyst [10]. The effect of H$_2$ and CO amounts on the overall performance of a commercial NSR catalyst was also investigated [14]. The performance of the catalyst improved with each incremental increase in H$_2$ concentration, with 5% H$_2$ the highest level evaluated. At high temperature, the performance also increased with increasing CO amounts, however at 200°C, increasing CO was found to decrease performance due to precious metal site poisoning.

The effect of the lean and rich times on the performance of a model NSR catalyst was also investigated, using H$_2$, CO, and C$_3$H$_6$ as reducing agents [15]. As an example of the results, at 300°C, when the lean time was increased from 45 to 135 sec while maintaining a constant rich time (1.5 sec), the overall conversion decreased from 93 to 40%. This was attributed to a lack of sufficient reductant during the 1.5 sec rich phase as the lean time was increased. In the same study, the rich time was increased from 1.5 to 4.5 sec with a constant reductant concentration (3%) and lean phase time (135 sec), and the NO$_X$ conversion increased from 41 to 98%. This was due to the Ba sites being more extensively regenerated with the longer regeneration time and therefore able to participate in trapping during the following lean phase. At lower operating temperatures (T≤250°C), the authors found that NO$_X$ conversion was less dependent on the lean/rich ratio. In another study, the effect of rich time vs. reductant amount on the overall NO$_X$
conversion performance of a powder Pt/Ba/Al₂O₃ catalyst was investigated [16]. With a fixed reductant-to-inlet NOₓ ratio at 400°C, the authors concluded that using longer regeneration times with lower reductant concentrations was more efficient compared to short regeneration times with higher reductant concentrations, which they attributed to two effects. The first was consumption of reductant by the oxygen at the lean/rich interface and the second was that the reduction process with the shorter regeneration time was not as efficient as that with longer regeneration.

The overall reduction of NOₓ and regeneration of trapping sites during the rich phase depends not only on the amount and type of reductant, but also on the amount of NOₓ released via decomposition of the surface nitrite and nitrate species. Primary causes of nitrate/nitrite decomposition and NOₓ release are changes in the gas phase composition, such as the absence of oxygen and NO and the presence of CO₂, H₂O and reductant during the rich phase, as well as heat generated from the exothermic reaction between reductants and oxygen stored on the catalyst surface. For the latter, in a previous study [17] the temperature patterns during cyclic operation of a commercial NSR catalyst were investigated. Just after the onset of the rich phase, the measured temperature rise observed within the first few millimeters of the catalyst surpassed 30°C. As the nitrite/nitrate species stability is a decreasing function of temperature, the increased temperature can lead to decomposition. Such large temperature rises are not typically observed over model Pt/Ba/Al₂O₃ samples due to a lack of significant oxygen stored on the surface, and therefore this exotherm driven decomposition could be insignificant on these model systems.
Nova and coworkers [18] clearly demonstrated the relative unimportance of a purely thermally driven decomposition versus reductant-induced decomposition on a model Pt/Ba/Al₂O₃ system. In their study little NOₓ desorption/nitrate decomposition was observed during temperature-programmed desorption experiments up to the temperature where NOₓ adsorption was performed. However, in the presence of H₂, decomposition could begin at temperatures 200°C lower than the adsorption temperature. Beyond the reductants, other gas-phase constituents influence nitrate stability as well. The presence of oxygen increases nitrate stability [19] and in its absence, the nitrates/nitrites become less stable and decompose. Similarly, it has been shown that CO₂ and H₂O can influence the stability of surface nitrate species, with CO₂ negatively impacting performance [20] via a reduction in nitrates formed, while H₂O has been observed to both decrease [21] and increase [5] NOₓ conversion performance. The effect of Pt on the thermal stability of nitrate and/or nitrite species has also been addressed [22-24, 18]. Results show that Pt induces decomposition of the Ba nitrite/nitrate during the regeneration phase and therefore NOₓ trapped close to Pt might be released faster. Along the same concept, two types of Ba nitrate have been observed; surface and bulk [25-27]. Previous studies have concluded that surface Ba nitrate species are not as thermally stable as a bulk nitrate species.

In this study, the effect of regeneration time, while keeping the total amount of reductant introduced during the regeneration phase the same, was investigated. The analysis includes experiments with and without reductant to monitor time dependent surface NOₓ species decomposition and reductant-induced decomposition. The trapping performance, NOₓ release and formation of NH₃ were measured.
6.3 Experimental Methods

The model Pt/BaO/Al₂O₃ sample used in this study was supplied by Johnson Matthey in monolithic form. The sample contains 0.12 g/cm³ Al₂O₃, 1.45% Pt and 20% BaO relative to the Al₂O₃. The sample was cut to 2.1 cm diameter with a length of 6.4 cm from a monolith block that had a cell density of 300 cpsi. The sample was inserted into a horizontal quartz tube, which was placed inside a Lindberg Minimite temperature-controlled furnace. The catalyst was wrapped with 3M insulation material to seal the catalyst in the quartz tube, to ensure that no gas slipped around the sample. For temperature measurements, 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. A third was placed ~ 2.5 cm upstream of the sample.

The gases and gas mixtures were supplied by Praxair and were metered with Bronkhorst mass flow controllers. A four-way, fast-acting solenoid valve was used to switch between the lean and rich mixtures, which were made in separate manifolds. After the dry gas mixture had been heated to >120°C, water was introduced downstream of this valve. Table 6.1 lists the gas compositions used in the cycling experiments. Small quartz tubes were inserted into the main quartz reactor tube to provide better heat transfer to the gas, such that at the catalyst position, temperature gradients were minimized along the length of catalyst.

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 gas mixture consisting of 5% H₂O, 5% CO₂, 1% H₂, and a balance of N₂ for 15 min at 500°C. 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 25,000 hr$^{-1}$. Different lean times were used at the different temperatures to reflect the different efficiencies at those temperatures, for example performance at 200°C is worse than at 300°C, so longer lean times were used at 300°C, which also matches application trends better. The gases exiting the reactor were maintained at >190°C to avoid condensation and NH$_3$ hold-up. The gas compositions were measured using a MKS MultiGas 2030 FT-IR analyzer at approximately a 2 Hz collection rate. CO, CO$_2$, NO, NO$_2$, N$_2$O, NH$_3$, and H$_2$O concentrations were measured.

**Table 6.1** Details of flow conditions used in the experiments

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<th>Regeneration (rich) phase</th>
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<td>25,000 hr$^{-1}$</td>
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<td>80 seconds</td>
<td>4, 8, 16 seconds</td>
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</table>

6.4 Results and Discussion

In the first set of experiments, 4, 8 and 16 second regeneration times were used, with 4, 2, and 1% H$_2$ as the reductant amounts, respectively. Thus the same amount of
reductant was introduced during each experiment. As previously shown [14], at low temperature CO as a reductant has a severe negative impact on NSR catalyst performance relative to H₂. However, the same study also demonstrated that if H₂ is added to the reductant stream, some performance can be maintained, and more H₂ led to better performance and less CO poisoning. So although CO was not added to the regeneration mixture in this study, the trends observed with H₂ will still be viable if H₂ is present in any amount in the regeneration gas mixture. The lean phase times at each temperature were maintained during these experiments, resulting in a constant inlet NOₓ-to-reductant amount in the cycles. However, different lean times were used at the different temperatures to avoid saturation and 0 ppm NOₓ slip at the performance extremes, better reflecting times and saturation levels used in practice. The performance of the catalyst was evaluated at different test temperatures, as listed in Table 6.2. The outlet NOₓ (the sum of NO + NO₂) concentrations as a function of time obtained during one of the cycles at an inlet temperature of 200°C are shown in Figure 6.1. The lean, or trapping, time was 40 seconds. The conversions and amounts of NOₓ trapped and the amount of un-reduced, released NOₓ during the rich phase, are listed in Table 6.2. The amount of unreduced NOₓ release is obtained by integrating the quantity of NOₓ released during the rich phase, which is defined by the trigger sent to switch the valve controlling which gas phase enters the reactor. All reported values and plotted data were obtained after steady cycle-to-cycle performance was attained.
Table 6.2 Calculated performance characteristics as a function of temperature, amount of H\textsubscript{2}, and regeneration time.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>H\textsubscript{2} (%)</th>
<th>Time (sec)</th>
<th>NO\textsubscript{X} Conversion (%)</th>
<th>NO\textsubscript{X} Trapped (μmoles)</th>
<th>NO\textsubscript{X} Released (μmoles)</th>
<th>NH\textsubscript{3} Released (μmoles)</th>
<th>CO Formed (μmoles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>4</td>
<td>4</td>
<td>40</td>
<td>42</td>
<td>44</td>
<td>4.9</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8</td>
<td>40</td>
<td>49</td>
<td>51</td>
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<tr>
<td></td>
<td>1</td>
<td>16</td>
<td>40</td>
<td>57</td>
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<td>31</td>
</tr>
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<td>99</td>
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<td>400</td>
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<td>120</td>
<td>78</td>
<td>226</td>
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<td>120</td>
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<td>120</td>
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<td>80</td>
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<td>84</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
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<td>2</td>
<td>8</td>
<td>80</td>
<td>35</td>
<td>88</td>
<td>23</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>16</td>
<td>80</td>
<td>30</td>
<td>91</td>
<td>34</td>
<td>10</td>
</tr>
</tbody>
</table>

The data plotted in Figure 6.1 show that the trapping performance was similar during the first few seconds of the lean phase, no matter the regeneration time, but differed after. The amounts of NO\textsubscript{X} trapped were 60, 51, and 44 μmoles for the 16, 8, and 4 second regeneration times, respectively. The amounts released as un reduced NO or NO\textsubscript{2} during the rich period were relatively small, but steadily increased as the regeneration time increased. This increase was expected since the amount of NO\textsubscript{X} released is a function of NO\textsubscript{X} trapped during the previous lean phase, and the amount of NO\textsubscript{X} trapped was larger with increasing regeneration time. The total inlet NO\textsubscript{X} during the 40 second lean time
was 93 μmoles. During the regeneration period, with 1, 2, and 4% H₂, 1124 μmoles of H₂ were introduced. If the reduction reaction is assumed to be Ba(NO₃)₂ + 5H₂ → N₂ + BaO + 5H₂O, then for 2 moles of NOₓ trapped, 5 moles of H₂ are required for reduction to N₂, or 232 μmoles to reduce all the entering NOₓ. The catalyst used in these experiments does not contain any oxygen storage components, such as ceria, so the amount of H₂ input was in large excess even if including that needed to consume the very small amount of oxygen stored on the catalyst surface (i.e. Pt oxides and possibly Ba peroxides at low temperatures).

Figure 6.1 NOₓ outlet concentrations obtained at 200°C with 1% H₂ and 16 sec, 2% H₂ and 8 sec, and 4% H₂ and 4 sec regeneration phases.
Similar experiments were carried out at 300, 400, and 500°C to investigate the effect of operating temperature on the storage, release, and reduction of NO\textsubscript{X} with the different regeneration protocols. The outlet NO\textsubscript{X} concentrations as a function of time at 300°C are shown in Figure 6.2. A summary of the results are also listed in Table 6.2. Again, there was initially little difference in the performance of the catalyst at the beginning of the lean phase with differences appearing as the lean time progressed. The trapping trends were similar to those observed at 200°C, where increased regeneration time led to increased amounts trapped. This increase in the amount trapped, with little impact on the amount released, led to higher overall conversions.

**Figure 6.2** NO\textsubscript{X} outlet concentrations obtained at 300°C with 1% H\textsubscript{2} and 16 sec, 2% H\textsubscript{2} and 8 sec, and 4% H\textsubscript{2} and 4 sec regeneration phases.
The total inlet NO\textsubscript{X} during the 80 second lean phase was 186 μmoles and the amount of H\textsubscript{2} required to reduce this NO\textsubscript{X}, if all was trapped, is 464 μmoles. The inlet H\textsubscript{2} during regeneration was 1120 μmoles, still in significant excess.

Figure 6.3 compares the outlet NO\textsubscript{X} concentrations at 400°C, with a lean phase duration of 120 seconds. At this temperature, the performances for all three regeneration times were similar for a larger portion of the lean phase, relative to that observed at the lower temperatures. Differences were still observed, just much later, and again trapping performance was improved with increasing regeneration time. The observed NO\textsubscript{X} release was higher than that observed during the 200 and 300°C tests, but this increase had little impact on the overall NO\textsubscript{X} conversions. The improved trapping performance at 400°C relative to 200 and 300°C is related to two main factors. First, at low operating temperature, NO oxidation is kinetically limited [5] [28] and most NSR catalyst types attain their maximum oxidation activity between 300 and 400°C. This would therefore result in higher NO\textsubscript{2} amounts and subsequently more rapid and extensive trapping of NO\textsubscript{X} as NO\textsubscript{2} is preferred relative to NO for trapping and nitrate formation [29]. Second, not only does the oxidation activity increase as the temperature increases, but also the extent of regeneration increases. As mentioned, with increasing temperature, nitrates become less stable and in the absence of O\textsubscript{2} and NO\textsubscript{X} in the gas stream, a more significant amount decomposes at 400°C relative to the lower temperatures. Furthermore, at high operating temperature, activation of reductants is not an issue [5], and hence the reductant can easily reduce decomposing nitrate species to N\textsubscript{2}. With more extensive regeneration, there is more trapping site availability expected in the subsequent lean phase portion of the cycle.
Figure 6.3 NO\textsubscript{X} outlet concentrations obtained at 400°C with 1\% H\textsubscript{2} and 16 sec, 2\% H\textsubscript{2} and 8 sec, and 4\% H\textsubscript{2} and 4 sec regeneration phases.

The data obtained at 500°C and an 80-second lean phase are shown in Figure 6.4. Again, improved trapping was observed with longer regeneration times coincident with increased release during the regeneration phase. At this high temperature, however, the NO\textsubscript{X} release increased significantly with each increase in regeneration time; 15, 23, and 34 \textmu{}moles with 4, 8, and 16 seconds of regeneration time, respectively. This increase in NO\textsubscript{X} release coincident with the relatively smaller increase in the trapping performance with longer regeneration times resulted in an overall decrease in NO\textsubscript{X} conversion as the regeneration time was increased. Although the reduction rate increases with temperature, the too rapid decomposition rate of the Ba nitrate species combined with decreasing
reductant concentration and its rapid consumption at the onset of the regeneration phase led to the increased significance of released and unconverted NO\textsubscript{X}.

**Figure 6.4** NO\textsubscript{X} outlet concentrations obtained at 500°C with 1% H\textsubscript{2} and 16 sec, 2% H\textsubscript{2} and 8 sec, and 4% H\textsubscript{2} and 4 sec regeneration phases.

In further detail, at the beginning of the trapping phase, NO\textsubscript{X} is trapped at sites located at upstream positions. These sites become saturated with time and then stop taking part in the trapping process, so downstream sites begin to participate. If the trapping phase is long enough, both upstream and downstream trapping sites will have participated in NO\textsubscript{X} trapping. At 500°C, nitrate decomposition is rapid and upon switching to the rich phase,
the reductant interacts with NO\textsubscript{X} species trapped at the upstream sites to reduce NO\textsubscript{X} and regenerate the surface. The evolved NO\textsubscript{X} species originating from the downstream trapping sites move through the catalyst without being reduced, as the reductant is being used to regenerate the upstream sites. This would in turn lead to the observed lower conversion of trapped NO\textsubscript{X} to N\textsubscript{2}. The amount released was higher with longer regeneration times at 500°C due to the lower local concentration of reductant throughout the catalyst at the onset of the rich phase, with the reduction reaction therefore more reductant limited during the rapid nitrate decomposition and NO\textsubscript{X} release. However, the amount trapped was still higher with longer regeneration time. At the lower test temperatures, the increased NO\textsubscript{X} release is at least partially due to the increase in the amount trapped, combined with lesser local reductant concentrations when nitrate decomposition begins as well.

The results show a marked increase in the trapping performance coincident with slight increases in NO\textsubscript{X} release and therefore overall performance improvement at all temperatures, except 500°C, with longer regeneration times even though the delivered reductant amounts were identical. The improvement in catalyst performance when using longer regeneration times can be primarily attributed to two effects. First, there will be an impact from gas mixing at the lean-to-rich transition interface, which will briefly lead to some reductant consumption. As mentioned in the Introduction, a previous study [16] investigated the effect of a longer regeneration pulse with a lower concentration of reductant vs. a shorter regeneration pulse with a higher concentration of reductant. The authors found that a better regeneration of the catalyst was achieved with the longer regeneration pulse and lower reductant concentration. One explanation proposed was the
consumption of reductants via combustion with oxygen at the interface between the lean and rich phase. With higher reductant concentrations, and the high level of O₂ used in the lean phases, more reductant can be lost compared to the lower reductant concentration case. Therefore, if indeed a significant amount of reductant was consumed at the interface when high concentrations (and a shorter rich pulse) were used in their study, the total amount of reductants delivered to the catalyst beyond the very upstream portion (where the oxidation will occur) will be lower than that when longer regenerations where less reductant concentration was used. Thus, a better regeneration could be expected with longer regeneration. If this mixing effect is significant, then in these experiments, as the rich time increased from 4 to 8 sec and 8 to 16 sec with decreasing reductant concentrations, the effect should have become less. But the difference between the 8 second, 2% H₂ experiment and the 16 second, 1% H₂ experiment was more significant than the difference between the 4 second, 4% H₂ experiment and the 8 second, 2% H₂ experiment. This indicates that this mixing impact on the observed trends is likely minimal, and there must at least be another factor. Furthermore, the temperature rises were relatively small, on the order of 2 to 6°C, and the temperature rise at the front of the catalyst was slightly higher during the shorter regeneration time experiments, relative to the longer regeneration times, in our study, indicating a higher combustion rate. This exotherm impact should, if a significant effect, have led to better regeneration with higher reductant concentrations, which was not observed.

The second effect is related specifically to the regeneration time and nitrate decomposition rate. The two reactions shown below, decomposition of the nitrate species,
as well as reduction of the nitrate species, describe an overall sense what occurs during the regeneration phase.

\[
\text{Ba(NO}_3\text{)}_2 \rightarrow \text{BaO} + 2\text{NO} + 1.5\text{O}_2 \quad (6-1)
\]

\[
\text{Ba(NO}_3\text{)}_2 + 5\text{H}_2 \rightarrow \text{N}_2 + \text{BaO} + 5\text{H}_2\text{O} \quad (6-2)
\]

Nitrate decomposition and NO\textsubscript{X} release, reaction (6-1), depend on several factors including temperature, the presence or absence of O\textsubscript{2}, H\textsubscript{2}O, CO\textsubscript{2} and NO\textsubscript{X}, and the inclusion of oxygen storage components such as Ce in the catalyst washcoat. There was little temperature rise during the rich phase of individual experiments, indicating little effect of changing temperature on NO\textsubscript{X} release, although this effect might play a more significant role in commercial catalysts [17]. Reaction 1 is the reverse of the trapping reaction, and the absence of oxygen during the regeneration phase can drive the decomposition of Ba nitrate as shown. An oxygen source is required for stabilization and formation of Ba nitrate and if oxygen is not introduced during the regeneration event, the decomposition reaction will be favored. The presence of CO\textsubscript{2} and H\textsubscript{2}O coincident with the absence of oxygen during regeneration event also induces the decomposition of Ba nitrate [30-34]. However, in each of these experiments, the inlet CO\textsubscript{2}, H\textsubscript{2}O and O\textsubscript{2} conditions were identical and therefore should not directly cause the observed changes in performance.

To clarify the effect of the rich-phase duration, a second set of cycling experiments at 200°C, where the most significant difference in overall performance was observed, was performed. The cycling experiments were identical to the previous experiments, but in the last cycle after steady cycle-to-cycle performance reached, the
reductant was not included during the regeneration phase. The NO\textsubscript{X} concentration data as a function of time for these experiments are not plotted, but the NO\textsubscript{X} ppm data from each experiment were identical for each incremental time frame. During this phase, the amounts of NO\textsubscript{X} trapped in the previous part of the cycle and that released without reductant present are shown in Table 6.3.

**Table 6.3** Calculated amount of NO\textsubscript{X} (µmoles) trapped and unreduced NO\textsubscript{X} released during regeneration at 200°C with and without reductant in the regeneration portion of the cycle.

<table>
<thead>
<tr>
<th>Regeneration Protocols</th>
<th>NO\textsubscript{X} Trapped</th>
<th>NO\textsubscript{X} Released</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 sec - 4% H\textsubscript{2}</td>
<td>45</td>
<td>7</td>
<td>38</td>
</tr>
<tr>
<td>8 sec - 2% H\textsubscript{2}</td>
<td>49</td>
<td>10</td>
<td>39</td>
</tr>
<tr>
<td>16 sec - 1% H\textsubscript{2}</td>
<td>57</td>
<td>16</td>
<td>41</td>
</tr>
</tbody>
</table>

The differences between the amount trapped with reductant used in the previous rich phase, and the amount released in the absence of H\textsubscript{2} in the regeneration phase are also listed. The amount of NO\textsubscript{X} released in the absence of reductant of course increased as the regeneration time increased. The difference represents the amount of NO\textsubscript{X} associated with trapping sites being regenerated during a rich phase when reductant is present, since steady cycle-to-cycle performance had been obtained. The values are quite similar with the three different regeneration times, indicating a similarity in the amount of regenerated trapping sites between the three experiments with three different regeneration times. This indicates that, in terms of a reductant dependency, the amount regenerated is a function of total reductant delivered, and not the concentration. Furthermore, this indicates that the
reduction process was not simply slower with short regeneration time or higher reductant levels. Finally, this also demonstrates that the extra regeneration observed with the longer regeneration time is solely due to the extra time for reaction 1 to continue.

Beyond just the amount of nitrate or nitrite species that decompose with time, there are other routes, still a function of the regeneration time, which might contribute to the improved performance with long regeneration times. The release/desorption and re-adsorption of the NO\textsubscript{X} species from trapping sites to adjacent or downstream Ba sites during regeneration events is one such possibility. At low operating temperatures, the desorption rate of NO\textsubscript{X} is slower than the reduction rate [5]. Therefore, extending the regeneration event could allow more released NO\textsubscript{X} to spillover to adjacent Pt sites for reduction, or be re-adsorbed at downstream Ba sites and then eventually reduced to N\textsubscript{2} as the reductant propagates from the front to back portion of the catalyst. Another scenario, along the same concept, but also related to the time effect related to reaction 1 and discussed above, is that NO\textsubscript{X} species can be trapped on two types of Ba sites; as proposed in the literature [35-37], one in close proximity to Pt sites, the other more remote from Pt sites. In previous studies [24], it was shown that Pt can catalyze the decomposition of nitrate species during the regeneration event. The nitrate species trapped on “distant” Ba sites can also be released, but at a slower rate than those proximal to Pt sites [5, 24]. Therefore, if the regeneration time is prolonged, it could lead to more NO\textsubscript{X} release from both Ba site types. With more NO\textsubscript{X} release, there are more sites available in the next trapping phase.
Figure 6.5 NH$_3$ and NO$_X$ outlet concentration data obtained at 200$^\circ$C during different regeneration protocols.
Although no differences in catalyst performance would be expected when either H₂ or NH₃ is used as the reductant source [38], the following brief discussion is only to relate the NH₃ formation trends with different regeneration protocols. The NH₃ concentrations as a function of time at 200°C and for the three different regeneration protocols are shown in Figure 6.5. Ammonia formation upon NOₓ reduction with H₂ over NSR catalysts has been widely reported [39-41]. Ammonia was consistently observed in our experiments shortly after the onset of the regeneration phase (about 1 to 2.5 sec after the onset) and reached a maximum when the released NOₓ concentration decreased to close to the baseline level, as shown in Figure 6.5. This result is consistent with NH₃ formed along the catalyst participating in the reduction of NOₓ following the selective catalytic reduction (SCR) mechanism. Ammonia formed at the front of the catalyst is used in the SCR mechanism to reduce downstream nitrate species. As the amounts of nitrates decrease and therefore the amount of NOₓ release begins to decrease, less NH₃ formed upstream reacts downstream and more is then observed. The amounts of NH₃ formed during the cycling experiments were calculated as a function of temperature and regeneration time and are listed in Table 6.2. At 200 and 300°C, total NH₃ formation was always higher when longer regeneration times were used. However, as shown in Figure 6.5, peak NH₃ concentrations were observed with the higher reductant levels, or shorter regeneration times. These trends can be related back to local reductant-to-NOₓ ratios, with the higher the ratio leading to more NH₃ formed [42-43], as well as nitrate exposure time to reductant. As shown in Figure 6.5, NOₓ release occurs at the onset of the regeneration phase. As the regeneration time progresses, less NOₓ is being released while reductant is still being delivered, and this results in NH₃ formation accelerating when the
observed NO\textsubscript{X} release was decreasing. Nitrates were still decomposing, as is evident by the NH\textsubscript{3} formation. Therefore, at later regeneration times, the local reductant-to-NO\textsubscript{X} ratio is higher thus the increase in NH\textsubscript{3} as NO\textsubscript{X} decreases. With the shorter regeneration time, but higher reductant level, the increased reductant-to-NO\textsubscript{X} ratio led to increased peak NH\textsubscript{3} formation values, while for the longer regeneration time experiments, the longer time led to a larger integral amount of NH\textsubscript{3} formed. At 400\textdegree C, there was not a significant change in the amount of NH\textsubscript{3} formed as a function of regeneration time, likely due to a balance in the more rapid release and reductant-to-NO\textsubscript{X} ratio. At 200 and 300\textdegree C, the reductant-to-NO\textsubscript{X} ratio was relatively higher due to the higher thermal stability of nitrate species. Therefore, more NH\textsubscript{3} was formed with longer regeneration time due to the increased total amount of NO\textsubscript{X} release. However, at 500\textdegree C, the weak stability of nitrate species, and the higher reductant concentration during the shorter regeneration protocol, resulted in higher NH\textsubscript{3} formation since both reactants for NH\textsubscript{3} formation were present in abundant quantities. Overall, at low operating temperatures, the longer regeneration time is a key factor controlling the total release of trapped NO\textsubscript{X} and to some extent the formation of NH\textsubscript{3} while at higher operating temperatures, where the thermal stability of nitrate species is weak, the higher reductant concentration is the more important parameter for NH\textsubscript{3} formation.

6.5 Conclusions

In this study, the effects of three different regeneration protocols between 200 and 500\textdegree C were investigated over a model NSR catalyst. The regeneration conditions were 4, 8 and 16 seconds with 4, 2, and 1% H\textsubscript{2} as the reductant amounts, respectively. The data showed an obvious improvement in the catalyst performance with increasing regeneration
time at 200, 300 and 400°C, with the effect related to improved NO\textsubscript{X} trapping. At 500°C, the weaker stability of nitrate species resulted in an overall lower conversion due to a more significant amount of NO\textsubscript{X} released with decreasing reductant concentrations, although the trapping performance was still better with longer regeneration time. The improved trapping performance with longer regeneration times was primarily due to prolonged regeneration conditions leading to more extensive nitrate decomposition, allowing more NO\textsubscript{X} to be trapped in the subsequent trapping phase. Total NH\textsubscript{3} formation at 200 and 300°C was also higher with longer regeneration time, while at 500°C, the trend was reversed, and was related to the local reductant-to-NO\textsubscript{X} ratios.

6.6 Acknowledgements

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References

36. M. Piacentini, M. Maciejewski and A. Baiker, Applied Catalysis B: Environmental 60(2005)265.
Chapter 7

Regeneration of a Model NO\textsubscript{X} Storage/Reduction Catalyst Using Hydrocarbons as the Reductant

7.1 Abstract

Regeneration of a model NSR catalyst using hydrocarbons, H\textsubscript{2}, or CO as reducing agents was investigated. As previously shown, at low temperature, 200°C, H\textsubscript{2} proved best, while both CO and hydrocarbons were found to poison Pt sites. At 250°C, again H\textsubscript{2} was better but the decreased performance with CO and hydrocarbons was also due to slow kinetics and not solely as a result of Pt site poisoning. At T \geq 300°C, hydrocarbons were found to regenerate the catalyst as efficiently as CO and H\textsubscript{2}. Hydrocarbon steam reforming experiments were performed to investigate the improved performance at T \geq 300°C. Steam reforming did not occur with either dodecane or m-xylene below 450°C. Additionally, although propylene steam reforming occurred at 375°C, the small amount of H\textsubscript{2} formed was insufficient for steam reforming to be the sole reason for improved regeneration. TPR experiments show that propylene was activated on the catalyst at T \geq 217°C and, under the conditions examined, the complete reduction of NO by propylene was achieved at 287°C. Furthermore, propylene was observed to reduce surface chemisorbed NO\textsubscript{X} species at T > 200°C, with high rates by 264°C, with this activity ultimately resulting in the comparable performance with either CO or H\textsubscript{2} at similar temperatures during NO\textsubscript{X} cycling experiments.

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7.2 Introduction

With increasing environmental regulation pressure, reducing vehicle emissions has become a significant challenge facing automobile manufactures. This includes NO\textsubscript{X}, CO and hydrocarbons, and there is increasing concern over vehicle CO\textsubscript{2} emissions as CO\textsubscript{2} is also considered a significant contributor to the greenhouse gas effect. One way to reduce vehicle CO\textsubscript{2} emissions and increase fuel economy is using lean-burn gasoline or diesel engines. However, lean-burn engine exhaust contains excess oxygen which makes NO\textsubscript{X} reduction challenging. One technology to reduce NO\textsubscript{X} emissions from lean-burn engines is NO\textsubscript{X} storage and reduction (NSR) catalysis. A NSR catalyst contains precious metals, such as Pt, Pd and Rh for the redox reactions, and alkali or alkaline metal earth components, such as Ba, that trap or store NO\textsubscript{X} as nitrite or nitrate species [1-4]. Overall, NO\textsubscript{X} is reduced to N\textsubscript{2} over NSR catalysts in five steps, two of which occur in the normal lean-burn exhaust environment, and the latter three in a reductant-rich mode, relative to oxygen [5-7]. These are called the lean and rich, or trapping and regeneration, phases of the cycle. The 5 steps are NO oxidation, NO\textsubscript{2} trapping, reductant evolution, nitrate decomposition and finally NO\textsubscript{X} reduction. In the lean phase, NO is oxidized to NO\textsubscript{2} and subsequently trapped by Ba in the form of a nitrate and/or nitrite. Upon saturation of some portion of the trapping material, the rich phase is required to regenerate the surface for further trapping capacity. In the rich phase, reductants, such as H\textsubscript{2}, CO, and hydrocarbons (HCs), are introduced to induce nitrate/nitrite decomposition and reduce the trapped or released NO\textsubscript{X} to N\textsubscript{2}.

Numerous approaches have been explored to achieve the net reducing environment in the rich phase to regenerate the catalyst and reduce the NO\textsubscript{X}. These
approaches include spraying diesel fuel into the exhaust (in-pipe injection) [8-10], using on-board fuel reformers to provide CO and H₂ [11-12], and in-cylinder injection of excess fuel (high F/A ratio) [13-14]. During this rich phase, it has been reported that diesel exhaust can, as an example, contain 2-6% CO, 1-2% H₂, 0.3-0.92% hydrocarbons and less than 0.5% O₂ [15-17]. In previous studies [17-18], different hydrocarbons species were detected in the diesel exhaust including formaldehyde, propylene, ethylene, acetylene, methane and dodecane. These hydrocarbons will be partially consumed by an upstream diesel oxidation catalyst (DOC) during the rich phase either via steam reforming or reacting with the small amount of oxygen in the gas or stored on the catalyst surface. However, some of these hydrocarbons will pass through the DOC to the downstream NSR catalyst. Researchers at Oak Ridge National Laboratory [18] have investigated the amount of reductant (CO, H₂, and HC) prior to and after the DOC and NSR catalysts, with the DOC placed upstream of the NSR catalyst. They found only a small change in reductant level across the DOC during the regeneration event, but a major decrease in the reductant levels across the NSR catalyst.

The hydrocarbons that pass through the DOC can be also be reformed during the rich phase over the NSR catalyst. Furthermore, several previous studies reported that the WGS reaction occurs on precious-metal based catalysts and on three way catalysts (TWCs) [19-23]. In one study, the WGS reaction over a commercial NSR catalyst [23] was investigated and the extent of the WGS reaction ranged from only 10% at 200°C to 91% at 400°C. This reductant amount change makes it difficult to determine whether the CO or H₂ is consistently the active reductant species. Previous work has demonstrated however, that isocyanate species form when CO is present, and these are hydrolyzed to
form N₂ product [24, 25]. This of course complicates the impact of CO, as it can react via the isocyanate route, or via the WGS reaction to form H₂. In terms of the hydrocarbon species, steam reforming can occur to produce H₂. Again, the H₂ produced can ultimately be used as the reductant source for NOₓ reduction. The proposed likelihood of steam reforming over NSR catalysts is based on the ease of hydrocarbon steam reforming over precious metal based catalysts [26-31]. For example, previous studies have shown that steam reforming of CH₄, C₃H₈ and C₃H₆ begins at approximately 325 to 350°C over Pd and Pt/Rh-based catalysts [30,31]. Such data indicate that if H₂ is a necessary reductant, then NSR catalyst regeneration using such hydrocarbon species may be limited at temperatures below ~350°C, which is in the range that some authors have seen equivalent performance between HCs and H₂.

Regeneration of NSR catalysts using different reductants, such as H₂, CO, and hydrocarbons, and mixture of these reductants, at different operating temperatures has been investigated [32-43]. At low temperatures, there is a consensus that H₂ is better in comparison to CO and HC, possibly due to precious metal site poisoning [40-41] or Ba site poisoning by residual isocyanates [38, 42]. At higher temperatures (T ≥ 300°C), H₂, CO, and HC are to some extent comparable in their regeneration and reduction efficiencies [41,43], therefore leaving the active reductant, whether it is H₂ or hydrocarbon, ambiguous.

Although NSR regeneration phenomena have been investigated, to the best of our knowledge, the effects of HCs as the reducing agent on performance and trends in performance have not been systematically studied. In the present study, the regeneration of a NSR catalyst using representative HCs, propylene for short chain, dodecane for long
chain and m-xylene for cyclic species, was evaluated. Hydrogen and CO were also used for comparison with the HCs. Hydrocarbon steam reforming and temperature programmed reduction (TPR) experiments were also performed to characterize the performance changes observed as a function of temperature.

7.3 Experimental Methods

A model Pt/BaO/Al$_2$O$_3$ monolith-supported sample, supplied by Johnson Matthey, was used in this study. The sample is composed of 2.0 g/in$^3$ Al$_2$O$_3$, 1.45% Pt and 20% BaO relative to the Al$_2$O$_3$. Via H$_2$ chemisorption, the Pt dispersion was found to be 12%. The sample had a cell density of 300 cpsi and was 2.1 cm in diameter and 6 cm in length. The catalyst was wrapped with 3M catalytic converter matting material and inserted into a horizontal quartz tube reactor, which was placed inside a Lindberg temperature-controlled furnace. Two K-type thermocouples were placed at the radial center of the catalyst. One was just inside the inlet face of the catalyst and one just inside the outlet face of the catalyst. A third was placed approximately 1” upstream of the sample. Small quartz tubes, 3 mm OD and 2 mm ID, were placed upstream of the catalyst to prevent fully developed flow patterns and to assist in heat transfer from the furnace to the gas phase. Preliminary experiments with just an inert phase demonstrated that the temperature difference between the front and back of the catalyst was less than 5°C for all flowrates and temperatures studied.

The gases and gas mixtures were supplied by Praxair. Bronkhorst mass flow controllers were used to meter the gases. For NSR cycling tests, a four-way, fast-acting solenoid valve was used to switch between the lean and rich mixtures, which were made
in separate manifolds. Water was introduced downstream of this valve after the dry gas mixture had been heated. In experiments using dodecane and xylene, the HCs were again metered with Bronkhorst mass flow controllers and introduced after the wet gas mixture had been heated to >170°C to avoid condensation, and at the reactor inlet to avoid reactions on the steel tubing upstream of the quartz tube.

To start each cycling experiment with a consistent surface, before each experiment, the sample temperature was ramped to 500°C and then cleaned, or conditioned, with a gas 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. Cycling experiments were performed at 170, 200, 250, 300, 400 and 500°C. Table 7.1 lists the gas compositions used in the cycling experiments. The gas compositions were measured using a MKS MultiGas 2030 FT-IR analyzer at approximately a 2 Hz collection rate. CO, CO₂, NO, NO₂, N₂O, NH₃, H₂O, C₃H₆, C₈H₁₀, and C₁₂H₂₆ concentrations were measured. In steam reforming experiments, spatially resolved capillary-inlet mass spectrometry (SpaciMS) was also used. The gases measured by the mass spectrometer were H₂, H₂O, C₃H₆, C₈H₁₀, C₁₂H₂₆ and Ar. Ar was used as a tracer in the mass spectrometer for calibration purposes. Spatial resolution was achieved by placing a silica capillary, connected to the sampling end of a 6’ capillary from a Hiden Analytical mass spectrometer via a zero dead volume steel union fitting, within one of the radially centered catalyst channels. The capillary dimensions were 0.3 mm I.D. and 0.43 mm O.D. Gases were collected at different positions by moving the silica capillary tip to different positions within the channel.
Two types of TPR experiments were performed; one evaluating the reaction chemistry when $C_3H_6$ and NO were both introduced together in the gas phase, and one a surface reaction experiment where NO$_X$ species were formed on the catalyst surface and $C_3H_6$ input after. In the former experiments, the catalyst was cleaned under the conditions described above and then cooled to 109°C. The catalyst was then heated from 109°C to 500°C at a rate of about 3°C/min in a mixture containing 1017 ppm $C_3H_6$, 257 ppm NO, 5% H$_2$O, and a N$_2$ balance. In the latter experiment, the catalyst was heated to 300°C and saturated with NO$_X$ using a mixture containing 350 ppm NO, 10% O$_2$, 5% CO$_2$, 5% H$_2$O, and balance N$_2$. Then the reactor was cooled to 115°C. The sample was then heated at about 2°C/min to 500°C in a mixture containing 55 ppm $C_3H_6$ and a N$_2$ balance. The products from the TPR experiments were monitored using the MKS MultiGas 2030 FT-IR analyzer.

Table 7.1 Details of flow conditions used in the cycling experiments

<table>
<thead>
<tr>
<th>Flow Conditions</th>
<th>Trapping (lean) phase</th>
<th>Regeneration (rich) phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space velocity</td>
<td>30,000 hr$^{-1}$</td>
<td>30,000 hr$^{-1}$</td>
</tr>
<tr>
<td>NO</td>
<td>350 ppm</td>
<td>0</td>
</tr>
<tr>
<td>$O_2$</td>
<td>10%</td>
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<tr>
<td>CO</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>$H_2$</td>
<td>0</td>
<td>1%</td>
</tr>
<tr>
<td>CO</td>
<td>0</td>
<td>1%</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>0</td>
<td>1% relative to C1</td>
</tr>
<tr>
<td>$N_2$</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>
7.4 Results and Discussion

7.4.1 NO\textsubscript{X} Cycling Experiments

Catalyst NO\textsubscript{X} trapping and reduction performance results using different reductants at different temperatures are characterized in this section. This includes evaluating different HCs at the different temperatures to determine when they become efficient as reductants in the regeneration phase. The data shown in Figure 7.1 were obtained at 170°C. The lean, or trapping, time was 40 seconds and the rich, or regeneration, time was 10 seconds. The amounts of reductants used were 1% H\textsubscript{2}, 1% CO, or 0.33% C\textsubscript{3}H\textsubscript{6} (1% on a C\textsubscript{1} basis). Although the amount of C\textsubscript{3}H\textsubscript{6} is greater than that of the CO or H\textsubscript{2} on a total reductant basis (in terms of the amount of O species that can be consumed via inclusion of H\textsubscript{2} and CO), an equivalent C\textsubscript{1} basis was chosen for these experiments. The conversions and amounts of NO\textsubscript{X} (the sum of NO and NO\textsubscript{2}) trapped and released during these experiments are listed in Table 7.2. All reported values and plotted data were obtained after steady cycle-to-cycle performance was attained. The data shown in the figure and table demonstrate that H\textsubscript{2} resulted in better trapping performance, consistent with previous work [33, 41, 44]. Furthermore, at the onset of the lean phase, the outlet NO\textsubscript{X} value reached 0 ppm for many seconds when H\textsubscript{2} was used, but not with CO and C\textsubscript{3}H\textsubscript{6}. With CO and C\textsubscript{3}H\textsubscript{6}, saturation of the available trapping sites occurred during the lean phase, whereas with H\textsubscript{2}, the outlet NO\textsubscript{X} level was still increasing at the end of the lean phase, not having reached the inlet value. The calculated NO\textsubscript{X} conversions were 55, 7 and 6\%, respectively, with differences primarily due to the significantly lower amounts trapped when using CO and C\textsubscript{3}H\textsubscript{6}. The total inlet NO\textsubscript{X} during the 40-second lean time
was 118 µmoles. With H₂ and CO, 841 µmoles were introduced during each regeneration period. Although fewer C₃H₆ moles were input, more was entered based on a C and H basis. The catalyst used in these experiments does not contain any oxygen storage components, such as ceria, so these reductant levels were in large excess relative to the amount required for complete reduction even if all the NOₓ was trapped. Therefore, it is inactivity of the CO and C₃H₆ toward regeneration, thus leaving the catalyst surface covered with nitrates, which caused their poorer performance.

![Graph](image-url)

**Figure 7.1** NOₓ outlet concentrations obtained at 170°C with 1% H₂, 1% CO, or 3333 ppm C₃H₆.
Table 7.2 Calculated performance characteristics as a function of temperature and reducing agent type. The calculated errors associated with these measurements was less than 1% for trapping conditions and less than 2% for regeneration conditions.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reductant</th>
<th>Time (sec)</th>
<th>NO\textsubscript{X} Trapped (µmoles)</th>
<th>NO\textsubscript{X} Released (µmoles)</th>
<th>NO\textsubscript{X} Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lean</td>
<td>Rich</td>
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<td>H\textsubscript{2}</td>
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<td></td>
<td>CO</td>
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<td>23</td>
<td>14</td>
</tr>
<tr>
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<td>C\textsubscript{3}H\textsubscript{6}</td>
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</tr>
<tr>
<td></td>
<td>C\textsubscript{8}H\textsubscript{10}</td>
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<tr>
<td></td>
<td>C\textsubscript{12}H\textsubscript{26}</td>
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<td>63</td>
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<td>CO</td>
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<tr>
<td></td>
<td>C\textsubscript{3}H\textsubscript{6}</td>
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<td>10</td>
<td>135</td>
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<tr>
<td></td>
<td>C\textsubscript{8}H\textsubscript{10}</td>
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<td>114</td>
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<td>C\textsubscript{12}H\textsubscript{26}</td>
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<td>135</td>
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<td>H\textsubscript{2}</td>
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<td>10</td>
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<td>24</td>
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<tr>
<td></td>
<td>CO</td>
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<td>10</td>
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<td>31</td>
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<td></td>
<td>C\textsubscript{3}H\textsubscript{6}</td>
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<td></td>
<td>C\textsubscript{8}H\textsubscript{10}</td>
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<td>10</td>
<td>250</td>
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</tr>
<tr>
<td></td>
<td>C\textsubscript{12}H\textsubscript{26}</td>
<td>120</td>
<td>10</td>
<td>251</td>
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<td>80</td>
<td>10</td>
<td>101</td>
<td>21</td>
</tr>
</tbody>
</table>

Experiments were carried out at higher temperatures to further investigate the effect of temperature on the storage, release, and reduction of NO\textsubscript{X} with the different reductants. The outlet NO\textsubscript{X} concentrations as a function of time at 250°C are shown in Figure 7.2. Dodecane and m-xylene were also tested as reductants at this temperature,
again with 1% on a C1 basis as their inlet concentrations. The summary of the results is also listed in Table 7.2. For this set of experiments, the trapping time was 60 seconds and the regeneration time was 10 seconds. With CO, C₃H₆, C₈H₁₀, and C₁₂H₂₆, the NOₓ breakthrough profiles during the lean phase were comparable. It should be mentioned that the catalyst performance improved, with CO and C₃H₆, compared to the performance observed at 170°C. It is apparent that both hydrocarbons and CO have some activity toward regenerating the catalyst, albeit significantly less than the H₂. For H₂, the NOₓ conversion was actually less than that observed at 170°C.

![Figure 7.2](image)

**Figure 7.2** NOₓ outlet concentrations obtained at 250°C with 1% H₂, 1% CO, 3333 ppm C₃H₆, 833 ppm C₁₂H₂₆, or 1250 ppm C₈H₁₀.
This can occur for two reasons. One is simply the longer lean time at 250°C, which will lead to lesser performance. Secondly, a similar trend has been noted before, where performance at temperatures as low as 100°C were as high as those at 200, 250 and 300°C. This trend was related to enhanced regeneration with H₂ when there are substantial hydroxyl amounts on the support surface and their promotion of the reductant spillover to the trapping sites [45].

To decouple the effect of poisoning and slow kinetics, a second set of cycling experiments was performed, at 200 and 250°C, where the rich-phase time was varied. The data obtained from experiments with CO and C₃H₆ at 200°C are shown in Figure 7.3. The lean phase was again 40 seconds but the regeneration times were 5, 10, and 20 seconds. No differences in trapping performance were observed when the regeneration time was increased from 5 to 20 seconds, using either reductant.
Figure 7.3 NOx outlet concentrations obtained at 200°C with different regeneration times; 5, 10, and 20 sec. (A) 3333 ppm C₃H₆ and (B) 1% CO.

Data obtained at 250°C are shown in Table 7.3 and Figure 7.4. The lean phase was 60 seconds and again the rich-phase duration was changed between 5, 10, and 20 seconds, with CO, C₃H₆, as well H₂. With all three reductants, increasing rich time resulted in increased performance, for example with CO, the amount trapped increased from 37 to 78 μmoles with the increase from 5 to 20 seconds in rich time. The results shown in Figure 7.4 also suggest that if the rich time was prolonged further, further regeneration might still occur.
Figure 7.4 NO\textsubscript{X} outlet concentrations obtained at 250°C with regeneration times; 5, 10, and 20 sec. (A) 3333 ppm C\textsubscript{3}H\textsubscript{6}, (B) 1% CO and (C) 1% H\textsubscript{2}.

Table 7.3 Calculated performance characteristics as a function of reductant type and regeneration time at 250°C

<table>
<thead>
<tr>
<th>Reductant Type</th>
<th>Time(sec)</th>
<th>NO\textsubscript{X} Trapped (μmoles)</th>
<th>NO\textsubscript{X} Released (μmoles)</th>
<th>NO\textsubscript{X} Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rich</td>
<td>Lean</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>5</td>
<td>60</td>
<td>37</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>10</td>
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<td>54</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>60</td>
<td>78</td>
<td>31</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6}</td>
<td>5</td>
<td>60</td>
<td>37</td>
<td>15</td>
</tr>
<tr>
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<td>10</td>
<td>60</td>
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<td></td>
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<td>H\textsubscript{2}</td>
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<td></td>
<td>20</td>
<td>60</td>
<td>98</td>
<td>6</td>
</tr>
</tbody>
</table>
The data obtained at 200°C indicate that it is not simply slow kinetics during the rich phase limiting the extent of regeneration, since increasing the rich-phase time had no effect. It is also not a lack of reductant activation as some regeneration does occur, nor is it diffusional resistance differences between the reductants as increased time had no effect for the CO and C₃H₆ species. The poor performance is due to Pt site poisoning by CO and C₃H₆, thereby inhibiting the release and reduction reactions. This is in line with previous NSR catalyst studies using CO and C₃H₆ at low temperature. Abdulhamid et al. [41] investigated the regeneration of a Pt/BaO/Al₂O₃ catalyst using CO at 150, 250, and 350°C and attributed the decrease in performance at low temperature to CO poisoning the Pt sites. In another study [46], surface IR results showed adsorbed CO and carbonate species when using CO or C₃H₆ at 200°C as reductants, which also resulted in a lower NOₓ storage rate after the switch from the rich phase to the lean phase. However, the results at 250°C indicate that the performance is limited by slow kinetics, although still possibly in combination with some residual Pt site poisoning. If poisoning was stronger/dominant, the performance would not have improved with each increase in the rich time, as was the case at 200°C. Surface diffusion limitations may play a role, but this would be coupled with poisoning. Previous work has shown isocyanate formation when CO was used as a reductant [42] and the authors concluded that these formed around the Pt sites, which could cause blocking of further surface transport. Such results also demonstrate that reductant spillover from the precious metal sites to the Ba trapping sites occurs, suggesting spillover direction.

The data obtained at 300°C are shown in Figure 7.5, with summary data listed in Table 7.2. There was an improvement in the catalyst performance with CO and
hydrocarbons, relative to 250°C, but H₂ still showed better activity in both trapping and reduction performance. With H₂, the calculated NOₓ conversion was 64%, while with CO it was 55%. Propylene and C₁₂H₂₆ led to slightly lower but similar conversions, indicating persistent kinetic limitations related to regeneration and reduction. With C₈H₁₀, the catalyst performance was significantly poorer, with the measured conversion being 34%. The poor performance with C₈H₁₀ compared to C₃H₆ or C₁₂H₂₆ is likely related to its cyclic nature, where it is assumed that activation of cyclic hydrocarbons is more difficult than the straight chain hydrocarbons [47].

![Graph](image)

**Figure 7.5** NOₓ outlet concentrations obtained at 300°C with 1% H₂, 1% CO, 3333 ppm C₃H₆, 833 ppm C₁₂H₂₆, or 1250 ppm C₈H₁₀.
At 300°C, NO$_X$ trapping and conversion performance was better with H$_2$ compared to CO and hydrocarbons and CO was better than the hydrocarbons. The reasons for the improved performance with CO as the temperature was increased has been previously studied and is explained by decreased CO poisoning and increased hydrolysis of cyanates, which form from direct reduction of the nitrate species by CO [40,48]. In general, the increased performance at 300°C when using the hydrocarbon reductants has been attributed to reductant activation vs. temperature [41]. Thus, as the temperature increased from 170 to 300°C, the activation of hydrocarbons on the Pt sites became easier and faster, and poisoning effects decreased, resulting in the higher reduction activity. This is in line with previous work that has shown similar trends and concluded that once C-H bond activation occurred, HCs could act as reductants [49]. In terms of improved performance for all the reductants, there is an increased surface diffusion rate with temperature [50-52], higher NO oxidation rates [53-54], and higher nitrate/nitrite decomposition rates during regeneration [5,54], all of which typically lead to improved NSR catalyst performance at test temperatures below 400°C.

Experiments at 400 and 500°C were also performed with summary data listed in Table 7.2. At 400°C, the amount of NO$_X$ released was actually higher with H$_2$ relative to m-xylene and dodecane, leading to overall similar conversions. With C$_3$H$_6$, the catalyst performance was better than that observed with the other reductants, due to the higher overall reductant level introduced when counting both the H and C components as reductants. Similarly, there is more when using the m-xylene and dodecane, and with their similar performance to H$_2$, suggests that there is still some limitation with their use. At 500°C, catalyst performance was lower than that observed at 300, 350, and 400°C,
with all reductants. The amounts of NOX trapped with H2, CO and C3H6 were comparable, but there were differences in the amounts of NOX released, with CO leading to higher release. Although the trapping performance was lower with C8H10 and C12H26 compared to that observed with H2, CO, and C3H6, the lower NOX release during the rich phase led to comparable conversions. The reason for the decreased performance relative to 300 and 400°C is due to nitrate stability. The nitrate species decompose rapidly at the onset of regeneration due to their low thermal stability at high operating temperatures [55-56]. As the reductant is being used to regenerate NOX species trapped at the upstream sites, NOX species are rapidly decomposing at downstream sites and will travel through the catalyst without being reduced, leading to a lower ratio of rate of reduction to rate of NOX release [57-58]. Also, due to their lower stability at higher temperature, less nitrates form during the trapping phase as well.

Two mechanisms have been proposed for reduction of NOX to N2 by hydrocarbons over the precious metal sites of NSR catalysts. The first mechanism [59] postulates that the reductant reduces the precious metal site, which then participates in NO decomposition. In the second mechanism [60], the reductant, C3H6 was selected as an example, is first adsorbed on the precious metal site and then breaks down to various types of reactive hydrocarbon sub-species [5]. The reactions pathways listed in reference [60] are shown below:

\[
\begin{align*}
\text{C3H6 (g) + Pt} & \rightarrow \text{Pt-C3H6} \\
\text{Pt-C3H6 +2Pt} & \rightarrow 3 \text{Pt-CH2} \\
\text{Pt-CH2 + 3Pt-NO} & \rightarrow 4 \text{ Pt + CO2 (g) + H2O (g) + 1.5 N2 (g)}
\end{align*}
\]
For the sake of simplicity, the authors suggested CH\textsubscript{2} as the hydrocarbon sub-species formed from propylene decomposition. They proposed that the bound intermediate CH\textsubscript{2} group reacts with the sorbed NO\textsubscript{X} species to form the reduction reaction products. In several IR characterization studies [49,61-64] nitro, organic nitro, nitrite and isocyanate surface species were observed on Ce-ZSM-5 and Pt/SiO\textsubscript{2} surfaces during lean- NO\textsubscript{X} reduction tests and were suggested intermediates in this reaction process, supporting the CH\textsubscript{2}-based mechanism shown above. However, a third possibility, due to the reaction mixtures imposed, is that hydrocarbons undergo steam reforming, producing CO and H\textsubscript{2}, which act as the actual reductant species. This is discussed in the following section.

\subsection*{7.4.2 Hydrocarbon Steam Reforming}

In cycling experiments, decreased catalyst performance at low temperatures using CO or hydrocarbons was related to Pt site poisoning, or slow kinetics as the temperature increased to 250\textdegree C. However, at higher operating temperatures (T ≥ 300\textdegree C), there was a significant improvement in the catalyst performance using hydrocarbons. A similar improvement was observed with CO as the reductant as well, which has been well explained in recent literature [40,48], thus the focus of this discussion will be on the hydrocarbons. In the rich phase, hydrocarbons and H\textsubscript{2}O are both present and therefore steam reforming could occur, leading to H\textsubscript{2} which could then act as the reductant. To investigate this possibility, hydrocarbon steam reforming was evaluated at different temperatures.

In this series of experiments, steam reforming of C\textsubscript{3}H\textsubscript{6}, C\textsubscript{12}H\textsubscript{16}, and C\textsubscript{8}H\textsubscript{10}, and mixtures of these, were investigated. The reaction gas mixtures used in these experiments
contain 5% H₂O, 1% hydrocarbon on a C1 basis, and a balance of N₂. Experiments were carried out at different test temperatures, ranging between 250 and 525°C with no reaction observed at less than 375°C. Spatially resolved capillary-inlet mass spectrometry (SpaciMS) was used to quantify the amount of hydrocarbons, CO₂, H₂O, and H₂ at different catalyst positions. The capillary tip was moved to seven different positions within the channel to study the axial distribution of the species. In the plotted data, the zero position represents the inlet of sample and 6 cm represents the end of sample.

![H₂ Production](image_url)

**Figure 7.6** H₂ concentrations obtained at different temperatures and lengths of the catalyst during steam reforming experiments. The inlet gas composition was 3333 ppm C₃H₆, 5% H₂O, and balance N₂.

Propylene steam reforming results, obtained along the catalyst length at different temperatures, are shown in Figure 7.6. At 375°C, C₃H₆ steam reforming occurs, but with
very low conversions. As the temperature was increased to 525°C, H₂ production monotonically increased, with more significant increases after 475°C. H₂ production steadily increased as a function of catalyst length.

Similar experiments were also carried out, but with dodecane or m-xylene as the hydrocarbons. The H₂ production data as a function of temperature and axial length of the catalyst are shown in Figures 7.7 and 7.8.

![Graph showing H₂ production vs catalyst position at different temperatures.](image)

**Figure 7.7** H₂ concentrations obtained at different temperatures and lengths of the catalyst during steam reforming experiments. The inlet gas composition was 833 ppm C₁₂H₂₆, 5% H₂O, and balance N₂.

Dodecane steam reforming started slightly below 450°C, higher than that observed with C₃H₆ (375°C). At 525°C, H₂ production was 91, 690, and 1195 ppm at 0, 3, and 6 cm respectively, while the amount of H₂ formed with C₃H₆ at 525°C was 172, 6551 and 7973
ppm. The outlet level with C₃H₆ was approximately 6.6 times higher than that observed with dodecane at the same temperature. M-xylene steam reforming started at just below 475°C and the amounts of H₂ formed were significantly lower than those with the other hydrocarbons. Again, H₂ formation increased with temperature, but even at 525°C, only 20, 238, and 507 ppm were formed at 0, 3, and 6 cm inside of the sample, respectively, much lower than those observed with C₃H₆ and C₁₂H₂₆.

![Figure 7.8](image.png)

**Figure 7.8** H₂ concentrations obtained at different temperatures and lengths of the catalyst during steam reforming experiments. The inlet gas composition was 1250 ppm C₈H₁₀, 5% H₂O, and balance N₂.

These results, as expected, show that different hydrocarbon types undergo steam reforming at different temperatures and with different rates on the NSR catalyst. It should
be noted that there is some measured conversion at the front of the catalyst. The capillary tip is positioned at the very edge of the sample, so will probe conversion that could occur at the face. Also, dodecane and m-xylene will homogeneously decompose in the reactor at temperatures above 320-330°C (based on empty reactor baseline experiments) and thus could lead to byproducts that are more easily reformed to H₂, even at or on the catalyst face.

H₂ production rates via steam reforming with a mixture of C₃H₆ and C₁₂H₂₆ were also investigated, with the data shown in Figure 7.9. According to the results obtained, there was no change in the amount of dodecane in any of these tests demonstrating that no dodecane steam reforming occurred. C₃H₆ steadily decreased along the catalyst length; therefore, the amount of H₂ measured originated solely as a result of C₃H₆ steam reforming. There were only slight differences in the amount of H₂ formed via C₃H₆ steam reforming in the absence and presence of dodecane at both 375 and 400°C. However, at the higher temperatures, significantly less H₂ was formed in the presence of dodecane. For example, at 525°C and in the absence of dodecane, the amount of H₂ formed was 7973 ppm whereas in presence of dodecane, the amount of H₂ produced was 3738 ppm. This indicates that dodecane inhibited C₃H₆ steam reforming, but at the same time C₃H₆ inhibited dodecane steam reforming. The latter is likely due to the higher reactivity of the C₃H₆ while the former is possibly due to the coverage of some metallic sites by the longer chain hydrocarbons, resulting in lower availability of metallic sites for adsorption of reactants.

These results show that steam reforming over a NSR catalyst can occur when hydrocarbons and water are present in the gas stream. Different hydrocarbon types have
different reactivities towards steam reforming. This could be related the extent of which the hydrocarbons can be activated on the surface of precious metals. Since steam reforming did not occur below 375°C for C₃H₆ and 450°C for C₁₂H₂₆ and C₈H₁₀, steam reforming cannot explain the improved performance in the cycling experiments at 300 to 400°C described above. Furthermore, even at 375 and 450°C, the amounts of H₂ produced were quite small, and built through the catalyst, such that at the catalyst front little H₂ was present until the higher temperatures.

![Graph](image)

**Figure 7.9** H₂ concentrations obtained at different temperatures and lengths of the catalyst during steam reforming experiments. The inlet gas composition was 3333 ppm C₃H₆, 833 ppm C₁₂H₂₆, 5% H₂O, and balance N₂.
These data therefore demonstrate that steam reforming does not play a critical role in NSR regeneration below 450°C. This is not to say that reforming is unimportant for NSR activity in general, as desulfation occurs at much higher temperatures, where steam reforming can have a more significant contribution.

7.4.3 TPR Experiments

In the previous section, hydrocarbon steam reforming was investigated and the data show that reforming to H₂ is not significant enough to explain the improved performance observed above 300°C when using hydrocarbons as reductants. To further investigate this issue, TPR experiments were performed with propylene selected as the reductant. Two types of experiments were performed; one where both the NO and C₃H₆ were simultaneously present in the gas phase and one where NO was first trapped on the catalyst and then C₃H₆ was input for the TPR.

In the first set of experiments, the catalyst was first cleaned with a gas mixture consisting of 5% H₂O, 5% CO₂, 1% H₂, and a balance of N₂ for 15 min at 500°C. The reactor was then cooled to down to 109°C. The catalyst was heated from 109°C to 500°C at approximately 3.3°C/min in a mixture containing 1017 ppm C₃H₆, 257 ppm NO, 5% H₂O, and a N₂ balance. The profiles of C₃H₆ and NO consumption as a function of temperature are shown in Figure 7.10. The reaction between C₃H₆ and NO started at approximately 200°C, but at low rates and lit-off beginning at 217°C. Full conversion of NO was observed by 287°C. In terms of a mass balance, if the reduction equation is assumed as follows, 9NO + C₃H₆ → 4.5 N₂ + 3CO₂ + 3 H₂O, then for 9 moles of NO, 1 mole of C₃H₆ is required for reduction to N₂. At 287°C, all inlet NO, 257 ppm, was
consumed and therefore ~29 ppm of C\textsubscript{3}H\textsubscript{6} should be consumed as well for the reduction. But, as shown in Figure 7.10, approximately 41 ppm of C\textsubscript{3}H\textsubscript{6} was consumed at 287°C. The excess amount of C\textsubscript{3}H\textsubscript{6} reacted went toward production of CO and other short chain hydrocarbons via partial oxidation and reaction, as both CO and ethylene were detected by FT-IR.

![Figure 7.10](image)

**Figure 7.10** NO and C\textsubscript{3}H\textsubscript{6} outlet concentrations obtained during a temperature programmed reduction experiment; the ramp rate was 3.3°C/min. The inlet gas composition was 1017 ppm C\textsubscript{3}H\textsubscript{6}, 257 ppm NO, 5% H\textsubscript{2}O, and balance N\textsubscript{2}.

There have of course been several studies focused on NO\textsubscript{X} reduction by hydrocarbons, but in the presence of O\textsubscript{2} (HC-SCR) [65-67]. Results from each of these studies indicate a similar temperature range in which C\textsubscript{3}H\textsubscript{6} begins to reduce NO\textsubscript{X}, even in the presence of
O₂, again suggesting the activation of C₃H₆, or the HC species in general, as a determining factor for regeneration temperature dependency. Furthermore, and as discussed earlier, with a Pt/Ba/Al₂O₃ catalyst [68], a mixture containing C₃H₆ and O₂ reacted with surface NOₓ species at approximately 230°C, again in the same range as that observed here.

In the second experiment, the catalyst was heated to 300°C and saturated with NOₓ using a mixture containing 350 ppm NO, 10% O₂, 5% CO₂, 5% H₂O, and a N₂ balance. Then the reactor was cooled to 115°C. The sample was then heated at 2.1°C/min to 500°C in a mixture containing 55 ppm C₃H₆ and a N₂ balance. Propylene consumption as a function of temperature is shown in Figure 7.11. Little to no change in the C₃H₆ concentration was observed before 175°C. Beyond that, there was a steady decrease in the C₃H₆ concentration until 264°C, where the maximum consumption of C₃H₆ was observed. The C₃H₆ consumption rate then decreased beyond 272°C as the surface NOₓ species, thus reaction reactant, were depleted. Anderson et al. performed TPR experiments on a Pt/Ba/Al₂O₃ catalyst with a stoichiometric C₃H₆/air mixture and observed maxima in NOₓ release just above 200°C [69]. This being done in an air-containing mixture resulted in some temperature increase due to the exotherm that would evolve from C₃H₆ combustion, thus their measured temperatures for NOₓ release would be lower than those observed in our study. Furthermore, NOₓ was not observed as a product with just C₃H₆ entering, indicating more complete reduction of the surface species. Jozsa et al. [33] also carried out TPR experiments, but on a commercial NSR catalyst, with C₃H₆, H₂, and CO. When the C₃H₆/N₂ mixture was used, NOₓ release reached a plateau at 250°C, slightly lower than that observed in our experiments. This is
likely attributed to the trapping conditions, where NO$_2$ was stored between 60 and 100°C. Saturating the catalyst at 300°C, as in our study, would lead to states with higher stability than those formed with exposure at lower temperatures.

![Temperature vs. C$_3$H$_6$ concentration graph](image)

**Figure 7.11** C$_3$H$_6$ outlet concentrations obtained during a temperature programmed reduction experiment; the ramp rate was 2.1°C/ min. The catalyst was first heated to 300°C and saturated with NO$_x$ using a mixture containing 350 ppm NO, 10% O$_2$, 5% CO$_2$, 5% H$_2$O, and a N$_2$ balance. The reactor was then cooled to 115°C to start the TPR experiment. The TPR gas composition contained 55 ppm C$_3$H$_6$ and a N$_2$ balance.

At 200°C, as shown in Figure 7.2, C$_3$H$_6$ and CO poisoning of Pt sites was evident by the lack of improvement with increased regeneration times. The TPR data in Figure
7.10 show that NO reduction with C$_3$H$_6$ begins at temperatures slightly above 200°C, with little activity at 200°C, in-line with the cycling experiment data. At T $\geq$ 217°C, the C$_3$H$_6$ and NO reaction is evident over the catalyst with complete reduction observed at 287°C. Similarly, when reducing the previously trapped NO$_X$ species (Figure 7.11), some reaction extent is observed $\sim$200°C, with increasing reactivity as the temperature was increased. Thus at 250°C (Figure 7.4), where extending the regeneration time did have a positive effect, it is related to slower kinetics, not complete poisoning by, or inactivity, of the hydrocarbon, nor to steam reforming of the hydrocarbon species. At T $\geq$ 287°C, based on the TPR and cycling experiments, the activation of C$_3$H$_6$ is not an issue and therefore a more comparable performance with H$_2$ would be expected.

7.5 Conclusions

In this study, the effects of different reducing agents (hydrocarbons, CO and H$_2$) on the performance of a model NSR catalyst were investigated. In cycling experiments, H$_2$ was the best reductant for catalyst regeneration at 170°C and the poor performance with hydrocarbons and CO was due to Pt site poisoning. At 250°C, H$_2$ was still superior and the poorer catalyst performance with hydrocarbons and CO was due to their slow reactivity and not solely because of poisoning effects. At T $\geq$ 300°C, hydrocarbons and CO were comparable with H$_2$. Hydrocarbon steam reforming experiment results show that steam reforming alone cannot explain the improved performance since steam reforming of dodecane and m-xylene occurred at T $\geq$ 450°C. With propylene, steam reforming occurred at 375°C, but the small amount of H$_2$ formed was not enough to result in comparable performance to CO and H$_2$ in regenerating the NSR catalyst. TPR
experiments were also performed and the results show that the reduction of NO by C$_3$H$_6$ can start at 217°C. Moreover, propylene can also induce nitrate decomposition and reduction at ~ 200°C. Thus as the reaction temperature exceeds 200°C, the hydrocarbons become directly active over the NSR catalyst, but are kinetically limited. At T > 300°C, the regeneration-phase reaction rates with hydrocarbons become appreciable enough to make the extent of regeneration comparable to that with H$_2$.

**7.6 Acknowledgements**

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References

Chapter 8

DeNO\textsubscript{X} Performance in Different Hybrid DOC+NSR Systems

8.1 Abstract

A combined, in series, DOC/NSR system was evaluated in terms of NO\textsubscript{X} trapping, release, and reduction. The evaluation included comparison between two configurations. In the first configuration, a DOC upstream of a NSR catalyst was tested in series. In the other configuration, the original DOC and NSR catalyst were divided into two equal volumes and placed in alternating series, i.e. DOC + NSR + DOC + NSR. Overall, the data show an improvement in NO\textsubscript{X} trapping, release, and reduction when the catalysts were split. At 200°C, these differences were slight due to poisoning effects by CO and hydrocarbons, though the performance with the second configuration was better for the first 10 cycles, before steady cycle-to-cycle performance was reached. At higher temperatures, the improved performance with the second configuration is related to NO\textsubscript{2} dose. “Extra” NO oxidation occurred over the 2\textsuperscript{nd} DOC, increasing the inlet amount of NO\textsubscript{2} to the 2\textsuperscript{nd} NSR catalyst. NH\textsubscript{3} formed from the 1\textsuperscript{st} NSR catalyst during the regeneration period is oxidized over the 2\textsuperscript{nd} DOC resulting in a negative impact, but this was overcome by the improved trapping due to the extra NO\textsubscript{2} formed. Also, the extents of the WGS reaction and/or C\textsubscript{3}H\textsubscript{6} steam reforming increased, resulting ultimately in more H\textsubscript{2} delivered to the downstream NSR catalyst.
8.2 Introduction

Minimizing fuel consumption has increased the interest in lean-burn engines, such as diesel engines. NO\textsubscript{X} and particulate matter emissions, however, are still considered a challenging issue in diesel engines [1-3]. Diesel particulate filters (DPFs) are being used to filter diesel particulate matter, and NO\textsubscript{2} and/or O\textsubscript{2} are used as an oxidant to oxidize the particulates on the filter [4-6]. For NO\textsubscript{X} emissions, two different technologies, selective catalytic reduction (SCR) and NO\textsubscript{X} storage and reduction (NSR), are being used.

NSR catalysts typically contain alkali and alkaline metal earth components that trap NO\textsubscript{X} in the form of nitrates and nitrites and precious metals, such as Pt, Pd and Rh for the redox reactions. Both are supported on a high surface area substrate such as γ-alumina [7-11]. A NSR catalyst operates in a cyclic mode; lean and rich. In the lean phase, or normal engine operation and exhaust, NO is oxidized to NO\textsubscript{2} over precious metal sites and the NO and/or NO\textsubscript{2} is subsequently stored on the trapping material as a nitrate and/or nitrite [12, 13]. When these trapping materials reach a certain level of saturation, the exhaust is switched to a fuel-rich mode [14, 15]. In the rich mode, reductants, such as H\textsubscript{2}, CO, and hydrocarbons (HCs) are introduced to induce the reduction of the stored NO\textsubscript{X} to N\textsubscript{2} [16]. It has been reported that diesel exhaust during this rich phase can contain 2-6% CO, 1-2% H\textsubscript{2}, and 0.3-0.92% HCs [17-19]. Numerous studies [20-31] have investigated the regeneration of NSR catalysts using different reductants. The general conclusion is that H\textsubscript{2} is the best reductant at low temperature, likely because CO and HCs poison Pt sites [20, 21] or Ba sites by residual isocyanates [31]. At high temperature (T ≥ 300°C), H\textsubscript{2}, CO, and HCs all have comparable efficiencies in reducing NO\textsubscript{X} to N\textsubscript{2} [20,22].
Diesel oxidation catalysts (DOCs) are commonly used in current diesel vehicles to reduce CO and HC exhaust emissions. DOCs can also oxidize NO to NO₂, which plays an important role in SCR, NSR and DPF aftertreatment technologies. In DPFs, NO₂ can oxidize soot at lower temperatures than O₂ [4-6]. In ammonia-SCR, it was found that the rate of SCR can be significantly increased if a portion of the NO contained in the exhaust is converted to NO₂, with an equimolar mix of NO and NO₂ being optimal [33]. Moreover, NO₂ can be readily stored, relative to NO, on NSR catalysts, especially at low operating temperatures [16, 34].

Both water and HCs are present in diesel exhaust, which possibly leads to steam reforming, producing more H₂. Hydrocarbon steam reforming has been extensively investigated over Pt, Pd, Rh, Ru, and Pt/Rd supported catalysts [35-43]. In one study [43], C₃H₆ and dodecane steam reforming was investigated over a Pt/Al₂O₃ catalyst during both steady-state and cycling experiments. C₃H₆ steam reforming started at 375°C while dodecane steam reforming began at 450°C. In another study, C₃H₈ steam reforming was investigated over Pd/CeO₂/Al₂O₃ and Pt-Rh/CeO₂/Al₂O₃ catalysts [40, 41] and reforming started at about 350°C. It should be noted that CO inherent to diesel exhaust or formed during steam reforming can also be consumed in the water gas shift (WGS) reaction to produce extra H₂. In a previous study [43], it was found that H₂ production from the water gas shift reaction over Pt/Al₂O₃ started at 225°C during both steady-state and cycling experiments.

In NSR catalysts, NO oxidation to NO₂ is an important step for overall performance. Additionally, H₂ has repeatedly been reported to be better than other reductant species (CO and HCs) in reducing surface NOₓ species to N₂ [20, 22]. Engine
out NO:NO₂ during the lean phase is on the order of 90:10 [16, 44] and H₂ concentrations are about 1-2% during the rich phase [17-19]. Therefore, if the amount of NO₂ during the lean phase and H₂ delivered to the NSR catalyst during the rich phase can be increased over the upstream DOC catalyst, the NOₓ reduction to N₂ performance over the downstream NSR catalyst could be improved.

The aim of this study is to evaluate overall NOₓ reduction performance when the DOC and NSR catalyst are placed in series, which represents the actual configuration in NSR-equipped diesel automobiles. Furthermore, performance was also evaluated with different configurations of the DOC and NSR catalyst, by splitting the samples and alternating the series, while keeping the overall catalyst volumes the same. The latter design was tested, under the hypothesis that any NO escaping the first NSR catalyst could be re-oxidized by the second DOC and then adsorbed on the fourth piece, another piece of NSR catalyst. Furthermore, at high temperatures where the WGS reaction could be thermodynamically limited, this arrangement could result in extra H₂ formed by eliminating hydrocarbon inhibition and again, with H₂ consumed in the first NSR catalyst, more could be made in the second DOC.

8.3 Experimental Methods

A commercial DOC supplied by Umicore AG and a model Pt/BaO/Al₂O₃ catalyst supplied by Johnson Matthey were used in this study. Both samples were in monolith form. The DOC contains 95 g/ft³ Pt supported on Al₂O₃. The monolith block that the sample was removed from had a cell density of 400 cpsi. The samples were 2.25 cm in diameter with lengths of 1, 2 and 4 cm depending on the test. The model Pt/BaO/Al₂O₃ sample contains 2.0 g/in³ Al₂O₃, 49.9 g/ft³ Pt and 20% BaO relative to the Al₂O₃.
sample was removed from a monolith block that had a cell density of 300 cpsi. The samples used were 2.23 cm in diameter with lengths of 2 and 4 cm. The samples were inserted into a horizontal quartz tube reactor, which was placed inside a Lindberg temperature-controlled furnace. The catalysts were wrapped with 3M matting material to cover the gap between the catalyst and the wall of the reactor to ensure that no gas slipped around the sample. K-type thermocouples were placed at the radial center of each catalyst; one just inside the inlet face of the catalyst and one just inside the outlet face of the catalyst.

The gases and gas mixtures, except N\textsubscript{2}, were supplied by Praxair and were metered with Bronkhorst mass flow controllers. The N\textsubscript{2} was produced using an On-Site nitrogen generator system. The dry gas mixture was then heated to > 120°C and water was then introduced using a Bronkhorst CEM system.

In these experiments, 250 ppm NO, 50 ppm NO\textsubscript{2}, 10% O\textsubscript{2}, 5% CO\textsubscript{2}, 5% H\textsubscript{2}O, and a balance of N\textsubscript{2} were used in the lean phase while in the rich phase 1% H\textsubscript{2}, 3% CO, 0.5% C\textsubscript{3}H\textsubscript{6}, 5% CO\textsubscript{2}, 5% H\textsubscript{2}O, and a balance of N\textsubscript{2} were used. The rich time was 6 seconds and the lean times were 40, 100, and 80 seconds with 200, 350, and 500°C respectively. The lean and rich gas mixtures were made in separate manifolds. A fourway, fast-acting solenoid valve was used to switch between the two. The calculated errors associated with these experiments were less than 1% for trapping conditions and less than 2% for regeneration conditions.

Before each experiment, the sample temperature was ramped to 500°C with 5% H\textsubscript{2}O, 5% CO\textsubscript{2}, and a balance of N\textsubscript{2} and then the catalyst was cleaned/conditioned with a
gas 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, 350 and 500°C with a space velocity, at standard conditions, of 25,000 h⁻¹. The gases exiting the reactor were maintained at > 190°C to avoid condensation and NH₃ hold-up.

The gas compositions were measured using a MKS MultiGas 2030 FTIR analyzer. Spatially resolved capillary-inlet mass spectrometry (SpaciMS) was also used to measure outlet H₂ amounts from each sample.

Figure 8.1 Catalyst configurations used in this study.

8.4 Results and Discussion

In this study, the DOC and NSR catalyst outlet concentrations of key reactant and product species were measured with different DOC/NSR configurations. In the first configuration, a 4 cm DOC and a 4 cm NSR catalyst were placed in series. In the second
configuration, the original DOC and NSR catalyst were divided into two equal volumes and then placed in series, so that the order of samples was: 2 cm DOC → 2 cm NSR → 2 cm DOC → 2 cm NSR. These two configurations are shown as group 1 in Figure 8.1.

8.4.1 Performance at 500°C

In the first set of experiments, the NO\textsubscript{X} performance obtained with configuration A of group 1 were compared to configuration B. The outlet NO\textsubscript{X} (the sum of NO + NO\textsubscript{2}) concentrations obtained using 1% H\textsubscript{2}, 3% CO, and 0.5% C\textsubscript{3}H\textsubscript{6} as the reductant mixture in the regeneration phase, and at an inlet temperature of 500°C are shown in Figure 8.2.

![Figure 8.2](image)

**Figure 8.2** NO\textsubscript{X} outlet concentrations obtained at 500°C with group 1 configurations. The lean gas mixtures were 250 ppm NO, 50 ppm NO\textsubscript{2}, 10% O\textsubscript{2}, 5% CO\textsubscript{2}, 5% H\textsubscript{2}O, and a balance of N\textsubscript{2}. The rich gas mixtures were 1% H\textsubscript{2}, 3% CO, and 0.5% C\textsubscript{3}H\textsubscript{6}, 5% CO\textsubscript{2}, 5% H\textsubscript{2}O, and a balance of N\textsubscript{2}.
For this set of experiments, the lean, or trapping, time was 80 seconds and the rich, or regeneration, time was 6 seconds. The conversions and amounts of NO$_X$ trapped and released for these experiments are listed in Table 8.1. All reported values and plotted data were obtained once steady cycle-to-cycle performance was observed. The data plotted in Figure 8.2 show that complete trapping was achieved over both sets for similar times, about 16 seconds. Both sets also reached trapping saturation by the end of the 80-second lean period. The amounts of NO$_X$ trapped were 101 and 115 μmoles, and the amounts released as unreduced NO or NO$_2$ during the rich period were 25 and 26 μmoles for configurations A and B, respectively. It should be noted that overall catalyst performance at 500°C is low because of the weak stability of nitrate species at 500°C [45].

There are several reasons for the improved performance with the “split” configuration (configuration B). First, in the split configuration, the NSR catalyst is ultimately exposed to higher NO$_2$ amounts. NO$_2$ concentrations at the outlet of each catalyst are plotted in Figure 8.3. In both configurations, the upstream DOC oxidizes the same amount of NO, hitting thermodynamic equilibrium. As would be expected, NO$_X$ breakthrough from the 1$^{\text{st}}$ NSR catalyst in the “split” configuration occurs earlier. Then some of the NO passing through the 1$^{\text{st}}$ NSR catalyst is oxidized to NO$_2$ over the 2$^{\text{nd}}$ DOC, which is more readily trapped on the 2$^{\text{nd}}$, most downstream NSR catalyst. This is consistent with a previous study [46], where the performance of a NSR catalyst was improved when NO$_2$ was used instead of NO. With NO$_2$ being a precursor or an intermediate in the trapping process, more NO$_X$ was trapped along the catalyst length and in conjunction with no NO$_2$/reactant concentration limitations, led to the improved performance. The data in Figure 8.3 demonstrate that ultimately the sum of the NSR
catalysts are exposed to a higher NO₂ flux during the trapping period compared to configuration A, where the single full size DOC and NSR samples are in series. Comparing the NOₓ profiles in Figure 8.3 for the final outlet amounts, it is apparent that the bigger difference is in the amount of NO, indicating that similar NO₂ conversions are attained, and since more NO₂ was generated in configuration B, more extensive trapping was attained.

**Table 8.1** Calculated performance characteristics as a function of temperature and catalyst configurations for group 1 in Figure 8.1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th><strong>Group (1)</strong></th>
<th>Time (sec)</th>
<th>NOₓ Trapped (μmoles)</th>
<th>NOₓ Released (μmoles)</th>
<th>NOₓ Conversion (%)</th>
<th>NH₃ Released (μmoles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>Configuration A</td>
<td>40 6</td>
<td>44</td>
<td>14</td>
<td>27.5</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>Configuration B (2\textsuperscript{nd} NSR)</td>
<td>40 6</td>
<td>47</td>
<td>15</td>
<td>29.4</td>
<td>0.55</td>
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<tr>
<td></td>
<td>Configuration B (1\textsuperscript{st} NSR)</td>
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<td>23</td>
<td>9</td>
<td>13.4</td>
<td>0.36</td>
</tr>
<tr>
<td>350</td>
<td>Configuration A</td>
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<td>3.6</td>
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<td>118</td>
</tr>
<tr>
<td></td>
<td>Configuration B (2\textsuperscript{nd} NSR)</td>
<td>100 6</td>
<td>267</td>
<td>3.3</td>
<td>95</td>
<td>105</td>
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<tr>
<td></td>
<td>Configuration B (1\textsuperscript{st} NSR)</td>
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<td>172</td>
<td>22.6</td>
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<td>66</td>
</tr>
<tr>
<td>500</td>
<td>Configuration A</td>
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<td>101</td>
<td>25</td>
<td>34</td>
<td>12</td>
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<tr>
<td></td>
<td>Configuration B (2\textsuperscript{nd} NSR)</td>
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<td>26</td>
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<td></td>
<td>Configuration B (1\textsuperscript{st} NSR)</td>
<td>80 6</td>
<td>62</td>
<td>9</td>
<td>24</td>
<td>12</td>
</tr>
</tbody>
</table>
Figure 8.3  NO and NO$_2$ outlet concentrations obtained at 500°C with group 1 configurations. The lean gas mixtures were 250 ppm NO, 50 ppm NO$_2$, 10% O$_2$, 5% CO$_2$, 5% H$_2$O, and a balance of N$_2$. The rich gas mixtures were 1% H$_2$, 3% CO, and 0.5% C$_3$H$_6$, 5% CO$_2$, 5% H$_2$O, and a balance of N$_2$.

Another contributing factor to the differences in performance relates to the amount of NH$_3$ formed. NH$_3$ formation during NO$_X$ reduction with H$_2$ over NSR catalysts has been extensively reported, and NH$_3$ also acts as a reductant [47-49]. As shown in Figure 8.4 for configuration B, NH$_3$ was observed at the upstream NSR catalyst outlet and 2$^{nd}$ DOC outlet about 1 to 2 seconds after the onset of the regeneration phase and for each, reached a maximum when the NO$_X$ concentration decreased close to the baseline level. As shown, more NO$_X$, during the regeneration phase, is observed at the outlet of the 2$^{nd}$ DOC, relative to that at the 1$^{st}$ NSR catalyst outlet, while at the same
time, there is less NH₃ at the 2nd DOC outlet. These data indicate that some of the NH₃ generated on the 1st NSR catalyst is oxidized to NOₓ over the downstream DOC, which also means less NH₃ is available for the most downstream NSR catalyst. If the only effect, this should actually lead to decreased performance, indicating that the enhancement observed with the extra NO₂ is somewhat decreased by this impact on the NH₃ generated.

![Graph](image)

**Figure 8.4** NOₓ and NH₃ outlet concentrations from the 1st NSR catalyst and 2nd DOC for configuration B of group 1, obtained at 500°C with 1% H₂, 3% CO, and 0.5% C₃H₆ used in the regeneration phase.

Another factor is the changes in reductant concentrations and/or extents of either the WGS or steam reforming reactions. Peak concentration data obtained between each piece of catalyst are listed in Table 8.2. The amount of H₂ at the inlet of the NSR catalyst
in configuration A was 1.16%, which is about the same as that at the inlet of the 1st NSR catalyst in configuration B, while the inlet H$_2$ to the 2nd NSR catalyst in configuration B was 2.2%. The CO shows the opposite trend, with a higher amount of CO at the inlet of the NSR for configuration A relative to the 2nd NSR catalyst in configuration B. The increase in H$_2$ and decrease in CO indicate that further WGS reaction extents are realized with configuration B. The likely reason for this is that the WGS reaction is inhibited by HCs [50], and by the 2nd DOC there is less HC since more HC would be consumed over the 1st DOC and NSR catalysts, or at least reduced in concentration, as indeed the data listed in Table 8.2 show. With configuration A, only 441 ppm of C$_3$H$_6$ were consumed over the upstream DOC while 277 ppm C$_3$H$_6$ were consumed over the 1st DOC of configuration B. However, a significant amount of C$_3$H$_6$ is also consumed through the NSR catalysts, with only 21 ppm at the outlet of configuration A and 840 ppm at the outlet of the 1st NSR catalyst in configuration B, with a drop to 480 ppm across the next DOC and 0 ppm exiting the 2nd NSR catalyst. Therefore, the 2nd DOC experiences less inhibition and the amount of H$_2$ formed is higher, possibly leading to more extensive regeneration of the 2nd NSR catalyst. This effect, however, is likely slight since at high temperatures CO, C$_3$H$_6$ and H$_2$ are considered equal in terms of reduction efficacy, although in general H$_2$ is considered better [20-31]. Furthermore, based solely on the changes in CO and H$_2$ observed, it would seem that the reduction/regeneration reactions are not limited by H$_2$ produced through the WGS reaction since the amounts of CO consumed and H$_2$ formed are similar, and therefore regeneration is not reductant limited. However, since steam reforming is also likely occurring (as discussed in the following paragraph), it is not possible to determine the exact source of the H$_2$ increase.
Table 8.2 Outlet reductant amounts as a function of temperature and catalyst configurations for group 1, Figure 8.1.

<table>
<thead>
<tr>
<th>Group 1 (Configuration A)</th>
<th>Temperature (ºC)</th>
<th>Reductant</th>
<th>Inlet DOC</th>
<th>Outlet DOC/Inlet NSR</th>
<th>Outlet NSR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>CO (%)</td>
<td>3</td>
<td>2.99</td>
<td>2.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂ (%)</td>
<td>1</td>
<td>0.99</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₃H₆ (ppm)</td>
<td>1667</td>
<td>1620</td>
<td>1610</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₂H₄ (ppm)</td>
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<td>4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₄ (ppm)</td>
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<td>4</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>CO (%)</td>
<td>3</td>
<td>2.9</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂ (%)</td>
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<td>1.13</td>
<td>0.75</td>
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<tr>
<td></td>
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<td>C₃H₆ (ppm)</td>
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<td>1524</td>
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<td>9</td>
</tr>
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<td></td>
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<td>CH₄ (ppm)</td>
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<td>40</td>
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</tr>
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<td>500</td>
<td>CO (%)</td>
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<td>2.90</td>
<td>1.65</td>
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<tr>
<td></td>
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<td>1.16</td>
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<td></td>
<td>C₃H₆ (ppm)</td>
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<td>1226</td>
<td>21</td>
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<td></td>
<td></td>
<td>C₂H₄ (ppm)</td>
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<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₄ (ppm)</td>
<td>0</td>
<td>720</td>
<td>1870</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group 1 (Configuration B)</th>
<th>Temperature (ºC)</th>
<th>Reductant</th>
<th>Inlet 1st DOC</th>
<th>Outlet 1st DOC</th>
<th>Outlet 1st NSR</th>
<th>Outlet 2nd DOC</th>
<th>Outlet 2nd NSR</th>
</tr>
</thead>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>CO (%)</td>
<td>3</td>
<td>2.99</td>
<td>2.97</td>
<td>2.93</td>
<td>2.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂ (%)</td>
<td>1</td>
<td>1.12</td>
<td>0.93</td>
<td>0.93</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
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<td>C₃H₆ (ppm)</td>
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<td>1638</td>
<td>1638</td>
<td>1627</td>
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<td></td>
<td>C₂H₄ (ppm)</td>
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<td>3</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₄ (ppm)</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>CO (%)</td>
<td>3</td>
<td>2.9</td>
<td>2.8</td>
<td>2.6</td>
<td>2.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂ (%)</td>
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<td>1.12</td>
<td>0.92</td>
<td>1.35</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₃H₆ (ppm)</td>
<td>1667</td>
<td>1550</td>
<td>1520</td>
<td>1430</td>
<td>1350</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₂H₄ (ppm)</td>
<td>0</td>
<td>15</td>
<td>18</td>
<td>19</td>
<td>25</td>
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<tr>
<td></td>
<td></td>
<td>CH₄ (ppm)</td>
<td>0</td>
<td>25</td>
<td>18</td>
<td>33</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>CO (%)</td>
<td>3</td>
<td>2.99</td>
<td>2.1</td>
<td>1.8</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂ (%)</td>
<td>1</td>
<td>1.15</td>
<td>1.9</td>
<td>2.2</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₃H₆ (ppm)</td>
<td>1667</td>
<td>1390</td>
<td>840</td>
<td>480</td>
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<td>C₂H₄ (ppm)</td>
<td>0</td>
<td>23</td>
<td>100</td>
<td>43</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₄ (ppm)</td>
<td>0</td>
<td>250</td>
<td>660</td>
<td>600</td>
<td>1930</td>
</tr>
</tbody>
</table>
As mentioned, H$_2$ can be produced by steam reforming over these catalysts. C$_3$H$_6$ steam reforming using the same DOC and NSR catalyst used in this study has been examined previously, and H$_2$ was observed via C$_3$H$_6$ steam reforming at T > 375°C [22, 43]. However, C$_3$H$_6$ as a reductant proved effective at lower temperatures indicating a direct reaction between C$_3$H$_6$ and surface nitrite/nitrate species [22]. As mentioned above, the data listed in Table 8.2 indeed show consumption in C$_3$H$_6$ amounts across the DOC and NSR catalysts, with ultimately more consumption observed with configuration B. Some of the increased C$_3$H$_6$ consumption with configuration B could be related to the increased amount of NO$_X$ trapped. The surface nitrates or released NO$_X$ could be reduced by the C$_3$H$_6$ and since more was trapped with configuration B, more might be consumed.

To further study the improvement observed with the split system, another set of configurations was studied, which are described in Figure 8.1 and labeled as “group 2”. It is clear from Figure 8.3 that the outlet amounts of NO and NO$_2$ from the 2 cm DOC are almost the same as those from the 4 cm DOC, indicating that only the first half, at most, of the DOC is utilized in NO oxidation. Therefore, for group 2, a 2 cm DOC was selected as the upstream DOC in configuration A, while in configuration B, the 2 cm DOC was divided into two equal parts and alternated with NSR samples to make configuration B. The conversions and amount of NO$_X$ trapped and released for these experiments are listed in Table 8.3. It is apparent that NO$_X$ performance is again better with configuration B, with similar trends to what was observed in group 1. The NO$_X$ conversions were 24 and 30% for configurations A and B, respectively. The reasons for such improvement were discussed above. Worth noting is that the outlet NO$_2$ amounts from the 1$^{st}$ DOC in configuration B was less than that from the larger DOC in configuration A (Figure 8.5).
Table 8.3 Calculated performance characteristics as a function of temperature and catalyst configuration for group 2, as shown in Figure 8.1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Group (2)</th>
<th>Time(sec)</th>
<th>NOX Trapped (µmoles)</th>
<th>NOX Released (µmoles)</th>
<th>NOX Conversion (%)</th>
<th>NH3 Released (µmoles)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Configuration A</td>
<td>Lean 6</td>
<td>41.5</td>
<td>17</td>
<td>22.5</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>Configuration B (2nd NSR)</td>
<td>40 6</td>
<td>43</td>
<td>16</td>
<td>24.5</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>Configuration B (1st NSR)</td>
<td>40 6</td>
<td>22</td>
<td>8</td>
<td>13</td>
<td>0.54</td>
</tr>
<tr>
<td>350</td>
<td>Configuration A</td>
<td>100 6</td>
<td>265</td>
<td>6.3</td>
<td>93.5</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>Configuration B (2nd NSR)</td>
<td>100 6</td>
<td>263</td>
<td>5.8</td>
<td>93</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>Configuration B (1st NSR)</td>
<td>100 6</td>
<td>158</td>
<td>29.5</td>
<td>46</td>
<td>77</td>
</tr>
<tr>
<td>500</td>
<td>Configuration A</td>
<td>80 6</td>
<td>75</td>
<td>23</td>
<td>24</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>Configuration B (2nd NSR)</td>
<td>80 6</td>
<td>96</td>
<td>29</td>
<td>30</td>
<td>19.6</td>
</tr>
<tr>
<td></td>
<td>Configuration B (1st NSR)</td>
<td>80 6</td>
<td>55</td>
<td>7.4</td>
<td>21</td>
<td>11</td>
</tr>
</tbody>
</table>

In terms of differences in outlet NOX concentrations between the two configurations, there were differences observed in both NO and NO2, with both being lower with configuration B. NH3 formation was also observed and the trend was similar to that observed in Figure 8.4 (data not shown for brevity). In terms of H2 production, the observations were also similar to those discussed above with group 1. As shown in Table 8.4, more H2 was produced either due to more extensive WGS reaction or C3H6 steam reforming. This eventually would lead to more deeply regenerated NSR catalysts, resulting in better NOX reduction performance.
Figure 8.5  NO and NO₂ outlet concentrations obtained at 500°C with group 2 configurations. The lean gas mixtures were 250 ppm NO, 50 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and a balance of N₂. The rich gas mixtures were 1% H₂, 3% CO, and 0.5% C₃H₆, 5% CO₂, 5% H₂O, and a balance of N₂.

CH₄ concentrations were also monitored. They are listed in both Table 8.2 and 8.4. The CH₄ formed is due to C₃H₆ partial decomposition and not due to methanation (CO + 3H₂ → CH₄ + H₂O). This was confirmed by two experiments, which were performed using a 1 cm DOC followed by a 2 cm NSR catalyst, the first two catalysts in configuration B in group 2. In the first experiment, 3% CO and 1% H₂ was used, while in the second experiment 0.5% C₃H₆ was added to 3% CO and 1% H₂. The CH₄ measured during these two experiments are plotted in Figure 8.6. Only 13 ppm CH₄ was detected in the absence of C₃H₆, indicating that the formed CH₄ during the regeneration period largely originated from C₃H₆ breaking down and not through the methanation reaction.
Table 8.4 Outlet reductant amounts as a function of temperature and catalyst configurations for group 2, as shown in Figure 8.1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reductant</th>
<th>Inlet DOC</th>
<th>Outlet DOC/Inlet NSR</th>
<th>Outlet NSR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group 2 (Configuration A)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>CO (%)</td>
<td>3</td>
<td>2.99</td>
<td>2.93</td>
</tr>
<tr>
<td></td>
<td>H₂ (%)</td>
<td>1</td>
<td>1</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>C₃H₆ (ppm)</td>
<td>1667</td>
<td>1650</td>
<td>1620</td>
</tr>
<tr>
<td></td>
<td>C₂H₄ (ppm)</td>
<td>0</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>CH₄ (ppm)</td>
<td>0</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>350</td>
<td>CO (%)</td>
<td>3</td>
<td>2.9</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>H₂ (%)</td>
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<td>1.12</td>
<td>0.78</td>
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<td>C₂H₄ (ppm)</td>
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<td>15</td>
<td>30</td>
</tr>
<tr>
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<td>CH₄ (ppm)</td>
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<td>55</td>
</tr>
<tr>
<td>500</td>
<td>CO (%)</td>
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<td>2.99</td>
<td>1.8</td>
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<td>H₂ (%)</td>
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<td>2</td>
</tr>
<tr>
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<td>C₃H₆ (ppm)</td>
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<th>Inlet 1st DOC</th>
<th>Outlet 1st DOC</th>
<th>Outlet 1st NSR</th>
<th>Outlet 2nd DOC</th>
<th>Outlet 2nd NSR</th>
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<td><strong>Group 2 (Configuration B)</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td>CO (%)</td>
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<td>2.95</td>
<td>2.94</td>
<td>2.93</td>
<td>2.88</td>
</tr>
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<td>H₂ (%)</td>
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<td>1</td>
<td>0.91</td>
<td>0.91</td>
<td>0.88</td>
</tr>
<tr>
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<td>C₃H₆ (ppm)</td>
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<td>1640</td>
<td>1638</td>
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<td>1620</td>
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<td>C₂H₄ (ppm)</td>
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<td>3</td>
<td>3</td>
<td>3.5</td>
</tr>
<tr>
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<td>CH₄ (ppm)</td>
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<td>1.5</td>
<td>3</td>
<td>3.5</td>
<td>6</td>
</tr>
<tr>
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<td>CO (%)</td>
<td>3</td>
<td>2.89</td>
<td>2.75</td>
<td>2.72</td>
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<td>1.1</td>
<td>0.90</td>
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<td>0.88</td>
</tr>
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<td>12</td>
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<td>30</td>
<td>17</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>500</td>
<td>CO (%)</td>
<td>3</td>
<td>2.9</td>
<td>2.1</td>
<td>2.24</td>
<td>1.82</td>
</tr>
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<td>H₂ (%)</td>
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<td>1.11</td>
<td>1.7</td>
<td>1.9</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
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<td>55</td>
<td>420</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>CH₄ (ppm)</td>
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<td>14</td>
<td>260</td>
<td>50</td>
<td>890</td>
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</table>
Figure 8.6 CH₄ concentrations obtained at 500°C with (A) 1% H₂, 3% CO and (B) 1% H₂, 3% CO, and 0.5% C₃H₆ used in the regeneration phase, using a 1 cm DOC followed by a 2 cm NSR catalyst.

8.4.2 Performance at 350°C

Similar experiments to those at 500°C were also carried out at 350°C to investigate the influence of temperature on the storage and reduction of NOₓ as a function of configuration. A summary of the results are also listed in Table 8.1. Again, the NOₓ performance improved when the catalysts were in the split configuration. The differences in trapping, in contrast with data at 500°C, were observed from the onset of the lean phase. The amounts trapped, however, were only slightly different, 261 and 267 μmoles, and the amounts released were 3.6 μmoles and 3.3 μmoles for configurations A and B, respectively. The data still show an improvement in overall NOₓ performance
with the split configuration, though these differences are smaller than those observed at 500°C. These small differences at 350°C compared to 500°C are related to high NO oxidation activity, with a lack of thermodynamic NO₂ limitation, coincident with immediate trapping of the formed NO₂ at 350°C [16], and thus the enhancement with the split configuration is less noticeable. For example, in a previous study [46], only small differences (on order of 2% in the NOₓ conversion) were observed in overall NSR performance with NO vs. NO₂ as the inlet NOₓ source at 300°C, indicating that NOₓ performance is independent of NOₓ source in this temperature region. Figure 8.7, again as observed at 500°C, shows that the amounts NO and NO₂ with the 4 cm and 2 cm DOC samples are the same.

![Graph showing NO and NO₂ concentrations](Image)

**Figure 8.7** NO and NO₂ outlet concentrations obtained at 350°C with group 1 configurations. The lean gas mixtures were 250 ppm NO, 50 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and a balance of N₂. The rich gas mixtures were 1% H₂, 3% CO, and 0.5% C₃H₆, 5% CO₂, 5% H₂O, and a balance of N₂.
Ammonia formation was again observed after the onset of the regeneration phase and reached a maximum when the released NO\textsubscript{X} concentration decreased to close to the baseline level. In terms of reductants, again there was an increase in the amounts of inlet H\textsubscript{2}, with a decrease in both CO and C\textsubscript{3}H\textsubscript{6} to the 2\textsuperscript{nd} half NSR compared with configuration A, as shown in Table 8.2. These smaller differences in H\textsubscript{2} amount, vs the slight decrease in CO and C\textsubscript{3}H\textsubscript{6}, also lead to the smaller differences observed between these two configurations in group 1 compared to what was observed with the 500ºC data.

NO\textsubscript{X} reduction performance was also investigated using configurations A and B in group 2. The detailed NO\textsubscript{X} performance data are shown in Table 8.3. It should be mentioned that the trapping performance for both configurations is at first similar, complete, for the first 16 seconds of the lean phase. However, by the end of the lean phase, more NO\textsubscript{X} was observed with configuration A at the outlet compared to configuration B. The calculated NO\textsubscript{X} conversions were comparable with both configurations. Figure 8.8 compares the outlet NO and NO\textsubscript{2} concentration profiles for each catalyst in group 2. It is apparent that there are now significant differences in the outlet amounts of NO and NO\textsubscript{2} between the DOC for configuration A and the smaller DOC for configuration B. As at 500ºC, the 2\textsuperscript{nd} DOC in configuration B did oxidize some NO. However, NO oxidation over the NSR is also appreciable at 350ºC [16, 45] and apparently this extra NO\textsubscript{2} from the DOC had less impact compared to 500ºC. Comparing the reductant amounts between these two configurations, again there were only small differences, as shown in Table 8.4, which contributes to the comparable performances. Overall, the strong performance at 350ºC normally noted with NSR catalysts [51] makes
any enhancement with the split configuration less noticeable under the conditions of these tests.

Figure 8.8  NO and NO₂ outlet concentrations obtained at 350°C with group 2 configurations. The lean gas mixtures were 250 ppm NO, 50 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and a balance of N₂. The rich gas mixtures were 1% H₂, 3% CO, and 0.5% C₃H₆, 5% CO₂, 5% H₂O, and a balance of N₂.

8.4.3 Performance at 200°C

The NOₓ storage and reduction performance was also investigated at 200°C using the configurations described in Figure 8.1. The cycle time was 40 seconds for storage and 6 seconds for regeneration. The outlet NOₓ concentrations obtained using configurations A and B in group 1, as described in Figure 8.1, after steady cycle-to-cycle performance had been attained, are shown in Figure 8.9. As shown, complete NOₓ uptake was not...
achieved. It is the presence of CO and C₃H₆ in the regeneration period that causes the decreased overall NSR catalyst performance, compared with those data at 350 and 500°C.

Figure 8.9 NOₓ outlet concentrations obtained at 200°C with group 1 configurations. The lean gas mixtures were 250 ppm NO, 50 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and a balance of N₂. The rich gas mixtures were 1% H₂, 3% CO, and 0.5% C₃H₆, 5% CO₂, 5% H₂O, and a balance of N₂.

Worth noting is a second NOₓ release peak during the transition from rich to lean, as highlighted in the figure. Such a feature has recently been reported [27, 52-54]. This NOₓ release peak originates from the oxidation of strongly bound isocyanate on barium sites [52], formed when CO was used as the reductant in the regeneration period (Ba(NO3)₂ + 8CO → Ba(NCO)₂ + 6CO₂). These surface isocyanates are readily
hydrolyzed by water into NH₃ at T ≥ 250°C [27, 52-54], which subsequently acts as a reductant for NOₓ reduction. This is consistent with the data in this study, where a second NOₓ release peak was not observed during the rich-to-lean transitions at T ≥ 350°C. At low temperature (~ T ≤ 250°C), Pt sites are strongly poisoned by CO, leading to decreased hydrolysis of the isocyanates to NH₃. These isocyanates, however, are readily oxidized to NOₓ at the onset of the subsequent lean phase [52], and due to the slow NO oxidation kinetics at T ≤ 250°C, some of the NOₓ is released. Again, this is consistent with the data presented here, where NOₓ release was detected at the each rich-to-lean transition at 200°C as shown in Figure 8.9.

![Figure 8.10](image_url) NO and NO₂ outlet concentrations obtained at 500°C with group 1 configurations. The lean gas mixtures were 250 ppm NO, 50 ppm NO₂, 10% O₂, 5% CO₂, 5% H₂O, and a balance of N₂. The rich gas mixtures were 1% H₂, 3% CO, and 0.5% C₃H₆, 5% CO₂, 5% H₂O, and a balance of N₂.
Overall, the data clearly show decreased performance at 200°C compared with 350 and 500°C. The conversion of NO to NO$_2$ was greater than 92% over both configurations, as shown in Figure 8.10, so the poor performance can not be explained by the low NO oxidation rates. It is the presence of CO and HC at low temperature poisoning Pt sites [20, 21] or Ba sites by residual isocyanates (NCO) [27, 31, 54] that causes this poor performance. For example, in a previous study [21] the effects of CO on NSR catalyst performance at 200°C were characterized, and a key inhibiting effect observed was that CO significantly inhibits the regeneration process by poisoning Pt-catalyzed nitrate decomposition.

![Figure 8.11](image.png)

**Figure 8.11** NO$_X$ outlet concentrations obtained before steady cycle-to-cycle performance was reached at 200°C with 1% H$_2$, 3% CO, and 0.5% C$_3$H$_6$ used in the regeneration phase with group 1 configurations.
In comparing the results obtained at 200°C for the two configurations (group 1), the differences were small and mainly observed in terms of trapping performance. The NO\textsubscript{X} conversions were 27.5 and 29.4% for the two configurations, with the split sample configuration being better. If improved NO oxidation, or an overall larger dose of NO\textsubscript{2}, leads to improved performance, but CO poisoning hinders regeneration, the first several cycles of the test should show more significant differences. The first 10 cycles of the test are plotted Figure 8.11.

Another set of experiments, identical to those described above, but using only 1% H\textsubscript{2} as a reductant to isolate the poisoning effects by HCs and CO, was also performed, with the data shown in Figure 8.12. Again, the performance improved with the split configuration.

The slight improvement with configuration B is still due to an overall larger dose of NO\textsubscript{2} for the total NSR catalyst amount. As shown in Figure 8.10, the differences in the NO and NO\textsubscript{2} concentrations are small, but some NO at the outlet of the 1\textsuperscript{st} NSR catalyst in configuration B is oxidized over the 2\textsuperscript{nd} DOC, resulting in more NO\textsubscript{2} for the 2\textsuperscript{nd} NSR catalyst. Little to no WGS or steam reforming is evident at 200°C (Table 8.2) leading to the similar extents of poisoning and therefore similar performance. This is consistent with a previous study [43] where the WGS reaction started at 225°C, but with little H\textsubscript{2} formed, which contributed little to improved performance, while C\textsubscript{3}H\textsubscript{6} steam reforming began at T ≥ 375°C. Another set of experiments were also carried out using configuration A and B in group 2, to confirm the above findings. The exact same trends were observed and therefore the results are not shown.
Figure 8.12 NO\textsubscript{X} outlet concentrations obtained before steady cycle-to-cycle performance reached at 200°C with 1% H\textsubscript{2} used in the regeneration phase with group 1 configurations.

It should be highlighted that it is repeatedly reported in the literature that increasing the amount of NO\textsubscript{2} upstream of an NSR catalyst will lead to improved NO\textsubscript{X} reduction performance, especially at low temperatures [55, 56]. This is because NO\textsubscript{2} is sometimes considered a precursor for nitrate formation, and necessary for the disproportionation reaction [16]. In this study, NO oxidation to NO\textsubscript{2} was significant, above 92% at 200°C with the DOC samples used. This clearly indicates that NO oxidation to NO\textsubscript{2} is not an issue with the system used in this study at 200°C. However, the performance is still poor. This clearly demonstrates that the poisoning effects of CO and HCs offset any gains that could be realized by higher NO\textsubscript{2} amounts. In application
diesel exhaust can contain 2-6% CO and 0.3-0.92% hydrocarbons during regeneration [17-19]. Therefore, the NSR catalyst formulations will always be poisoned by CO and HCs at 200°C, which hinders regeneration and ultimately leads to poor catalyst performance.

8.5 Conclusions

In this study, NO\textsubscript{X} reduction using two different DOC/NSR configurations was evaluated. Overall performance was improved with the catalysts in a split configuration while maintaining the same overall catalyst volumes (DOC \rightarrow NSR versus DOC \rightarrow NSR \rightarrow DOC \rightarrow NSR). The differences in NO\textsubscript{X} conversion were more apparent at the highest temperature tested, 500°C, due to the NSR catalyst being exposed to a larger amount of NO\textsubscript{2} and some of the CO and C\textsubscript{3}H\textsubscript{6} being converted to H\textsubscript{2} for better regeneration. At 200°C, there were differences in both NO\textsubscript{X} trapping and release for the first several cycles, but then CO poisoning of Pt and Ba sites slowed regeneration to such an extent that the extra NO\textsubscript{2} generated with the split configuration made little difference. At 350ºC, little difference in performance was observed under the conditions tested, since NO oxidation is significant, i.e. not kinetically or thermodynamically limited, and the poisoning effects of the CO and HC species are minimal.

8.6 Acknowledgements

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Chapter 9

9. Conclusions and Recommendations

9.1 Conclusions

The focus of this research was to provide a systematic and comprehensive understanding of both DOC and NSR catalysts when they are used individually and in series. The extent of inhibition reactions between reactant gases in simulated diesel exhaust was investigated over a monolith-supported DOC. A detailed discussion was provided, explaining why and how this inhibition occurred. Overall, there was inhibition between CO, hydrocarbons, and NO both individually and in mixtures with NO₂. CO was less influenced among the other species because its light-off temperature was lower than that of the other species. DOCs are always placed upstream of NSR, DPF, and SCR catalysts. During the lean phase, or normal diesel exhaust conditions, DOCs can oxidize HCs, CO and NO. During the rich phase, reductants, such as HCs and CO, are available in appreciable amounts (e.g. 2-6% CO and 0.5% HCs) with H₂O. Therefore, the second objective was to investigate H₂ production from both HC steam reforming and water gas shift reactions over a DOC. The results showed that C₃H₆ and dodecane steam reforming started at 375 and 450°C, respectively, whereas the water gas shift reaction started at 225°C. The formed H₂ can be used as a reductant to reduce NOₓ species during the rich phase over a downstream NSR catalyst.

For NSR evaluation, investigations included using NO or NO₂ as the NOₓ source, different regeneration protocols, and evaluating different reducing agents (hydrocarbons, H₂, or CO). Overall, the performance of catalyst was improved when NO₂ was used as the NOₓ source. The primary reason for this improvement is that the monolith is an
integral reactor. With NO\textsubscript{2} as the NO\textsubscript{X} source, NO\textsubscript{2} can be readily trapped at the very inlet and along the catalyst length. This results not only in higher trapping amounts, but also in more interaction between reductant and stored NO\textsubscript{X} along the catalyst length. The next objective was to study the influence of different regeneration protocols on NSR catalyst performance. Different regeneration times were tested, 4, 8 and 16 seconds with 4, 2, and 1\% H\textsubscript{2} as the reductant amounts, respectively, with constant lean times. With longer regeneration times, more nitrite/nitrate decomposition occurred, leading to a cleaner surface for the next lean phase. This led to improved catalyst performance at all temperatures except 500\textdegree C, where decomposition was more rapid than reduction so that the significant release of NO\textsubscript{X} during the rich phase led to poorer performance. The efficiency of hydrocarbons, H\textsubscript{2}, or CO as reducing agents to reduce NO\textsubscript{X} species to N\textsubscript{2} was also investigated. At T \leq 250\textdegree C, H\textsubscript{2} was found best, while at higher temperatures both CO and HCs were comparable to H\textsubscript{2} in regenerating the catalyst. The decreased performance with CO and HCs at 200\textdegree C was due to Pt site poisoning and at 250\textdegree C was caused by slower kinetics associated with CO and HC activation. Since the onset of propylene steam reforming occurred at 375\textdegree C, and with dodecane and m-xylene at even higher temperatures, the relatively good performance with HCs at T \geq 300\textdegree C was not due to H\textsubscript{2} production from HC steam reforming. The likely reason is the direct reaction of HCs with NO\textsubscript{X} species, as was proved during TPR experiments between NO and propylene.

The performance when both the DOC and NSR catalyst are placed in series was also investigated. The performance was evaluated based on two different configurations. In one configuration, a DOC and NSR catalyst were placed in series whereas in the other
configuration, the DOC and NSR catalysts were divided into two equal volumes and placed in alternating series. The results show an improvement in the NO\textsubscript{X} performance with the split configuration at all temperatures tested, with small changes at 200°C due to poisoning effects of Pt and Ba sites by CO and hydrocarbons. The reasons for the improved performance with the split configuration were due to more NO\textsubscript{2} being delivered to the downstream NSR, H\textsubscript{2} production from steam reforming and WGS reactions increased, and reduced inhibition of the WGS reaction by hydrocarbons that were consumed over the first DOC and NSR catalysts.

### 9.2 Recommendations

The ultimate goal of this research was to offer detailed mechanisms, provide further understanding, and determine optimal conditions for the performance of both DOC and NSR catalysts individually, and in series. However, there are still some issues and questions that need to be answered. The following are a number of recommendations proposed for future opportunities:

- Diesel engine exhaust will typically contain SO\textsubscript{2}. The extent of inhibition and how the chemistry will differ over DOC catalysts when introducing SO\textsubscript{2} into the inlet gases should be evaluated.

- Along the same concept, what is the effect of thermal aging, arising from the desulphation process, on the performance of the DOC catalyst?

- To better understand NSR chemistry, NO\textsubscript{X} trapping, release, and reduction characteristics, and formation of byproducts such as NH\textsubscript{3} and N\textsubscript{2}O along the
length of an NSR catalyst when either NO or NO\textsubscript{2} is used as a NO\textsubscript{X} source, should be characterized using spatially-resolved capillary-inlet mass spectrometry (SpaciMS). This is especially critical for NO\textsubscript{2} vs NO performance to discern if it is simply NO\textsubscript{2} being trapped better at the front of the catalyst or if other chemistry is significant.

- During our experiments over NSR catalysts, a high amount of NH\textsubscript{3} was formed especially at high operating temperature. Therefore, it is would be beneficial to study the performance improvements with a downstream SCR catalyst in place.

- When the DOC and NSR catalyst are placed in series, what would be the performance of the system after thermal aging? Is the improved performance with the split configuration the same?

- According to the data obtained in this research, CO and HC\textsubscript{s} can regenerate the NSR catalyst as efficiently as H\textsubscript{2} at T \geq 300^\circ\text{C}, but not at low temperatures due poisoning of Pt and Ba sites. Therefore, it seems critical to find a catalyst that can preferentially reduce the amount of CO and HC\textsubscript{s} at low temperature to avoid the downstream poisoning effect and improve overall performance.
Appendix A:

Statistical Analysis and Uncertainties

This experimental study involved many sample calculations to evaluate the performance of the DOC and NSR technologies. Statistical analysis and uncertainty (error) are very important in experimental studies, where they can be used to identify significant errors and hence provide guidance as to where more effort is needed to improve an experiment and assess the significance in the measurements.

Most of statistical analysis, including the one used in this section, is applied when the data are considered to follow a normal distribution. One simple test to check whether the data (sample) follows a normal distribution is using the normal probability plot. In applying this test, two sample sets were chosen; one from the diesel oxidation catalyst and the other from the NO\textsubscript{X} storage and reduction catalyst. In the second part of this section, the reproducibility and calculated standard deviation of some selected data for both catalysts are presented. This was to check and ensure that any performed experiment is representative of the mean results. In the last section, the associated error or uncertainty with each measurement (instrument) is provided.

A.1 Normal probability plot

A normal probability plot is a graphical technique to determine if a distribution is approximately normal. When the distribution is close to normal, the plotted points will lie close to a line. Systematic deviations from a line indicate a non-normal distribution.
To apply this test, the output data (response) should be first ordered from smallest to highest. Then, each value is ranked, with the smallest starting with 1. The probability of the data’s rank is subsequently calculated with the following equation:

\[
P(\text{rank}) = \frac{(i - 0.5)}{N}
\]

where \( i \) is the rank of the data and \( N \) is the total number of data points.

The next step is finding the expected value of the probability, the \textbf{Z-value} that corresponds to each value of “\( P \)” using a normal probability distribution table. Last, the output data (responses) are plotted against a theoretical expected value of normal distribution in such a way that the points should form an approximate straight line, if it follows a normal distribution. One sample calculation will be provided for one selected data set for each catalyst type.

1. **Diesel Oxidation Catalyst (DOC)**

The sample calculation and normal probability plot is provided for \( \text{C}_3\text{H}_6 \) oxidation. In this set of experiments, \( \text{C}_3\text{H}_6 \) conversions were obtained during a temperature programmed oxidation (TPO) experiment with 1080 ppm \( \text{C}_3\text{H}_6 \), 10 % \( \text{O}_2 \), 5% \( \text{CO}_2 \), 5% \( \text{H}_2\text{O} \), and balance \( \text{N}_2 \). The conversions (response) along with other calculations are listed in Table A.1
**Table A.1** Normal probability plot table for C$_3$H$_6$ conversions

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<th>Conversion (%)</th>
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<th>P(rank)</th>
<th>Expected Value</th>
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<td>0.005</td>
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</table>
The points on this plot form a nearly linear pattern with a correlation coefficient, $r = 0.985$, the square root of $R^2$ (the coefficient of determination), which indicates that the normal distribution is a good model for this data set.

2. **NO$_x$ storage and reduction (NSR) catalyst**

The sample calculation and normal probability plot is provided for the outlet NO$_x$ concentration during the lean phase when H$_2$ was used as the reducing agent at 300°C. The detailed experiment conditions and flows are listed in Table A.2. The outlet NO$_x$ concentrations along with other calculations are listed in Table A.3.
Table A.2 Details of flow conditions used in the experiments

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<th>Regeneration (rich) phase</th>
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<td>25,000 hr⁻¹</td>
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<tr>
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<td>Cycling ratio (sec)</td>
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Table A.3 Normal probability plot table for NOx concentration

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<th>Expected Value</th>
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<td>12</td>
<td>0.548</td>
<td>0.120</td>
</tr>
<tr>
<td>34.357</td>
<td>13</td>
<td>0.595</td>
<td>0.241</td>
</tr>
<tr>
<td>39.414</td>
<td>14</td>
<td>0.643</td>
<td>0.366</td>
</tr>
<tr>
<td>43.135</td>
<td>15</td>
<td>0.690</td>
<td>0.497</td>
</tr>
<tr>
<td>47.813</td>
<td>16</td>
<td>0.738</td>
<td>0.637</td>
</tr>
<tr>
<td>52.410</td>
<td>17</td>
<td>0.786</td>
<td>0.792</td>
</tr>
</tbody>
</table>
Again, the points on this plot form a nearly linear pattern with a correlation coefficient $r = 0.954$, the square root of $R^2$ (the coefficient of determination), which indicates that the normal distribution is a good model for this data set.

**A.2 Reproducibility between repeated experiments**

In this section, the reproducibility, via standard deviation measurements, of selected experiments for a DOC and NSR catalyst were performed to ensure no significant variations in the measured performances.
Standard deviation (σ) is a statistical term that measures the dispersion of a set of values about the mean value. If the standard deviation for the data is small, the data values are close to the mean value, while large standard deviation means that the data points are far from the mean. Standard deviation (σ) and mean can be calculated by the following equations:

$$\sigma = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (x_i - \bar{x})^2}$$

$$\bar{x} = \frac{x_1 + x_2 + \cdots + x_N}{N} = \frac{1}{N} \sum_{i=1}^{N} x_i$$

Where $\bar{x}$ is 50% conversion, or amounts of NOX trapped or released depending on the experiment. $\overline{x}$ is the mean of $x$.

(1) Diesel oxidation catalyst

In this study, the oxidation of NO, CO, and different types of hydrocarbons was investigated individually and in mixtures with NO2. Hydrogen production via hydrocarbon steam reforming and water gas shift reactions was also investigated. Table A.4 shows the 50% conversions for the selected experiments and their replicates. The mean and standard deviation for each repeated experiment were calculated and are reported in Table A.4. The repeated experiments of hydrogen production via C3H6 steam reforming and the water gas shift reaction during steady state and cycling experiments at 450°C at the middle point of the catalyst (3cm) are shown in Table A.5 along with their mean and standard deviation. Table A.6 shows CO2 formation obtained during temperature programmed oxidation (TPO) experiments after C3H6 steam reforming at
450°C for 180 min and at 2 and 4 cm from the front of catalyst. Again, the mean and standard deviation associated with these experiments were calculated and reported in Table A.6. The detailed experimental descriptions were reported in previous chapters; Chapter 3 for Table A.4 and Chapter 4 for Tables A.5 and A.6.

Table A.4  Statistical analysis for the 50% conversion for the selected repeated set of experiments

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Experiment (1)</th>
<th>Experiment (2)</th>
<th>Experiment (3)</th>
<th>mean</th>
<th>Standard Deviation (˚C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>145</td>
<td>143.8</td>
<td>146.5</td>
<td>145.1</td>
<td>± 1.35</td>
</tr>
<tr>
<td>C3H6</td>
<td>162</td>
<td>163</td>
<td>162</td>
<td>162</td>
<td>± 1</td>
</tr>
<tr>
<td>CO + C3H6</td>
<td>170.1 a</td>
<td>172.2 a</td>
<td>173.1 a</td>
<td>171.8 a</td>
<td>± 1.52 a</td>
</tr>
<tr>
<td></td>
<td>176 b</td>
<td>177.7 b</td>
<td>175.7 b</td>
<td>176.47 b</td>
<td>± 1.04 b</td>
</tr>
<tr>
<td>C3H6 + Dodecane</td>
<td>168 b</td>
<td>169.5 b</td>
<td>167 b</td>
<td>168.2 b</td>
<td>± 1.26 b</td>
</tr>
<tr>
<td></td>
<td>164.4 c</td>
<td>166.3 c</td>
<td>165 c</td>
<td>165.3 c</td>
<td>± 0.84 c</td>
</tr>
<tr>
<td>Dodecane + NO c</td>
<td>164</td>
<td>162.2</td>
<td>165</td>
<td>163.7</td>
<td>±1.38</td>
</tr>
<tr>
<td>C3H6 + NO b</td>
<td>182</td>
<td>184</td>
<td>182.4</td>
<td>182.8</td>
<td>±0.95</td>
</tr>
<tr>
<td>C3H6 + NO + NO2 b</td>
<td>198</td>
<td>199.5</td>
<td>197.3</td>
<td>198.3</td>
<td>±1.11</td>
</tr>
</tbody>
</table>

a: the 50% conversion of CO.
b: the 50% conversion of C3H6.
c: the 50% conversion of dodecane.
*: a mixture of 200 ppm NO and 200 ppm NO2.
Table A.5  Statistical analysis for hydrogen production (in ppm) for the selected repeated set of experiments.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Experiment (1)</th>
<th>Experiment (2)</th>
<th>Experiment (3)</th>
<th>mean</th>
<th>Standard Deviation (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{3}H\textsubscript{6} \textsuperscript{a}</td>
<td>84</td>
<td>88</td>
<td>86</td>
<td>86</td>
<td>± 2</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6} \textsuperscript{b}</td>
<td>474</td>
<td>480</td>
<td>478</td>
<td>477.3</td>
<td>± 2.36</td>
</tr>
<tr>
<td>CO \textsuperscript{a}</td>
<td>1005</td>
<td>1010</td>
<td>1007</td>
<td>1007.3</td>
<td>± 2.12</td>
</tr>
<tr>
<td>CO \textsuperscript{b}</td>
<td>1124</td>
<td>1127.5</td>
<td>1123</td>
<td>1124.8</td>
<td>± 2.32</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: Steady state experiment at 450°C
\textsuperscript{b}: Cycling experiment at 450°C

Table A.6  Statistical analysis for CO\textsubscript{2} formation (in ppm) obtained during (TPO) experiments at 2 and 4 cm from the front of catalyst after C\textsubscript{3}H\textsubscript{6} steam reforming experiments at 450°C for 180 min.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Experiment (1)</th>
<th>Experiment (2)</th>
<th>Experiment (3)</th>
<th>mean</th>
<th>Standard Deviation (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{3}H\textsubscript{6} \textsuperscript{a}</td>
<td>80.6</td>
<td>82.4</td>
<td>78.5</td>
<td>80.5</td>
<td>± 1.95</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6} \textsuperscript{b}</td>
<td>164</td>
<td>167</td>
<td>169</td>
<td>166.7</td>
<td>± 1.95</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: CO\textsubscript{2} formation at 2 cm
\textsuperscript{b}: CO\textsubscript{2} formation at 4 cm
(2) NOₓ storage and reduction catalyst

In this study, the performance of the NOₓ storage and reduction catalyst was investigated based on (1) whether the NOₓ source was NO or NO₂, (2) regeneration time and H₂ concentration, and (3) reductant type. For Table A.7, the experiments were repeated three times when either NO or NO₂ was the NOₓ source at 500°C. In Table A.8, two regeneration protocols; 4 sec rich and 4% H₂ and 8 sec rich and 2% H₂, were repeated at 400°C. In Table A.9, the reproducibility of the catalyst performance was investigated with either C₁₂H₂₆ or H₂ used as the reductant at 250°C. The lean time was 60 sec and rich time was 10 sec. The detailed experiment descriptions are reported in previous chapters; Chapter 5 for Table A.7, Chapter 6 for Table A.8, and Chapter 7 for Table A.9.

According to the standards deviations listed in the tables, experiments were reproducible and show very little variation in the repeated experiments, as indicated by the small values of standard deviation. For example, H₂ production during cycling C₃H₆ steam reforming experiments was higher than that during steady state experiments over the DOC at 450°C, as shown in Table A.5. The average H₂ formed during cycling experiments was 477.3 ppm (with σ = ± 2.36 ppm) whereas 86 ppm (with σ = ± 2 ppm) were formed during steady state experiments. Therefore, even if the standard deviation is added/subtracted, these differences are still significant. Table A.9 shows the differences in the NOₓ trapping and released when either C₁₂H₂₆ or H₂ was used as the reducing agent at 250°C. The average NOₓ trapped with C₁₂H₂₆ was 63.2 μmoles (with σ = ± 0.67 μmoles) while 82.13 μmoles were trapped (with σ = ± 0.67 μmoles) with H₂. Again, these differences are significant.
**Table A.7** Statistical analysis of the effect of NO\textsubscript{X} source (NO or NO\textsubscript{2}) on the catalyst performance at 500\degree C with 80 sec lean and 4 sec rich. 3\% H\textsubscript{2} was used as reducing agent.

<table>
<thead>
<tr>
<th>Performance ((\mu)moles)</th>
<th>Experiment (1)</th>
<th>Experiment (2)</th>
<th>Experiment (3)</th>
<th>mean</th>
<th>Standard Deviation ((\mu)moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{X} Trapping</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>163</td>
<td>166</td>
<td>164</td>
<td>164.3</td>
<td>(\pm 1.2)</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>189</td>
<td>192</td>
<td>190.4</td>
<td>190.5</td>
<td>(\pm 1.22)</td>
</tr>
<tr>
<td>NO\textsubscript{X} release</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>30.5</td>
<td>33</td>
<td>31</td>
<td>31.5</td>
<td>(\pm 1.2)</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>23</td>
<td>26</td>
<td>24</td>
<td>24.3</td>
<td>(\pm 1.3)</td>
</tr>
</tbody>
</table>

**Table A.8** Statistical analysis of the effect regeneration time on the catalyst performance. Comparison between condition A: 4 sec rich and 4\% H\textsubscript{2} and Condition B: 8 sec rich and 2\% H\textsubscript{2} at 400\degree C.

<table>
<thead>
<tr>
<th>Performance ((\mu)moles)</th>
<th>Experiment (1)</th>
<th>Experiment (2)</th>
<th>Experiment (3)</th>
<th>mean</th>
<th>Standard Deviation ((\mu)moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{X} Trapping</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>226</td>
<td>229</td>
<td>227.5</td>
<td>227.5</td>
<td>(\pm 1.2)</td>
</tr>
<tr>
<td>B</td>
<td>237</td>
<td>239</td>
<td>237.5</td>
<td>237.8</td>
<td>(\pm 0.92)</td>
</tr>
<tr>
<td>NO\textsubscript{X} release</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>10</td>
<td>12</td>
<td>11</td>
<td>84</td>
<td>(\pm 0.81)</td>
</tr>
<tr>
<td>B</td>
<td>16</td>
<td>18</td>
<td>16.7</td>
<td>16.9</td>
<td>(\pm 0.87)</td>
</tr>
</tbody>
</table>
Table A.9  Statistical analysis of the regeneration of a model NO\textsubscript{X} storage/reduction catalyst using C\textsubscript{12}H\textsubscript{26} and H\textsubscript{2} as the reductant at 250ºC. The lean time was 60 sec and rich time was 10 sec.

<table>
<thead>
<tr>
<th>Performance ((\mu)moles)</th>
<th>Experiment (1)</th>
<th>Experiment (2)</th>
<th>Experiment (3)</th>
<th>mean</th>
<th>Standard Deviation ((\mu)moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{X} Trapping</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{12}H\textsubscript{26}</td>
<td>62.5</td>
<td>64</td>
<td>63</td>
<td>63.2</td>
<td>(\pm 0.67)</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>81.4</td>
<td>83</td>
<td>82</td>
<td>82.13</td>
<td>(\pm 0.68)</td>
</tr>
<tr>
<td>NO\textsubscript{X} release</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{12}H\textsubscript{26}</td>
<td>18</td>
<td>20</td>
<td>18.5</td>
<td>18.8</td>
<td>(\pm 0.92)</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>7.3</td>
<td>9.8</td>
<td>7.9</td>
<td>8.3</td>
<td>(\pm 1.16)</td>
</tr>
</tbody>
</table>

A.3 Uncertainty with measurements

Every measurement has a degree of error or uncertainty associated with it. Propagating the instrument’s error is an important step to check whether the calculated differences between the experiments are significant or not, especially if a high error degree for the instrument is reported. The instruments used in this study can be divided into three categories; namely, the feed delivery system, reactor system, and gas analyzers. The uncertainties associated with each instrument are reported in Table A.10 and were obtained from the associated manuals.

In all experiments, the gas flow rate was greater than 10 L/min, so the listed values are considered small, and therefore their effects are negligible. For the heating
systems and thermocouples, any differences smaller than 2°C during the experiments were considered insignificant. Uncertainties associated with the gas analyzers were also very small.

**Table A.10 Uncertainties associated with instruments**

<table>
<thead>
<tr>
<th>Instrument Type</th>
<th>Associated Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Delivery system</strong></td>
<td></td>
</tr>
<tr>
<td>Main feed delivery system</td>
<td>± (2-4) ml</td>
</tr>
<tr>
<td>Mass flowerers</td>
<td></td>
</tr>
<tr>
<td><strong>Water system</strong></td>
<td></td>
</tr>
<tr>
<td>Mass flowerers</td>
<td>± 2.5 ml</td>
</tr>
<tr>
<td>Heating System</td>
<td>± 0.8°C</td>
</tr>
<tr>
<td><strong>Hydrocarbon system</strong></td>
<td></td>
</tr>
<tr>
<td>Mass flowerers</td>
<td>± 2.5ml</td>
</tr>
<tr>
<td>Heating System</td>
<td>± 0.9°C</td>
</tr>
<tr>
<td><strong>Reactor</strong></td>
<td></td>
</tr>
<tr>
<td>Thermocouples (K-type)</td>
<td>± 1°C</td>
</tr>
<tr>
<td><strong>Gas Analyzers</strong></td>
<td></td>
</tr>
<tr>
<td>FTIR (MKS)</td>
<td>± 0.9 %</td>
</tr>
<tr>
<td>Mass spectrometry</td>
<td>± 2-5%</td>
</tr>
<tr>
<td></td>
<td>of the reading</td>
</tr>
</tbody>
</table>
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<td>Meshari AL-Harbi</td>
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