NOx storage and reduction over a lean-burn automotive catalyst
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**NO\textsubscript{x} storage and reduction over a lean-burn automotive catalyst**

**Summary**

Nowadays, there is an increased interest in lean-burn technologies, i.e. diesel and lean-burn gasoline engines, mainly due to their higher fuel efficiency compared to conventional gasoline engines. Lean-burn engines work under excess oxygen and consequently produce oxygen-rich exhaust. This oxygen-rich environment favors the catalytic oxidation of CO and HC to water and CO\textsubscript{2} over the reduction of NO\textsubscript{x} into N\textsubscript{2} and the conventional three-way catalyst technology is not able to reduce NO\textsubscript{x} under these circumstances. Therefore, new catalytic systems have been developed. Among the most promising approaches is the so-called NO\textsubscript{x} storage reduction (NSR) catalyst along with mixed lean combustion, where the fuel combustion is altered between lean (oxygen excess) and rich (fuel excess) conditions. During the relatively long lean periods, NO\textsubscript{x} is stored on a storage component, e.g. barium. As the NO\textsubscript{x} storage component gets saturated, the catalyst needs to be regenerated. This is done during short rich operation of the engine resulting in oxygen-deficient exhaust. Consequently, the stored NO\textsubscript{x} is released and reduced over noble metals like Pt into the harmless N\textsubscript{2}. For real-life application, it is crucial to understand the NSR mechanism in order to minimize both fuel penalty and emissions.

In this thesis, the NSR mechanism on an automotive catalyst is investigated, using both experimental and modelling methods. Lean/rich cycling experiments are performed in a packed bed reactor using an automotive Pt-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3} (1 wt.% Pt and 30 wt.% Ba) catalyst. Emphasis is given in understanding the catalyst behavior, the role of multiple storage sites, the influence of CO\textsubscript{2} and H\textsubscript{2}O and the influence of different reducing agents (CO, H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4}) on NO\textsubscript{x} storage and reduction.

Lean/rich cycling results show that in the absence of CO\textsubscript{2} and H\textsubscript{2}O, almost 100\% of barium is involved in NO\textsubscript{x} storage when the catalyst is exposed to 9 h lean conditions and both bulk and surface barium sites
participate in NO\textsubscript{x} storage. The subsequent rich phase shows incomplete regeneration of stored NO\textsubscript{x}, even after 15 h rich exposure with H\textsubscript{2}. Due to this incomplete regeneration, less barium participates in the following lean phase. Additionally, the NO oxidation efficiency of the catalyst decreases upon lean exposure till steady cycling is achieved. Furthermore, the BET surface area, pore volume and Pt dispersion decrease by about 40%. Similar findings are observed for 30 min lean and 120 min rich cycling experiments.

In the absence of added CO\textsubscript{2} and H\textsubscript{2}O, NO\textsubscript{x} can be stored on γ-Al\textsubscript{2}O\textsubscript{3}, BaO, BaCO\textsubscript{3} and Ba(OH)\textsubscript{2}. However, in the presence of CO\textsubscript{2}, NO\textsubscript{x} is stored on γ-Al\textsubscript{2}O\textsubscript{3} and BaCO\textsubscript{3} sites. Bulk barium sites are inactive in NO\textsubscript{x} trapping in the presence of CO\textsubscript{2} and only 30% of total barium participates in NO\textsubscript{x} storage. Ba(NO\textsubscript{3})\textsubscript{2} is then always completely regenerated during the subsequent rich phase and the Pt dispersion, BET surface area and pore volume remain unchanged.

A global reaction kinetic model is developed to describe the NO\textsubscript{x} storage/reduction process in the presence of CO\textsubscript{2} with H\textsubscript{2} as reducing agent at a temperature of 300 0\textdegree\text{C}. The model considers that NO\textsubscript{x} storage occurs on three types of barium sites, viz. surface, semi-bulk and bulk barium sites. Fast NO\textsubscript{x} storage occurs at surface BaCO\textsubscript{3} sites, determined by the reaction kinetics. Slow NO\textsubscript{x} storage occurs at semi-bulk sites, where diffusion plays a major role. Bulk sites are inactive in NO\textsubscript{x} trapping. It is assumed that surface and semi-bulk sites correspond with a dispersed barium phase and bulk barium sites with crystalline BaCO\textsubscript{3} sites.

The model elucidates that the initial complete NO\textsubscript{x} uptake can be mainly ascribed to NO storage on surface barium sites in the form of nitrites. As the surface coverage increases, NO breakthrough can be seen. The NO storage process continues with the involvement of semi-bulk barium sites but at a lower rate due to diffusion limitation. Meanwhile NO\textsubscript{2} is consumed in oxidizing surface nitrites into nitrates with release of NO and by getting stored on semi-bulk barium sites. As a result, delay in NO breakthrough can be seen and the NO concentration passes through a maximum.

In the presence of CO\textsubscript{2}, CO poisons the catalyst in the rich phase through carbon decomposition on the Pt sites and formation of strongly bound isocyanates at 300 0\textdegree\text{C}. Under these conditions, stored NO\textsubscript{x} is not fully
removed in the rich phase. C\textsubscript{2}H\textsubscript{4} also poisons the catalyst, but to a lesser extent as all the stored NO\textsubscript{x} in the preceding lean phase is released and reduced. The type of reducing agent also affects the NO\textsubscript{x} breakthrough profile observed in the following lean phase. After catalyst regeneration with CO, the NO\textsubscript{x} breakthrough profile shows simultaneous NO and NO\textsubscript{2} breakthrough and both NO and NO\textsubscript{2} concentrations increase gradually in time. The NO\textsubscript{x} breakthrough profile with C\textsubscript{2}H\textsubscript{4} as reductant, shows a combination of the profiles observed for CO and H\textsubscript{2}.

H\textsubscript{2}O in the lean phase inhibits NO oxidation and no NO\textsubscript{2} formation is observed. Less NO is stored in the presence of H\textsubscript{2}O, which supports the higher storage capacity towards NO\textsubscript{2} than NO. Lean/rich cycling experiments with H\textsubscript{2}O and CO\textsubscript{2} and H\textsubscript{2} as reducing agent show that H\textsubscript{2} is efficient in catalyst regeneration for temperatures between 200 and 300 °C. Experiments with CO show that at temperatures above 250 °C, the water gas shift reaction takes place and H\textsubscript{2} acts as reductant instead of CO. At 200 °C, CO and C\textsubscript{2}H\textsubscript{4} are not able to regenerate the catalyst. At higher temperatures, C\textsubscript{2}H\textsubscript{4} is capable of reducing all stored NO, although C\textsubscript{2}H\textsubscript{4} poisons the Pt sites at 250 °C. H\textsubscript{2}O prevents catalyst poisoning by C\textsubscript{2}H\textsubscript{4} at 300 °C.

The previous developed model is adapted to describe lean/rich cycling in the presence of CO\textsubscript{2} and H\textsubscript{2}O for temperatures between 200 and 300 °C and for different reductants (CO, H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4}). The model can be used to simulate and optimize the catalyst at transient operating conditions.
Samenvatting

Sinds enige tijd is er een toenemende belangstelling voor de zogenaamde “lean-burn”-technologie, waaronder dieselmotoren en “lean-burn”-benzinemotoren vallen. Dit kan voornamelijk worden toegeschreven aan het feit dat deze motoren zuiniger zijn vergeleken met de conventionele benzinemotoren. “Lean-burn”-motoren werken onder overmaat zuurstof en produceren dan ook zuurstofrijke uitlaatgassen. In deze zuurstofrijke omgeving verloopt de katalytische oxidatie van CO en koolwaterstoffen naar water en CO₂ beter dan de reductie van NOₓ naar N₂. De conventionele drie-weg katalysator is niet in staat om NOₓ te reduceren onder deze omstandigheden. Er is dan ook vraag naar nieuwe katalytische systemen. Onder de meest belovende systemen bevindt zich de zogenaamde “NOₓ storage reduction (NSR)”-katalysator, waarbij de brandstofverbranding alternerend plaatsvindt in zuurstofrijke (“lean” (arme)) en brandstofrijke (“rich” (rijke)) condities. Gedurende de relatief lange “lean” periodes, wordt NOₓ opgeslagen op een opslagcomponent, zoals barium. Zodra de opslagcomponent verzadigd raakt, dient de katalysator geregenereerd te worden. Dit wordt gedaan tijdens de korte rijke periode waarbij een zuurstofarm uitlaatgas ontstaat. Hierbij komt de opgeslagen NOₓ vrij en deze wordt vervolgens gereduceerd tot N₂ over een edelmetaal zoals platina. Voor praktijktoepassing van dit katalysatorsysteem is het belangrijk om het NSR-mechanisme goed te begrijpen, zodat zowel het brandstofverbruik als de emissies tot een minimum beperkt kunnen worden.

In dit proefschrift wordt het NSR-mechanisme onderzocht, gebruikmakend van zowel experimenten als modelleerwerk. “Lean”/”rich” cyclische experimenten zijn uitgevoerd in een gepakt-bed reactor met een Pt-Ba/γ-Al₂O₃ (1 gew.% Pt en 30 gew.% Ba) katalysator. Nadruk ligt hierbij vooral op het begrijpen van het gedrag van de katalysator, de rol van de verschillende opslag-“sites”, de invloed van CO₂ en H₂O en de invloed van verschillende reductanten (CO, H₂ en C₂H₄) op de NOₓ-opslag en -reductie.
“Lean”/“rich” cycli laten zien dat in de afwezigheid van CO₂ en H₂O nagenoeg alle barium meedoet aan de NOₓ-opslag, indien de katalysator voor 9 uur aan “lean”-condities wordt blootgesteld. Zowel oppervlakte- als bulk-barium-sites zijn actief in NOₓ-opslag. De volgende rijke fase toont echter onvolledige regeneratie van de opgeslagen NOₓ, zelfs na 15 uur blootstelling aan H₂. Door deze incomplete regeneratie doet minder barium mee in de navolgende “lean”-fase. Verder neemt ook de efficiëntie van de NO-oxidatie af in de “lean”-fase totdat de cyclisch-stationaire toestand is bereikt. Bovendien dalen het BET-oppervlak, het porievolume en de Pt-dispersie met 40%. Gelijkse resultaten zijn gevonden met 30 min “lean” en 120 min “rich” cyclische experimenten.

In afwezigheid van CO₂ en H₂O, kan NOₓ worden opgeslagen op γ-Al₂O₃, BaO, Ba(OH)₂ en BaCO₃. In aanwezigheid van CO₂ wordt NOₓ opgeslagen op γ-Al₂O₃ en BaCO₃ sites. Verder zijn de bulk-barium-“sites” inactief in NOₓ-opslag in de aanwezigheid van CO₂ en maar 30% van de totale hoeveelheid barium doet mee aan NOₓ-opslag. Overigens wordt onder deze condities Ba(NO₃)₂ altijd volledig geregenereerd tijdens de volgende rijke fase en blijven de Pt-dispersie, het BET-oppervlak en het porievolume gelijk.

Een model gebaseerd op globale reactiekinetiek is ontwikkeld om NOₓ-opslag en -reductie te beschrijven bij 300 °C in de aanwezigheid van CO₂ met H₂ in de rijke fase. In het reactiemodel kan NOₓ-opslag plaatsvinden op drie verschillende barium-“sites”, nl. oppervlakte, semi-bulk en bulk “sites”. Snelle NOₓ-opslag vindt plaats op oppervlakte “sites”, bepaald door de reactiekinetiek. Langzame NOₓ-opslag gebeurt op semi-bulk “sites”, waarbij diffusie een belangrijke rol speelt. Bulk “sites” zijn inactief in NOₓ-opslag. Oppervlakte en semi-bulk “sites” komen overeen met een gedispergeerde bariumfase en bulk-barium “sites” met kristallijn BaCO₃.

In het reactiemodel komt naar voren dat de initiële complete NOₓ-opslag toegeschreven kan worden aan NO-opslag op oppervlakte “sites” in de vorm van nitrieten. Zodra de oppervlakte “sites” vollopen, is er NO-doorbraak te zien. Het NO-opslag proces gaat dan door met semi-bulk “sites”, maar met een lagere snelheid als gevolg van diffusielimitering. Ondertussen wordt NO₂
geconsumeerd in de oxidatie van nitriet naar nitraat, waarbij NO vrijkomt en door opslag op semi-bulk barium-“sites”. Hierdoor vertoont de NO₂-doorbraak een vertraging en laat de NO-concentratie een maximum zien.

In de aanwezigheid van CO₂, toont de rijke fase bij 300 °C met CO katalysatorvergiftiging door koolstofafzetting op de Pt-“sites” en vorming van isocyanaten. Bij deze condities wordt opgeslagen NOₓ niet volledig vrijgemaakt in de rijke fase. C₂H₄ toont ook katalysatorvergiftiging maar minder aangezien de opgeslagen NOₓ in de voorafgaande “lean”-fase volledig wordt vrijgemaakt en gereduceerd. Het type reductant in de rijke fase heeft onder deze condities ook effect op het NOₓ-doorbraakprofiel in de volgende “lean”-fase. Na regeneratie met CO, laat het NOₓ-doorbraakprofiel gelijktijdig NO- en NO₂-doorbraak zien en zowel de NO- als de NO₂-concentratie neemt toe in de tijd. Het NOₓ-doorbraakprofiel na C₂H₄ in de rijke fase toont een combinatie van de profielen waargenomen bij CO en H₂.

H₂O in de “lean”-fase hindert NO-oxidatie en NO₂-vorming wordt niet waargenomen. Minder NO wordt opgeslagen in de aanwezigheid van H₂O, hetgeen overeenkomt met de betere opslagcapaciteit voor NO₂ dan voor NO. “Lean”/“rich” cyclische experimenten in aanwezigheid van H₂O en CO₂ en met H₂ in de rijke fase laten zien dat H₂ in staat is de katalysator te regenereren voor temperaturen tussen 200 °C en 300 °C. Experimenten met CO tonen dat bij temperaturen boven 250 °C, de “water gas shift”-reactie plaatsvindt en dat H₂ de reductant is i.p.v. CO. C₂H₄ en CO zijn niet in staat de katalysator te regenereren bij 200 °C. Bij hogere temperaturen is C₂H₄ wel in staat om de opgeslagen NO te reduceren, hoewel C₂H₄ de Pt-“sites” vergiftigt bij 250 °C. In de aanwezigheid van H₂O wordt er geen katalysatorvergiftiging waargenomen bij 300 °C.

Het reactiemodel is verder aangepast om “lean”/“rich”-experimenten in de aanwezigheid van CO₂ en H₂O te beschrijven voor temperaturen tussen 200 °C en 300 °C met verschillende reductanten (CO, H₂ en C₂H₄). Dit model kan gebruikt worden voor simulaties en optimalisatie van de katalysator bij transiënte condities.
Nomenclature

- $A_{Ba}$: specific barium surface, ($m^2_{Ba} m^{-3}_{reactor}$)
- $A_r$: surface area of the reactor, ($m^2_{reactor}$)
- $d_{Ba}$: diameter semi-bulk barium cluster, ($m_{Ba}$)
- $D_{eff}$: diffusion coefficient, ($m_{gas}^3 m^{-1}_{Ba} s^{-1}$)
- $f$: volume fraction, ($m^4_{Ba} m^{-3}_{reactor}$)
- $F_v$: volumetric flow rate, ($m^3_{gas} s^{-1}$)
- $K_{carbon}$: Poisoning Pt sites ($m^3 mol^{-1} s^{-1}$)
- $K_{CO}$: Regeneration Pt sites by CO ($m^3 mol^{-1} s^{-1}$)
- $K_{C2H4}$: Regeneration Pt sites by C$_2$H$_4$ ($m^3 mol^{-1} s^{-1}$)
- $K_{H2}$: Regeneration Pt sites by H$_2$ ($m^3 mol^{-1} s^{-1}$)
- $K_{O2,store}$: O$_2$ adsorption Pt sites ($m^3 mol^{-1} s^{-1}$)
- $K_{oxi, equilibrium}$: NO oxidation equilibrium
- $k_{ox,f}$: forward NO oxidation, ($m^{4.5}_{gas} mol^{-0.5}_{i} mol^{-1}_{Pt} s^{-1}$)
- $k_{ox,b}$: backward NO oxidation, ($m^{1}_{gas} mol^{-1}_{Pt} s^{-1}$)
- $k_{red}$: NO$_x$ reduction, ($m^{6}_{gas} mol^{-2}_{i} s^{-1}$)
- $k_{reg, nitrate, bulk}$: Ba(NO$_3$)$_2$ regeneration of bulk barium sites, ($m^3_{gas} mol^{-1}_{i} s^{-1} mol_{Ba} m^3_{Ba}$)
- $k_{reg, nitrate, semibulk}$: Ba(NO$_3$)$_2$ regeneration of semi-bulk barium sites, ($m^3_{gas} mol^{-1}_{i} s^{-1} mol_{Ba} m^3_{Ba}$)
- $k_{reg, nitrate, surface}$: Ba(NO$_3$)$_2$ regeneration of surface barium sites, ($m^3_{gas} mol^{-1}_{i} s^{-1}$)
- $k_{reg, nitrite, semibulk}$: Ba(NO$_2$)$_2$ regeneration of semi-bulk barium sites, ($m^3_{gas} mol^{-1}_{i} s^{-1} mol_{Ba} m^3_{Ba}$)
- $k_{reg, nitrite, surface}$: Ba(NO$_2$)$_2$ regeneration of surface barium sites, ($m^3_{gas} mol^{-1}_{i} s^{-1}$)
- $k_{as, dis, semibulk}$: nitrite oxidation on semi-bulk barium sites, ($m^6_{gas} mol^{-2}_{i} s^{-1} mol_{Ba} m^3_{Ba}$)
- $k_{as, dis, surface}$: nitrite oxidation on surface barium sites, ($m^6_{gas} mol^{-2}_{i} s^{-1}$)
- $k_{as, NO, semibulk}$: NO storage on semi-bulk barium sites, ($m^{7.5}_{gas} mol^{-2.5}_{i} s^{-1} mol_{Ba} m^3_{Ba}$)
- $k_{as, NO, surface}$: NO storage on surface barium sites, ($m^{7.5}_{gas} mol^{-2.5}_{i} s^{-1} mol_{Ba} m^3_{Ba}$)
- $k_{as, NO2, bulk}$: NO$_2$ storage on bulk sites, ($m^{7.5}_{gas} mol^{-2.5}_{i} s^{-1} mol_{Ba} m^3_{Ba}$)
- $k_{as, NO2, semibulk}$: NO$_2$ storage on semi-bulk barium sites, ($m^{7.5}_{gas} mol^{-2.5}_{i} s^{-1} mol_{Ba} m^3_{Ba}$)
- $k_{as, NO2, surface}$: NO$_2$ storage on surface barium sites, ($m^{7.5}_{gas} mol^{-2.5}_{i} s^{-1}$)
- $k_{WGS}$: Water Gas Shift Reaction ($m^3 mol^{-1} s^{-1}$)
- $L_{Ba, bulk}$: moles of Ba bulk sites / $m^3$ reactor, ($mol m^{-3}_{reactor}$)
- $L_{Ba, semi-bulk}$: moles of Ba semi-bulk sites / $m^3$ reactor, ($mol m^{-3}_{reactor}$)
- $L_{Ba, surface}$: moles of Ba surface sites / $m^3$ reactor, ($mol m^{-3}_{reactor}$)
- $L_{Ba, total}$: moles of total Ba sites / $m^3$ reactor, ($mol m^{-3}_{reactor}$)
- $L_{Pt}$: moles of Pt surface sites / $m^3$ reactor, ($mol m^{-3}_{reactor}$)
- $L_{reactor}$: reactor length, ($m_{reactor}$)

Greek symbols

- $\varepsilon_b$: bed porosity, ($m^3_{gas} m^{-3}_{reactor}$)
- $\varepsilon_{cluster}$: cluster porosity, ($m^3_{gas} m^{-3}_{Ba}$)
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Introduction

Abstract
Nowadays, there is an increased interest in lean-burn technologies, i.e. diesel and lean-burn gasoline engines, mainly due to their higher fuel efficiency compared to conventional gasoline engines. These engines work under excess oxygen and consequently produce oxygen-rich exhaust. However, effectively reducing NO\textsubscript{x} in oxygen-rich exhaust is a challenging endeavor, because the conventional three-way catalyst technology is not able to reduce NO\textsubscript{x} efficiently under these circumstances. Therefore, new catalytic systems have been developed. Several approaches have been suggested, and among the most promising is the so-called NO\textsubscript{x} storage reduction (NSR) concept. In order to explain the motivation of the research described in this thesis, the reader is introduced briefly about the need to control the NO\textsubscript{x} emission of lean-burn gasoline and diesel engines. Additionally, the working principle of the NSR catalyst is given in a few words. Furthermore, the scope of the research and the layout of the thesis are described.
1.1. Legislation of air pollutants

One of the most important environmental concerns is air pollution. Due to the huge numbers of vehicles in the world, their emissions of air pollutants contribute a significant fraction of the total amount of emissions. In European urban areas e.g. the toxic compound CO is produced almost entirely (90 %) from road traffic emissions [1]. Major air pollutants in exhaust gas are nitrogen oxides (NO$_x$), carbon oxides (CO$_x$), hydrocarbons (HC), sulfur oxides (SO$_x$), and particulate matter (PM). The term particulate matter refers to fine particles that are released from the engine, mostly based on carbonaceous matter. These fine particles can be carried deep into the lungs where they can cause inflammation and a worsening of heart and long diseases [2]. SO$_x$ refers mainly to SO$_2$, what gives rise to formation of H$_2$SO$_3$ which is known to cause acid rain [3]. HC are known to be involved in the formation of ozone, which is a major component of smog [4]. HC harm the human health, as they are toxic and extremely carcinogen. CO$_x$ consists of carbon monoxide (CO) and carbon dioxide (CO$_2$). CO is also extreme toxic and may reduce the oxygen-carrying capacity of the blood. This can lead to a significant reduction in the supply of oxygen to the heart, particularly in people suffering from heart diseases [5].

Table 1.1.
Tailpipe maximum EU emission standards for passenger cars in g/km [9-12]

<table>
<thead>
<tr>
<th>Tier</th>
<th>Year</th>
<th>CO</th>
<th>HC</th>
<th>HC+NO$_x$</th>
<th>NO$_x$</th>
<th>PM</th>
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<table>
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<tr>
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</table>

CO$_2$ is a so-called greenhouse gas and is expected to contribute to the global warming [6]. NO$_x$ emissions, both nitrogen monoxide (NO) and nitrogen dioxide (NO$_2$), contribute to the formation of smog and acid rain [3,7]. In
addition, excessive exposure to NO\textsubscript{x} may affect the human respiratory system and may increase the risk of respiratory allergies.

The negative impact of these emissions on the human health and on the climate led to legislation to control and limit the emissions. Emission limits in the European Union have been introduced in 1970 [8] and since then the legislation has become more and more stringent. Table 1.1. shows the most important amendments.

![Figure 1.1: Fuel consumption and 3-way performance of a gasoline engine as a function of air-fuel (A/F) ratio [15]](image)

Figure 1.1: Fuel consumption and 3-way performance of a gasoline engine as a function of air-fuel (A/F) ratio [15]

to the original directives including EURO 1, EURO 2, EURO 3, and EURO 4 standards [9-11] and the most recent EURO 5 limits [12]. The emission limits for CO, HC, NO\textsubscript{x} and PM are given for gasoline and diesel engine equipped passenger cars. Legislation of the exhaust gas emissions led to the development of exhaust after treatment systems. Today, the three-way catalyst (TWC) oxidizes CO and HC to CO\textsubscript{2} and H\textsubscript{2}O and simultaneously reduces NO\textsubscript{x} into the harmless N\textsubscript{2} with high efficiency for gasoline engines [13,14]. The stoichiometric air-fuel ratio of 14.5:1 of gasoline engines produces exhaust gas that contains the right balance of CO, H\textsubscript{2} and HC to reduce NO\textsubscript{x} and O\textsubscript{2} (Fig. 1.1). However, diesel engines operate at air-fuel ratios of 25:1 and above, resulting in exhaust gas with oxygen excess (Table 1.2).
Table 1.2. Exhaust gas composition [26]

<table>
<thead>
<tr>
<th></th>
<th>Conventional gasoline engine</th>
<th>Diesel engine</th>
<th>Lean-burn gasoline engine</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ vol. %</td>
<td>0.2 – 2</td>
<td>5 – 15</td>
<td>4 – 18</td>
</tr>
<tr>
<td>CO₂ vol. %</td>
<td>10 – 13.5</td>
<td>2 – 12</td>
<td>2 – 12</td>
</tr>
<tr>
<td>H₂O vol. %</td>
<td>10 – 12</td>
<td>2 – 10</td>
<td>2 – 12</td>
</tr>
<tr>
<td>N₂ vol. %</td>
<td>70 – 75</td>
<td>70 – 75</td>
<td>70 – 75</td>
</tr>
<tr>
<td>CO vol. %</td>
<td>0.1 – 6</td>
<td>0.01 – 0.1</td>
<td>0.01 – 0.08</td>
</tr>
<tr>
<td>HC vol. % C₁</td>
<td>0.5 – 6</td>
<td>0.005 – 0.05</td>
<td>0.002 – 0.015</td>
</tr>
<tr>
<td>NOₓ vol. %</td>
<td>0.04 – 0.4</td>
<td>0.003 – 0.06</td>
<td>0.01 – 0.05</td>
</tr>
<tr>
<td>SOₓ</td>
<td>Dependent on fuel S content</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The oxygen-rich environment of lean-burn engines favors the catalytic oxidation of CO and HC to water and CO₂ over the reduction of NOₓ into N₂, and the normal TWC is not capable of reducing NOₓ. It has therefore been necessary to restrict NOₓ emissions by sophisticated diesel engine control measures and to use an oxidation catalyst to convert excess HC and CO to water and CO₂.

1.2. **Lean-burn gasoline and diesel engines**

Because of the three-way catalyst, the emission of NOₓ by gasoline engines has decreased significantly. However, this gain is counteracted by the continuing rise in vehicle numbers and distances traveled, particularly by the increase in the number of diesel engines that are not equipped with a catalyst to reduce NOₓ emission. The latest quarterly pricing survey by PricewaterhouseCoopers and eurocarprice.com [16,17] shows that diesel cars accounted for 49 % of the total European car market at the end of 2005. It is expected that the number of diesel engines continues to grow, potentially achieving 55-60 % of the total market. There are several reasons for the increased interest in diesel engines. The lean-burn combustion of diesel engines results in higher fuel efficiency compared to conventional gasoline engines and consequently significantly lower amounts of the greenhouse gas CO₂ [18]. In addition, diesels have superior performance regarding CO and HC. Therefore, supported by the European environmental community, governments encourage the use of diesel technology. Tax regimes make diesel fuel cheaper than gasoline and encourage the sales of diesel engines. These advantages are, however, country dependent. The demand for diesel
engines has also been fuelled by their better performance as modern diesel engines have more power at lower engine speeds and are more durable than gasoline engines. Moreover, the latest diesel technology results in quiet engines, eliminating the noise from early diesel cars.

The diesel engine is a so-called lean-burn engine, as there is an excess of air and combustion is completed in an oxidizing atmosphere. Another modern type of lean-burn engine is the lean-burn gasoline engine. Contrary to a conventional gasoline engine, combustion takes places with excess of air resulting in a more efficient combustion, improved power, and 20 to 35 % higher fuel efficiency [19]. It is expected that these lean-burn gasoline engines will increasingly compete with diesels in terms of overall efficiency.

1.3. Control of NO\textsubscript{x} for lean-burn engines

The nowadays increased interest in lean-burn combustion has prompted research on the development of a new catalyst that is capable of reducing NO\textsubscript{x} in excess O\textsubscript{2} to meet future legislation. Selective catalytic reduction (SCR) of NO\textsubscript{x} using ammonia (NH\textsubscript{3}) or urea (CO(NH\textsubscript{2})\textsubscript{2}) is a well-known process in industry, as well as in stationary diesel engine applications [20]. In the presence of O\textsubscript{2}, NH\textsubscript{3} prefers to react with NO\textsubscript{x} to form N\textsubscript{2}. Urea, which is safer in use than NH\textsubscript{3}, can be used as NH\textsubscript{3} source and urea-based systems are already applied for heavy-duty trucks [21]. However, application of this process in passenger cars has disadvantages such as the need for additional space for an urea tank and the development of an urea distribution network [22]. Another technique is SCR with hydrocarbons, with e.g. noble metal or Cu/ZSM-5 catalysts. However, these catalysts also have serious drawbacks such as low catalytic activities, narrow temperature windows and insufficient hydrothermal stability [23].

An alternative approach is the use of NO\textsubscript{x} storage-reduction (NSR) catalysts along with mixed lean combustion, where the air-fuel ratio is altered between lean (oxygen excess) and rich (fuel excess) conditions [15,24]. During the relatively long lean periods, NO\textsubscript{x} is stored on a storage component, e.g. barium. In the presence of O\textsubscript{2}, HC, and CO are readily oxidized into H\textsubscript{2}O and CO\textsubscript{2}. As the NO\textsubscript{x} storage component gets saturated, the catalyst needs to be regenerated. This is done during short rich operation of the engine with the
stoichiometric air-fuel mixture. The resulting exhaust becomes comparatively oxygen-deficient and HC, H₂ and CO remain un-oxidized. The stored NOₓ is released and reacts with HC, H₂ and CO over noble metals like Pt into the harmless N₂, H₂O, and CO₂.

Using the NSR catalyst seems to be very promising to achieve high NOₓ conversion, even under lean atmosphere. Nevertheless, a number of issues arises from implementation of this concept, such as fuel penalty for the rich events, sensitivity for fuel sulfur levels and control under transient engine operation. To keep the fuel consumption as well as the exhaust gas emissions to a minimum, a model-based controller can be used. It is necessary for a proper control model to understand in detail the NSR mechanism.

1.4. Aim and lay-out of the thesis

The NSR process has been the focus of several kinetic studies (see [25] and references herein). However, there is still no clear agreement on the steps through which NOₓ storage and reduction occurs. The aim of this thesis, and part of the STW project STW/CW 790.35.774, is therefore to obtain more insight in the NSR mechanism, using both experimental methods and modeling. The focus was on NOₓ storage and reduction on an automotive Pt-Ba/γ-Al₂O₃ (1 wt. % Pt and 30 wt. % Ba) catalyst. Lean/rich cycling experiments were performed in a packed bed reactor. Catalyst characterization using thermogravimetric analysis (TGA) combined with mass spectrometry (MS), XRD, BET analysis and Pt dispersion measurement has been done to support the model results.

Chapter 2 shows the NOₓ storage and reduction behavior of the Pt-Ba/γ-Al₂O₃ catalyst during different lean/rich cyclic timings, in the absence of CO₂ and H₂O. To achieve a better understanding of the NOₓ storage process, excess H₂ and long regeneration times were used during the rich phase of the cycle to ensure complete catalyst regeneration. Lean/rich cycles were repeated until cyclic steady state is reached. Multiple storage sites are active in the NOₓ trapping process. In practice, the vehicle exhaust gas always contains CO₂ and H₂O. In order to better clarify the influence of CO₂ and H₂O and to understand the role of the multiple storage sites, Chapter 3 presents
lean/rich cycling experiments in the absence and presence of CO$_2$ and H$_2$O. Chapter 4 demonstrates a global reaction kinetic model based on a multiple storage sites mechanism for the NSR process in the presence of CO$_2$. The model provides better understanding of the reaction steps and barium utilization during the NO$_x$ storage process. Chapter 5 describes a comparative study on the NO$_x$ reduction/regeneration capabilities of the Pt-Ba/$\gamma$-Al$_2$O$_3$ catalyst. Different reductants (H$_2$, CO, and C$_2$H$_4$) are used in the absence and presence of H$_2$O in the rich phase. CO$_2$ was always present in both the lean and rich phase. Subsequently, in Chapter 6 the global reaction kinetic model is used to understand and describe the NSR process in the presence of CO$_2$ and H$_2$O at different temperatures (200 – 300 $^\circ$C) and different reductants (H$_2$, CO, and C$_2$H$_4$). Finally, the main conclusions of this thesis and the outlook are presented in Chapter 7.

Please note that each chapter presented in this thesis is presented in the form as they are published or intended to be published in scientific journals. Each chapter can be read separately from the rest of this thesis. Consequently, this may cause some overlaps or repetitions in some of the sections of the chapters, e.g. in the introduction and modeling parts.

References
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* All mentioned internet pages accessed on February 3, 2007
** Downloads available at http://europa.eu.int/eur-lex
2

NO\textsubscript{x} storage/reduction in the absence of CO\textsubscript{2} and H\textsubscript{2}O

This chapter has been published as:

Abstract
This paper shows the behavior of a Pt/Ba/γ-Al\textsubscript{2}O\textsubscript{3} automotive catalyst in a fixed bed reactor during cyclic operation at lean and rich gas phase conditions at short (seconds) and long (hours) cycling times at different temperatures. Reactor exit gas phase concentrations have been measured and catalyst properties have been determined before and after selective cycling experiments. The experimental results indicate that: (i) Upon 9 h lean and 15 h rich cycling, the NO oxidation efficiency of the catalyst decreases with time while incomplete regeneration is seen, even after 15 h rich exposure with H\textsubscript{2}. The cyclic steady state is reached after 3 lean/rich cycles, at which only 60 \% of the available barium is involved in the NO\textsubscript{x} storage/reduction. (ii) The BET surface area, pore volume, and Pt dispersion decrease by approximately 40 \%, which may be a result of masking of Pt sites or blocking of pores of the barium clusters as BaCO\textsubscript{3} becomes Ba(NO\textsubscript{3})\textsubscript{2}. Experiments with catalyst pellet sizes of 180 and 280 μm along with XPS measurements show that
blocking of catalyst pellet pores is not taking place. (iii) When applying lean/rich cycling in the order of seconds, it appears that catalyst history and lean/rich timing affect the number of cycles required to arrive at a closed N balance. XRD results after lean exposure confirm the formation of barium nitrate in the bulk of the barium cluster.

2.1. Introduction

Higher fuel efficiency and reduced emissions of the greenhouse gas CO₂ make diesel and lean-burn engines attractive compared to conventional gasoline engines. However, controlling the exhaust NOₓ emission has been recognized as one of the most challenging aspects for lean-burn engine technology as the conventional three-way catalyst is not effective in reducing NOₓ in a lean exhaust due to the high oxygen level. A NOₓ storage/reduction (NSR) catalyst [1] is among the most promising solutions to control NOₓ in lean exhaust. The NSR catalyst contains a storage component in order to store NOₓ under lean conditions. Catalyst regeneration is necessary as the storage capacity of the adsorbing component gets saturated. Regeneration takes place by the introduction of a short period of rich driving, as injections of extra fuel cause decomposition of stored NOₓ and subsequent reduction into N₂. A critical aspect of the NSR technology is the catalyst deactivation by sulfur [2,3]. A detailed understanding about the NOₓ storage and reduction mechanism is important for improving catalyst regeneration times and preventing catalyst deactivation.

The NSR catalytic system most often contains γ-Al₂O₃ as the supporting material, the precious metal Pt for oxidation and reduction, and barium as the NOₓ adsorbing component [1]. The generally proposed mechanism for NOₓ storage, the disproportionation mechanism [2,3,4], suggests that the first step in the NOₓ storage process is the oxidation of NO into NO₂ over precious metals, followed by the storage of NO₂ on the storage component in the form of nitrates. In recent work [8,9] it is suggested that NOₓ storage is accomplished via two parallel routes: (i) the disproportionation route (“nitrate route”), and (ii) the “nitrite route”, where NO is oxidized in the presence of oxygen to form nitrite species, followed by oxidation to nitrates.
Many versions of these mechanisms can be found in the literature with varying level of complexity [10]. In most cases the NO\textsubscript{x} storage/reduction mechanism is based on a single type of barium site [7,8]. The shrinking core mechanism has been used to describe the NO\textsubscript{x} storage process [13-16]. Hepburn et al. [11], Olsson et al. [12], and Tuttlies et al. [13] have developed global models based on this mechanism. They assume that NO\textsubscript{x} diffusion inside the barium clusters is the rate controlling step in the NO\textsubscript{x} storage process. In these models no distinction is made between reactivity of surface and bulk barium sites towards NO\textsubscript{x} storage. However, there is clear evidence in the literature that multiple types of barium sites exist, which differ in reactivity [9,17]. Barium sites close to Pt sites are considered to be more reactive than barium sites located further away [6,9]. Barium can be present in the catalyst as BaO, Ba(OH)\textsubscript{2}, or BaCO\textsubscript{3}, depending on the reaction conditions. NO\textsubscript{x} storage occurs preferentially at BaO, then at Ba(OH)\textsubscript{2}, followed by BaCO\textsubscript{3} sites [19].

The effect of reductants for catalyst regeneration has also been investigated in the literature [20,21]. James et al. [20] found that CO facilitates Ba(NO\textsubscript{3})\textsubscript{2} decomposition, but not NO\textsubscript{x} reduction. However, H\textsubscript{2} enables both to take place, with high conversion to N\textsubscript{2}. Further, Liu and Anderson [21] proposed the order of efficiency in terms of stored NO\textsubscript{x} reduction as H\textsubscript{2} > CO > propene.

In this paper, the focus is to understand how the barium utilization may be affected by NO\textsubscript{x} diffusion from the surface of the barium cluster to the bulk barium sites and which barium containing species are involved in the NO\textsubscript{x} storage/reduction process. Experiments are performed exposing 1 wt \% Pt / 30 wt \% Ba / γ-Al\textsubscript{2}O\textsubscript{3} catalyst to 9 h lean/15 h rich cycling conditions. Additionally, cycle times in the order of seconds are used, to mimic automotive reaction conditions. NO is used as NO\textsubscript{x} source, while H\textsubscript{2} is used as a reductant. For better understanding of catalyst behavior, catalyst characterization using XPS, XRD, BET, Pt and barium dispersion measurements have been done.
2.2. Experimental

2.2.1. Alternation of lean and rich flows

Lean/rich cycling experiments are performed with a fixed bed reactor made of titanium. The catalyst bed is retained by two sintered plates and has a length of 15 mm and a diameter of 14 mm. The reactor tube is heated by an electric coil, wrapped around the reactor jacket. The temperature in the catalyst bed is measured with thermocouples at three different axial positions: in the center of the reactor, and 3 mm above and 3 mm below the center, to assure isothermal conditions. Radial temperature profiles are monitored by a thermocouple located on the outside of the reactor wall. This thermocouple is used as input for a PID controller, which sets the reactor temperature. The reactor has two separate feed lines, each with its own set of mass flow controllers, which allows periodical alterations between lean and rich gas compositions. The gas lines are heated before entering the reactor in a preheater in order to maintain the desired temperature in the reactor.

The gas composition is measured with an online quadrupole mass spectrometer (ESS) at the beginning and at the end of the catalyst bed. A fixed amount of argon is fed as an internal standard during experiments and calibration to compensate for any intensity loss of the mass spectrometer. The mass spectrometer is calibrated weekly. Gas analysis is performed on m/e 2 (H₂), 17 (NH₃), 18 (H₂O), 28 (N₂ + CO₂), 30 (NO + NO₂), 32 (O₂), 40 (Ar), 44 (CO₂ + N₂O) and 46 (NO₂).

A NOₓ storage catalyst, Pt/Ba/Al₂O₃ (1/30/100, w/w/w), is used in powder form as provided by Engelhard. The catalyst is sieved to obtain size fractions with average pellet diameters of 180 and 280 μm, respectively. Typically 1.9 gram of catalyst is used in the NOₓ storage/reduction experiments. The fresh catalyst is pre-treated at 773 K with 1 vol. % of oxygen in helium during 1 h, followed by 0.5 h in helium, and finally by reduction with 2 vol. % of hydrogen in helium for 2 h. The total gas flow during the experiments is kept constant at 0.743 mmol/s, resulting in a gas space velocity (GHSV) of 29,000 h⁻¹ (standard conditions 298 K, 1 bar). During the lean phase, the feed gas contains a mixture of 0.2 vol. % NO, 4 vol. % O₂ and 1 vol. % Ar in a helium carrier. The rich phase contains 0.8 vol. % H₂ and 1
vol. % Ar in a helium carrier. During the experiments, the reactor temperature and the lean/rich timing are varied.

2.2.2. Catalyst characterization

Surface area, pore volume, and pore size distribution are determined of fresh catalyst samples, pretreated catalyst samples, and catalyst samples used in lean/rich cycling experiments. Samples used in lean/rich cycling experiments are obtained after the cyclic steady state was reached. The surface area is determined with the BET method at 77 K with N\textsubscript{2} as the adsorbent using a Tristar Micromeritics instrument. The BJH pore size distribution and pore volume are calculated from the N\textsubscript{2} desorption isotherm. Pt dispersion is obtained from CO chemisorption at 298 K using an ASAP-2000 Micromeritics instrument and is determined for pretreated catalyst samples and catalyst samples used in lean/rich cycling experiments. CO\textsubscript{2} chemisorption is used to estimate the barium dispersion, according to the method described by Li et al. [15]. Powder X-ray diffraction is measured with a Rigaku Geigerflex diffractometer. Typically, an XRD spectrum is recorded in the range 15\textdegree < 2\theta < 75\textdegree using Cu-K\textsubscript{\alpha} radiation. XPS measurements are performed on a VG-Escalab spectrometer using an aluminum anode (Al K\textsubscript{\alpha} = 1486.3 eV) operating with a background pressure of 2*10^{-9} mbar. A takeoff angle of 90\textdegree (between the sample surface and the axis of the analyzer lens) is used. Spectra are recorded within 2 min in order to minimize radiation damage of the sample. Peak fitting is done with CasaXPS Version 2.19 software.

2.3. Results

2.3.1. Lean/rich cycling in the order of hours

The pretreated catalyst was exposed to lean/rich cycling experiments with 9 h lean flow and 15 h rich flow at 643 K. The measured reactor outlet NO, NO\textsubscript{2}, H\textsubscript{2}O and CO\textsubscript{2} concentrations are displayed as a function of time in Figure 2.1a.
In the first lean phase (cycle 1), complete NO\textsubscript{x} storage is observed for 14.1 min. Immediate formation of H\textsubscript{2}O in the gas phase is observed, followed by CO\textsubscript{2} formation after 5 min. The evolution of H\textsubscript{2}O and CO\textsubscript{2} suggests that Ba(OH)\textsubscript{2} and BaCO\textsubscript{3} take part in the formation of Ba(NO\textsubscript{3})\textsubscript{2}. The delay in CO\textsubscript{2} evolution might be due to a lower reactivity of BaCO\textsubscript{3} for NO\textsubscript{x} trapping compared to BaO and Ba(OH)\textsubscript{2}. Lietti et al. [19] found similar results, although
H₂O evolution was not observed. The discrepancy with our results can be explained by absence of Ba(OH)₂ in case of Lietti et al., which might be the result of difference in catalyst pretreatment. Lietti et al. oxidized the catalyst before lean/rich cycling experiments while in our case the catalyst was oxidized followed by reduction with H₂. During reduction with H₂, Ba(OH)₂ can form. At the end of the lean phase 93 % of the total barium present participates in the NOₓ storage process assuming that two moles of NOₓ are stored per mole barium and negligible capacity of γ-Al₂O₃ for NOₓ storage at 643 K [23]. The involvement of different barium containing species is also presented in Table 2.1, where major contribution of BaCO₃ can be clearly seen.

<table>
<thead>
<tr>
<th>Cycle no</th>
<th>% Ba active</th>
<th>% Ba active as BaO</th>
<th>% Ba active as Ba(OH)₂</th>
<th>% Ba active as BaCO₃</th>
<th>% reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>93</td>
<td>6</td>
<td>11</td>
<td>76</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>71</td>
<td>37</td>
<td>26</td>
<td>8</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>36</td>
<td>24</td>
<td>-</td>
<td>59</td>
</tr>
</tbody>
</table>

*Lean phase: 0.2 vol. % NO, 4 vol. % O₂ and 1 vol. % Ar in He, 9 hrs.*

*Rich phase: 0.8 vol. % H₂ and 1 vol. % Ar in He, 15 hrs. T=643 K.*

*Pretreated catalyst was used. See also Figure 1.*

NO₂ breakthrough is observed after 16.5 min and shows a delay compared to the NO breakthrough (after 14.1 min). After NO₂ breakthrough, the NO₂ outlet concentration reaches to a maximum of 0.096 vol. %, which then decreases to a value of 0.068 vol. % at the end of the lean phase. This indicates that the NO oxidation efficiency is changing with time during NOₓ storage. This issue is discussed later on in detail.

The subsequent rich phase is shown in Figure 2.1b. Upon switching from lean to rich, immediate N₂ formation and NOₓ release along with H₂O and O₂ production can be seen. During the period of N₂ production, the fed H₂ is completely consumed (not shown), while simultaneously Ba(NO₃)₂ is converted into Ba(OH)₂ and BaO. No N₂O is detected during the entire rich
phase, while NH₃ formation is seen once the N₂ production declines. The NH₃ formation indicates that the selectivity towards N₂ decreases with time, which seems to be in concinnity with diminishing quantity of NOₓ and O₂. Even though H₂ is a strong reductant [21], the N balance shows that only 79 % of the total barium is regenerated after 15 h rich phase (Table 2.1). As a result, 21 % of the barium will be inactive for further NOₓ storage and reduction.

The subsequent lean phase (cycle 2) shows complete NO storage for 28.8 min, as against 14.1 min for the first lean cycle. This may be the result of an increase in the number of BaO and Ba(OH)₂ sites compared to BaCO₃ sites, as can be seen through a greater extent of H₂O evolution and less CO₂ formation compared to the first cycle. BaO and Ba(OH)₂ are more active in NOₓ trapping [19], which increases the catalyst reactivity towards NOₓ storage. Additionally, due to an increase of the number of the more reactive barium containing species, complete NO₂ storage is seen for 44.6 min, as against 16.5 min for the first lean phase. However, as a result of further decrease in the oxidation activity of the catalyst, the NO₂ concentration at the end of the lean phase is 0.05 vol. %. The total barium participation in the second lean phase is 71 % (Table 2.1). This may be explained by incomplete regeneration in the first cycle. The subsequent rich phase shows similar trends as observed for the previous cycle. In this case only 60 % of the total barium is regenerated (Table 2.1).

The lean phase of the third cycle shows H₂O evolution at the same extent as the previous cycle, but with negligible CO₂ formation. Interestingly, NO and NO₂ breakthrough is observed after 24.6 and 26.5 min, as against 28.8 and 44.6 min, respectively, for cycle 2. This may be due to the incomplete regeneration of the catalyst along with changes in NO oxidation efficiency, as seen in the previous cycles. The end NO₂ concentration in the third cycle is even lower, i.e. 0.04 vol. %. The subsequent cycles show the same phenomena as observed in the third cycle, indicating that the cyclic steady state has been reached. The N balance for these cycles closes within 5% and approximately 60 % of the total barium participates in NOₓ storage and reduction.

A decrease in NO oxidation efficiency of the catalyst and incomplete regeneration of stored NOₓ at rich conditions are also seen when exposing a
pretreated catalyst to lean/rich cycling at different temperatures. However, the number of lean/rich cycles before the cyclic steady state is reached differs since temperature has an effect on the NO\textsubscript{x} storage and reduction, e.g. at a temperature of 513 K with 9 h lean exposure, 30 % of total barium was involved in the NO\textsubscript{x} storage process when cyclic steady state was reached. This percentage increases up to 60 % for a temperature of 643 K.

![Figure 2.2: Top) Outlet NO, NO\textsubscript{2} and NO\textsubscript{x} concentrations during NO\textsubscript{x} storage. Lean: 0.2 vol. % NO, 4 vol. % O\textsubscript{2} and 1 vol. % Ar in He, 9 h, T=513 K. Bottom) Outlet N\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O and NO\textsubscript{x} concentrations during the first 10 min of the reduction period. Rich: 0.8 vol. % H\textsubscript{2} and 1 vol. % Ar in He, 15 h, T=513 K. The cyclic steady state was reached.](image)

2.3.2. Lean and rich characteristics

In general, three different time periods can be distinguished in the 9 h lean phase, as presented in Figure 2.2a. In the first period (< 7 min), complete storage of NO\textsubscript{x} can be seen. As there is no NO nor NO\textsubscript{2} breakthrough, it is unlikely that NO\textsubscript{x} is stored through the disproportionation route only. Accordingly, and in line with observations in the literature, NO\textsubscript{x} can also be stored via the nitrite route [8, 9]. During the second period (7 – 150 min) NO\textsubscript{x} breakthrough with considerable NO\textsubscript{x} storage can be seen. The third period (>
150 min) is characterized by a slow but still measurable uptake of NO\textsubscript{x}, which could be caused by diffusion of NO\textsubscript{x} from the surface of the barium clusters to bulk barium sites [13-15, 24].

Upon switching from lean to rich conditions, immediate formation of N\textsubscript{2} and NO\textsubscript{x} is seen (Figure 2.2b). This is followed by H\textsubscript{2}O and O\textsubscript{2} formation with a delay of 36 s. Prinetto et al [25] observed that O\textsubscript{2} is not evolved with nitrite decomposition. This implies that O\textsubscript{2} formation observed in our results is due to nitrate decomposition. The delay in H\textsubscript{2}O and O\textsubscript{2} formation might be explained with re-adsorption of H\textsubscript{2}O and O\textsubscript{2} onto the catalyst. It is remarkable that O\textsubscript{2} is observed in the gas phase as it could be expected that O\textsubscript{2} competes with NO\textsubscript{x} for reduction by H\textsubscript{2}. This indicates that H\textsubscript{2} is selective towards NO\textsubscript{x} reduction in contrast to CO that prefers to react with O\textsubscript{2} instead of NO\textsubscript{x} [20].

Table 2.2. BET surface area, pore volume and Pt dispersion.

<table>
<thead>
<tr>
<th></th>
<th>BET (m\textsuperscript{2}/g)</th>
<th>Pore volume (cm\textsuperscript{3}/g)</th>
<th>Pt dispersion (%)</th>
<th>Ba dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh catalyst</td>
<td>71</td>
<td>0.22</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pretreated catalyst</td>
<td>70</td>
<td>0.22</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>After lean phase</td>
<td>43</td>
<td>0.15</td>
<td>11</td>
<td>-</td>
</tr>
<tr>
<td>After rich phase</td>
<td>45</td>
<td>0.18</td>
<td>11</td>
<td>-</td>
</tr>
</tbody>
</table>

The data shown for the catalyst after a lean phase and a rich phase are data measured after the catalyst had reached the cyclic steady state.

2.3.3. Changes in catalyst activity for NO\textsubscript{x} storage/reduction

Catalysts containing platinum and barium are less capable in oxidizing NO compared to catalysts only containing Pt [5,12]. This could be due to masking of the Pt sites by barium [12]. During the NO\textsubscript{x} storage, Ba(NO\textsubscript{3})\textsubscript{2} is formed which has a molar volume twice that of BaCO\textsubscript{3} [13,16], covering even more Pt sites or blocking of catalyst pores. Consequently, NO oxidation efficiency decreases with time. The rich phase (Table 2.1) indicates that not all of Ba(NO\textsubscript{3})\textsubscript{2} is decomposed, resulting in incomplete catalyst regeneration. The measured Pt dispersion after the lean/rich phase, at cyclic steady state, shows a decrease of 40 % compared to the Pt dispersion of the fresh catalyst (Table 2.2). This signifies that Pt is essential for NO oxidation/reduction as well as for Ba(NO\textsubscript{3})\textsubscript{2} decomposition, in agreement with the literature [6].
Measurements also show a decrease of 40 % in the catalyst BET surface area and pore volume.

![Figure 2.3: Top: NO\textsubscript{x} outlet concentrations during the lean period for average pellet sizes of 180 \, \mu m and 280 \, \mu m respectively. Lean: 0.2 vol. % NO, 4 vol. % O\textsubscript{2} and 1 vol. % Ar in He, 9 h. Bottom: N\textsubscript{2} concentrations during the rich period for average pellet sizes of 180 and 280 \, \mu m. Rich: 0.8 vol. % H\textsubscript{2} and 1 vol. % Ar in He, 15 h. T= 643 K. Cyclic steady state was reached.](image)

Lean/rich cycling experiments with different catalyst pellet sizes show the same extent of NO\textsubscript{x} storage and reduction behavior for both pellet sizes (Figure 2.3). This excludes diffusion limitation on the scale of the catalyst pellet and is an indication of volumetric effects, meaning that the surface of the catalyst pellet behaves the same as the inner part. This is supported by an XPS measurement for milled and non-milled catalyst pellets (Figure 2.4) after a lean phase. The milled and non-milled samples show the same XPS pattern with identical Ba(NO\textsubscript{3})\textsubscript{2} peaks. This excludes the possibility that the decrease in catalyst activity is due to pore blocking at the scale of catalyst pellets, as suggested as one of the possible reasons for diffusion limitation by Muncrief et al. [24]. However, it may still be possible that pore blocking at the scale of the barium clusters is taking place, as a result of the increase in the molar volume of the barium clusters during NO\textsubscript{x} storage.
Figure 2.4: XPS measurement of the catalyst after lean exposure. Cyclic steady state was reached. Lean: 0.2 vol. % NO, 4 vol. % O₂ and 1 vol. % Ar in He, 9 h. T=573 K. Black: pellets as taken out of the reactor. Grey: Crushed pellets. The right-hand side shows an enlargement of the N-signal.

Figure 2.5: Outlet NOₓ and N₂ concentrations during lean/rich cycling starting with a pretreated catalyst. Selected cycles out of a series of 200 cycles are shown. Lean: 0.2 vol. % NO, 4 v% O₂ and 1 vol. % Ar in He, 60 s. Rich: 0.8 vol. % H₂ and 1 vol. % Ar in He, 15 s.
2.3.4. Lean and rich cycling in the order of seconds

The pretreated catalyst was exposed to alternating cycles of lean and rich flows with cycle periods in the order of seconds. Figure 2.5 shows selected NO\textsubscript{x} storage and reduction data out of a series of 200 cycles with a lean flow of 60 s and a rich flow of 15 s. During the first few storage/reduction cycles all fed NO\textsubscript{x} is stored. During the catalyst regeneration period, N\textsubscript{2} formation and NO\textsubscript{x} desorption are observed. NO\textsubscript{x} stored during each lean period is not fully reduced during the subsequent rich period as can be concluded from the N balance per complete cycle (lean and rich phase) as shown in Figure 2.6. As a result nitrates accumulate inside the catalyst. For the first cycles the N balance shows a deviation around 50 % indicating that steady cyclic operation has not been reached yet. After approximately 28 cycles the deviation drops steeply to 10 % around cycle 50 and then slowly decreases. Just then, NO\textsubscript{x} immediately breaks through after switching to lean conditions. At that moment, the nitrates accumulation corresponds with 17 % of the total number of barium sites. As mentioned in Table 2.2, the barium dispersion, as estimated from CO\textsubscript{2} chemisorption, is 10 %. This suggests that even with lean/rich cycling in the order of seconds, bulk barium sites play a role in the NO\textsubscript{x} storage process. The XRD pattern of the catalyst after lean exposure (Figure 2.7) shows crystalline barium nitrate, indicating as well that bulk barium nitrates are formed.

Table 2.3. Number of cycles before the cyclic steady state is reached for different lean/rich timing.

<table>
<thead>
<tr>
<th>Lean/rich timing</th>
<th>Number of cycles before cyclic steady state is reached</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean 60 s / Rich 15 s</td>
<td>120</td>
</tr>
<tr>
<td>Lean 240 s / Rich 60 s</td>
<td>Immediately</td>
</tr>
<tr>
<td>Lean 120 s / Rich 30 s</td>
<td>24</td>
</tr>
</tbody>
</table>

*Lean phase: 2000 ppm NO and 4 v% O\textsubscript{2}. Rich phase: 8000 ppm H\textsubscript{2}; T = 623 K.*

Pretreated catalyst was exposed to 60 s lean/15 s rich, followed by 240 s lean/60 s rich and 120 s lean/30 s rich.

As the lean/rich cycling proceeds, the NO\textsubscript{x} concentration at the reactor outlet increases until the system reaches a state of steady cycling and all observed phenomena are reproducible in succeeding cycles. It should be
noted that, as shown in Figure 2.5, the increase in the NO\textsubscript{x} concentration is very small over two successive cycles. Nevertheless the catalyst might still be far from the cyclic steady state, as is apparent from the N balance (Figure 2.6).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.6}
\caption{N balance per full cycle for lean/rich cycling as shown in Figure 2.5.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.7}
\caption{XRD pattern after lean/rich cycling, ending with lean exposure. Lean: 0.2 vol. \% NO, 4 v\% O\textsubscript{2} and 1 vol. \% Ar in He, 60 s. Rich: 0.8 vol. \% H\textsubscript{2} and 1 vol. \% Ar in He, 15 s. The cyclic steady state was reached. * corresponds with Ba(NO\textsubscript{3})\textsubscript{2}.}
\end{figure}

Only after 100 cycles the N balance closes within 5\%. When the lean and rich timings are increased to 240 s and 60 s respectively, it appears that the cyclic
steady state is reached immediately (Table 2.3). When changing the lean time to 120 s and the rich time to 30 s, 24 lean/rich cycles are needed before the cyclic steady state is reached (Table 2.3). It seems that this number of cycles depends on the history of the catalyst and the experimental conditions. More cycles are necessary, if the lean phase is shorter or the rich phase is longer.

2.4. Conclusions

NO\textsubscript{x} storage/reduction has been investigated in a fixed bed reactor over Pt/Ba/γ-Al\textsubscript{2}O\textsubscript{3} catalyst with alternating flows of NO-O\textsubscript{2}-He and H\textsubscript{2}-He between 513 and 643 K. Approximately 93 % of barium is involved in NO\textsubscript{x} storage as the pretreated catalyst is exposed to 9 h lean conditions. The subsequent rich phase shows incomplete regeneration of stored NO\textsubscript{x}, even after 15 h rich exposure with H\textsubscript{2}. Cyclic steady state is reached after 3 lean/rich cycles, at which only 60 % of the total barium is involved in the NO\textsubscript{x} storage. The NO oxidation efficiency of the catalyst decreases till steady cycling is achieved. The BET surface area, pore volume, and Pt dispersion decrease by approximately 40 %, which may be a result of masking of Pt sites or blocking of the pores of the barium clusters as BaCO\textsubscript{3} becomes Ba(NO\textsubscript{3})\textsubscript{2}. Experiments with different catalyst pellet sizes along with XPS measurements show that blocking of the catalyst pellet pores is not taking place. In general, even after 9 h of lean exposure, NO\textsubscript{x} storage slowly continues which points to a diffusional process and formation of bulk barium nitrate. Switching from lean to rich, a NO\textsubscript{x} breakthrough peak is observed, followed by a period of simultaneous evolution of N\textsubscript{2}, O\textsubscript{2}, and H\textsubscript{2}O, and decaying amounts of NO\textsubscript{x}. Apparently, the reaction of H\textsubscript{2} with NO\textsubscript{x} is favored over H\textsubscript{2} consumption by O\textsubscript{2}. When applying lean/rich cycling in the order of seconds, it appears that the catalyst history and the lean/rich timing affect the number of cycles required to arrive at a closed N balance. XRD measurement after lean exposure confirms formation of bulk barium nitrate.

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References

Influence of CO\textsubscript{2} and H\textsubscript{2}O on NO\textsubscript{x} storage/reduction

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Abstract
In this paper, the effect of CO\textsubscript{2} and H\textsubscript{2}O on NO\textsubscript{x} storage and reduction over a Pt-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3} (1 wt. % Pt and 30 wt. % Ba) catalyst is shown. The experimental results reveal that in the presence of CO\textsubscript{2} and H\textsubscript{2}O, NO\textsubscript{x} is stored on BaCO\textsubscript{3} sites only. Moreover, H\textsubscript{2}O inhibits the NO oxidation capability of the catalyst and no NO\textsubscript{2} formation is observed. Only 16 % of the total barium is utilized in NO storage. The rich phase shows 95 % selectivity towards N\textsubscript{2} as well as complete regeneration of stored NO. In the presence of CO\textsubscript{2}, NO is oxidized into NO\textsubscript{2} and more NO\textsubscript{x} is stored as in the presence of H\textsubscript{2}O, resulting in 30 % barium utilization. Bulk barium sites are inactive in NO\textsubscript{x} trapping in the presence of CO\textsubscript{2}. NH\textsubscript{3} formation is seen in the rich phase and the selectivity towards N\textsubscript{2} is 83 %. Ba(NO\textsubscript{3})\textsubscript{2} is always completely regenerated during the subsequent rich phase. In the absence of CO\textsubscript{2} and H\textsubscript{2}O, both surface and bulk barium sites are active in NO\textsubscript{x} storage. As lean/rich cycling proceeds, the selectivity towards N\textsubscript{2} in the rich phase decreases from 82 % to
47 % and the N balance for successive lean/rich cycles shows incomplete regeneration of the catalyst. This incomplete regeneration along with a 40 % decrease in the Pt dispersion and BET surface area, explains the observed decrease in NOx storage.

3.1. Introduction

Diesel and lean burn gasoline engines have a better fuel economy and lower emissions of gaseous pollutants than the conventional gasoline engines, which operate at stoichiometric air to fuel ratios. However, due to the excess O2 in the exhaust gas, the 3-way catalyst is ineffective in NOx reduction. One promising solution to reduce NOx during lean exhaust operation is the use of a NOx storage reduction (NSR) catalyst [1]. The NSR catalytic systems usually investigated are Pt-based oxidation catalysts, which contain barium as a storage component [2]. NSR catalytic systems operate under cyclic conditions, during which NOx is stored under lean conditions and subsequent catalyst regeneration takes place during periodic, brief fuel-rich excursions of the engine. Understanding the NSR mechanism is crucial for reducing catalyst regeneration times.

The NSR process has been the focus of several kinetic studies [2 and references herein] and different mechanisms have been proposed for the NOx storage. It is generally believed that first NO is oxidized to NO2 over Pt sites. NO2 can be stored via a disproportionation route resulting in nitrate formation and NO release in the gas phase [3-5], or via a direct route without NO release [6,7]. It is also suggested that NO can be stored as barium nitrites [3,8,9]. Nitrites can be further oxidized into nitrates with NO2 as oxidizing agent [10-12]. Upon switching to rich conditions, stored NOx will be released and reduced into N2. Several studies have been performed to understand the effect of different reductants in the rich phase. The order of efficiency in terms of stored NOx reduction is mostly reported as H2 > CO > hydrocarbons [13-15].

The complete NOx breakthrough profile during lean exposure can be divided into three time periods of different length. In the first period, complete NOx storage is seen. During the second period, NOx breakthrough with still considerable NOx storage is observed. The third period is characterized by a
slow NOx storage and is active for a longer time as the other two periods. The three different time periods indicate the presence of multiple types of barium sites with different activity towards NOx storage. Barium can be present in the catalyst as BaO, Ba(OH)2, and BaCO3, depending on the reaction conditions [7]. NOx storage occurs preferentially at BaO, then at Ba(OH)2, followed by BaCO3 sites. It is also reported that, depending on the barium loading, barium is present both as a crystalline, bulk-like phase and as a well-dispersed barium phase [16,17]. The well-dispersed phase shows a higher activity towards NOx storage and reduction than the bulk-like phase [18,19].

In practice, the vehicle exhaust gas always contains CO2 and H2O. However, relatively few studies have reported the effect of CO2 and H2O on NOx storage and reduction. It has been shown that CO2 affects both the NOx trapping and the reduction phases [20]. CO2 inhibits NOx storage [7,20-22], while it promotes NOx release at rich conditions [20,23,24]. In the temperature range of 250 to 400 °C, the presence of 8 % H2O shows an inhibiting effect on NOx storage [22]. However, 1 % H2O shows a promoting effect on NOx trapping at 200 °C and an inhibiting effect at higher temperatures [7].

In order to better clarify the influence of CO2 and H2O on the NSR mechanism and to understand the role of the multiple storage sites, 30 min lean and 120 min rich cycling experiments at 300 °C have been carried out over a Pt-Ba/γ-Al2O3 (1 wt. % Pt and 30 wt. % Ba) catalyst, in the absence and presence of CO2 and H2O. NO is used as NOx source, while H2 is used as reducing agent. To achieve a better understanding of the NOx storage process, excess H2 and long regeneration times have been used during the rich phase of the cycle to ensure complete catalyst regeneration. The catalyst was exposed to a longer lean period as used in real-life application to ensure considerable NOx breakthrough. Additionally, cycle times of 9 h lean and 15 h rich exposures have been used to deduce the effect of CO2 and H2O on the complete NOx breakthrough profile and on the barium utilization. Catalyst characterization using XRD, BET analysis, and Pt dispersion measurements has been done to support the experimental results.
3.2. Experimental

3.2.1. Alternation of lean and rich flows

Lean/rich cycling experiments are performed in a packed bed reactor, which is described in detail elsewhere [25]. The gas composition of reactants and products is measured with an online quadrupole mass spectrometer (ESS). A fixed amount of argon is fed as an internal standard during experiments to compensate for any intensity loss of the mass spectrometer. Gas analysis is performed on m/e 2 (H₂), 17 (NH₃ + H₂O), 18 (H₂O), 28 (N₂ + CO₂ + CO), 30 (NO + NO₂), 32 (O₂), 40 (Ar), 44 (CO₂ + N₂O), and 46 (NO₂). A high resolution magnetic sector mass spectrometer (Jeol JMS GCmate) is also used for the analysis of N₂ + CO and CO₂ + N₂O. A NOₓ storage catalyst, Pt-Ba/γ-Al₂O₃ (1 wt. % Pt and 30 wt. % Ba), is used in powder form as provided by Engelhard. Typically, 1.9 gram of catalyst with average pellet diameter of 180 μm is used. The pressure drop over the bed is less than 5 % of the inlet pressure. The fresh catalyst is pre-treated at 500 °C with 1 vol. % O₂ in He during 1 h, followed by 0.5 h in He, and finally by reduction with 2 vol. % of H₂ in He for 2 h. The total gas flow during the experiments is kept constant at 0.743 mmol/s, resulting in a gas space velocity (GHSV) of 29,000 h⁻¹ (standard conditions 298 K, 1 bar). The lean phase of the cycle contains 0.2 vol. % NO, 4 vol. % O₂, 1 vol. % Ar, 0 or 10 vol. % CO₂, 0 or 10 vol. % H₂O, and a balance of He. The rich phase includes 0.8 vol. % H₂, 1 vol. % Ar, 0 or 10 vol. % CO₂, 0 or 10 vol. % H₂O, and a balance of He. Actually, in practice CO and hydrocarbons make up a significant portion of the reductant in the rich phase. However, quantification of the data with H₂ as reductant is less complicated as H₂ shows no mass overlap at m/e 28 and therefore H₂ is used in this study. H₂ is fed at higher concentrations as typically present in a real exhaust gas to ensure complete catalyst regeneration. NO is also fed at higher concentrations to guarantee enough sensitivity of the mass spectrometer for the gas phase component NO₂. The other experimental conditions are representative for conditions in diesel and lean-burn exhaust gases.
Table 3.1. BET surface area, pore volume and Pt dispersion.

<table>
<thead>
<tr>
<th></th>
<th>BET (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pt dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>71</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>Pretreated</td>
<td>70</td>
<td>0.22</td>
<td>20</td>
</tr>
<tr>
<td>After lean, without CO₂</td>
<td>43</td>
<td>0.15</td>
<td>11</td>
</tr>
<tr>
<td>After rich, without CO₂</td>
<td>45</td>
<td>0.18</td>
<td>11</td>
</tr>
<tr>
<td>After lean, with CO₂</td>
<td>70</td>
<td>0.22</td>
<td>20</td>
</tr>
<tr>
<td>After rich, with CO₂</td>
<td>70</td>
<td>0.22</td>
<td>20</td>
</tr>
<tr>
<td>After lean, with CO₂ + H₂O</td>
<td>70</td>
<td>0.22</td>
<td>20</td>
</tr>
<tr>
<td>After rich, with CO₂ + H₂O</td>
<td>70</td>
<td>0.22</td>
<td>20</td>
</tr>
</tbody>
</table>

Lean exposure without CO₂: 30 min, 0.2 vol. % NO, 4 vol. % O₂, and 1 vol. % Ar. T = 300°C. Rich exposure without CO₂: 120 min, 0.8 vol. % H₂, and 1 vol. % Ar. T = 300°C. Characterization was done after 25 lean/rich cycles. Lean exposure with CO₂: 9 h, 0.2 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂ and 1 vol. % Ar. T = 300°C. Rich exposure with CO₂: 15 h, 0.8 vol. % H₂, 10 vol. % CO₂ and 1 vol. % Ar. T = 300°C. Characterization was done after 3 lean/rich cycles. Lean exposure with CO₂ + H₂O: 9 h, 0.2 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂ and 1 vol. % Ar. T = 300°C. Rich exposure with CO₂ + H₂O: 15 h, 0.8 vol. % H₂, 10 vol. % CO₂ and 1 vol. % Ar. T = 300°C. Characterization was done after 3 lean/rich cycles.

3.2.2 Catalyst characterization

Surface area, pore volume, and pore size distribution are determined of fresh catalyst samples and catalyst samples used in the lean/rich cycling experiments. The surface area is determined with the BET method at 77 K with N₂ as the adsorbent using a Tristar instrument (Micromeritics). The BJH pore size distribution and pore volume are calculated from the N₂ desorption isotherm. Pt dispersion is obtained from CO chemisorption at 298 K with an ASAP-2000 instrument (Micromeritics) using CO chemisorption stoichiometries of 1 CO per Pt atom. The Pt dispersion is determined for pretreated catalyst samples and catalyst samples used in the lean/rich cycling experiments. The BET surface area, pore volume, and Pt dispersion are listed in Table 3.1. Powder X-ray diffraction is measured with a Rigaku Geigerflex diffractometer. Typically, an XRD spectrum is recorded in the range 15° < 20 < 75° using Cu-Kα radiation.
3.3. NO\textsubscript{x} storage-reduction performance

3.3.1. Absence of CO\textsubscript{2} and H\textsubscript{2}O

The pretreated catalyst is exposed to lean/rich cycling experiments with 30 min lean and 120 min rich flow at 300 °C without CO\textsubscript{2} and H\textsubscript{2}O present in the gas feed. Data collected during lean/rich cycle nrs 1, 5, 10, and 25 are shown in Figure 3.1.

![Figure 3.1: Lean outlet concentrations of NO\textsubscript{x}, CO\textsubscript{2} and H\textsubscript{2}O during lean/rich cycling experiments. Lean phase: 0.2 vol. % NO, 4 vol. % O\textsubscript{2} and 1 vol. % Ar, 30 min. Rich phase: 0.8 vol. % H\textsubscript{2}, and 1 vol. % Ar, 120 min.](image)

In the first lean phase (cycle 1), complete NO\textsubscript{x} storage is observed for 15.1 min. Immediate formation of H\textsubscript{2}O is seen, followed by CO\textsubscript{2} formation after 15.0 min. The evolution of H\textsubscript{2}O and CO\textsubscript{2} suggests that Ba(OH)\textsubscript{2} and BaCO\textsubscript{3} take part in the formation of Ba(NO\textsubscript{3})\textsubscript{2}. The delay in CO\textsubscript{2} evolution might be due to a lower activity of BaCO\textsubscript{3} for NO\textsubscript{x} trapping compared to BaO and Ba(OH)\textsubscript{2} [7]. As shown in Figure 3.2, H\textsubscript{2}O evolution is seen during the entire lean period, but changes in H\textsubscript{2}O formation rates suggest that H\textsubscript{2}O evolution occurs through more than one type of site. The first release of H\textsubscript{2}O occurs immediately after switching to lean conditions. This release peak is the same for all lean phases indicating a fixed number of NO\textsubscript{x} trapping sites and probably occurs because of NO\textsubscript{x} trapping on γ-Al\textsubscript{2}O\textsubscript{3} via surface hydroxyl...
groups. This is supported by findings in literature [22,26]. The second H₂O release becomes apparent after 1 min lean phase operation and starts declining after 15 min. This second H₂O release is also present in the fifth lean phase (Figure 3.1), but the H₂O concentration decreases only after 22.1 min, as against 15.1 min for the first lean phase.

![Figure 3.2: H₂O evolution during the first lean phase. See also Figure 3.1.](image)

Catalyst regeneration with H₂ produces N₂ and H₂O. Upon switching to rich conditions, immediate N₂ formation can be seen (Figure 3.3). However, the H₂O signal shows a delay of about 40 s. Most likely, the delay in H₂O formation is due to adsorption of H₂O onto γ-Al₂O₃. After the delay of 40 s, the H₂O concentration increases to the level of 0.64 vol. % and it remains constant until the N₂ production declines. As H₂ is completely consumed during N₂ production (not shown), the H₂O concentration of 0.64 vol. % corresponds to that expected from reaction (1), and is lower than that derived from reaction (2):

\[
\text{Ba(NO}_3\text{)}_2 + 5\text{H}_2 \rightarrow \text{Ba(OH)}_2 + \text{N}_2 + 4\text{H}_2\text{O} \tag{1}
\]

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

This indicates that Ba(OH)₂ is formed during the rich phase. Accordingly, the number of Ba(OH)₂ sites increases compared to BaCO₃ sites, as can be seen through a greater extent of H₂O evolution and less CO₂ formation in the fifth cycle compared to the first lean phase (Figure 3.1). Ba(OH)₂ is more active in NOₓ trapping as BaCO₃ [7], which increases the catalyst activity towards NOₓ.
trapping and more NO\textsubscript{x} is stored (Table 3.2). Additionally, complete NO\textsubscript{x} storage is seen for 22.1 min, as against 15.1 min for the first lean phase. The tenth lean phase shows the same NO\textsubscript{x} breakthrough profile as the fifth lean phase. However, as lean/rich cycling proceeds, the NO\textsubscript{x} trapping activity of the catalyst decreases and less NO\textsubscript{x} is stored (cycle 25). Moreover, complete NO\textsubscript{x} storage is observed for 18.5 min, as against 22.1 min for the tenth lean phase.

Table 3.2. Barium utilization for lean and rich phases in the absence of CO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Cycle no</th>
<th>Lean</th>
<th>1</th>
<th>5</th>
<th>10</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stored NO\textsubscript{x} (μmol/gcat)</td>
<td>1112</td>
<td>1256</td>
<td>1243</td>
<td>1160</td>
<td></td>
</tr>
<tr>
<td>Released H\textsubscript{2}O (μmol/gcat)</td>
<td>395</td>
<td>606</td>
<td>608</td>
<td>575</td>
<td></td>
</tr>
<tr>
<td>Released CO\textsubscript{2} (μmol/gcat)</td>
<td>157</td>
<td>22</td>
<td>9</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

Rich

<table>
<thead>
<tr>
<th>Cycle no</th>
<th>Lean</th>
<th>1</th>
<th>5</th>
<th>10</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles NO\textsubscript{x} released and reduced (μmol/gcat)</td>
<td>1060</td>
<td>1169</td>
<td>1157</td>
<td>1164</td>
<td></td>
</tr>
<tr>
<td>Reduction efficiency (%)</td>
<td>82</td>
<td>73</td>
<td>68</td>
<td>47</td>
<td></td>
</tr>
</tbody>
</table>

Lean: 0.2 vol. % NO, 4 vol. % O\textsubscript{2} and 1 vol. % Ar in He, 30 min. Rich: 0.8 vol. % H\textsubscript{2} and 1 vol. % Ar in He, 120 min. T=300 °C. Pretreated catalyst has been used. See also Figures 3.1 and 3.3.

The decrease in NO\textsubscript{x} trapping activity may be explained by the results obtained during the rich phase operation. Besides N\textsubscript{2} formation, the rich phase also shows immediate NO release (Figure 3.3). NH\textsubscript{3} production is observed once the N\textsubscript{2} formation declines. The N balance for the first cycle (lean and rich) closes within 5 % (Table 3.2). However, data of the fifth rich phase indicate that not all Ba(NO\textsubscript{3})\textsubscript{2} formed in the preceding lean phase is reduced. In a similar series of experiments, the temperature in the rich phase starts at 300 °C. As soon as the reduction process has stopped, the temperature is increased to 500 °C. At 500 °C, part of the remaining Ba(NO\textsubscript{3})\textsubscript{2} is regenerated, which seems to indicate that as lean/rich cycling continues more stable nitrates form that cannot be completely regenerated at temperatures below 500 °C. These barium sites will be inactive for further NO\textsubscript{x} storage and reduction. Also, the N balance of the tenth cycle is not fully closed, demonstrating an increased number of inactive barium sites. This incomplete regeneration along with a decrease in the Pt dispersion and BET
surface area, as can be seen in Table 3.1, may explain the decreased NO\textsubscript{x} trapping capacity as lean/rich cycling proceeds.

\[
\text{Reduction efficiency} = \frac{[2N_2]}{[2N_2] + [NH_3] + [NO_x]} \times 100\%
\]

The first rich phase shows a reduction efficiency of 82% (Table 3.2). The reduction efficiency decreases to 47% for the twenty fifth rich phase. Castoldi et al. [27] reported that the formation of ammonia depends on the formulation and properties of the catalyst. However, as the reduction process is very complex, its mechanism and selectivity is still not understood.

### 3.3.2. Presence of CO\textsubscript{2}

Figures 3.4 and 3.5 show 30 min lean and 120 min rich cycles for an experiment with pretreated catalyst at 300 °C in the presence of CO\textsubscript{2}. In the first lean phase (Figure 3.4, cycle 1), complete NO\textsubscript{x} storage is seen for 7.1
min. Formation of H₂O after 20 s, indicates the participation of γ-Al₂O₃ sites and/or Ba(OH)₂ in the NOₓ storage process. During the pretreatment with H₂, Ba(OH)₂ can form. CO₂ evolution due to nitrate formation on BaCO₃ sites is hard to detect as CO₂ is fed in excess, and is thus not shown. The amount of NOₓ stored (Table 3.3) during the first lean phase in the presence of CO₂ is 828 μmol/g catalyst, as against 1112 μmol NOₓ/g catalyst without CO₂ present in the gas feed. It is reported that CO₂ competes with NOₓ for the same barium sites inhibiting the NOₓ storage [7,20]. The subsequent rich phase is shown in Figure 3.5. Upon switching from lean to rich conditions, N₂ formation and NO release can be seen.

\[ \text{Ba(NO}_3\text{)}_2 + 5\text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{N}_2 + 5\text{H}_2\text{O} \]  \hspace{1cm} (4)

Figure 3.4: Lean outlet concentrations of NOₓ and H₂O during lean/rich cycling experiments. Lean phase: 0.2 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂ and 1 vol. % Ar, 30 min. Rich phase: 0.8 vol. % H₂, 10 vol. % CO₂ and 1 vol. % Ar, 120 min.

The H₂O formation shows a delay of 40 s, due to adsorption of H₂O on alumina sites. After 40 s, the H₂O concentration increases to 0.8 vol. %, as expected from reaction (4).

This suggests that in the presence of CO₂, no Ba(OH)₂ is formed. The H₂O concentration decreases to 0.22 vol. %, once the N₂ production declines. At
the same time, NH₃ and CO formation (not shown) is observed. The CO formation is accompanied by the parallel consumption of H₂ and CO₂ (not shown) and by the parallel production of H₂O. This suggests that the reverse water gas shift (RWGS) reaction takes place. Notably, the reduction process is initially selective to N₂ and once the N₂ production is terminated, NH₃ and CO appear. The reduction efficiency is 79% for the first rich phase. The N balance (Table 3.3) shows that NOₓ stored during the lean phase is completely regenerated during the rich phase.

![Figure 3.5](image-url)

*Figure 3.5: Rich outlet concentrations of NOₓ, N₂, H₂O and NH₃ during lean/rich cycling experiments. Lean phase: 0.2 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂ and 1 vol. % Ar, 30 min. Rich phase: 0.8 vol. % H₂, 10 vol. % CO₂ and 1 vol. % Ar, 120 min.*

The fifth lean phase shows immediate H₂O formation. As shown in Figure 3.6, this H₂O evolution (curve C) is larger as the H₂O evolution (curve A) observed in lean/rich cycling experiments without CO₂ present. On the other hand, during rich exposure the same delay in H₂O formation is seen for both type of experiments, indicating that the same amount of H₂O is trapped on γ-Al₂O₃ sites. However, Figure 3.6 also shows H₂O desorption (curve B) when exposing the catalyst to an inert phase after rich conditions in the presence of CO₂. Curves A and B added give curve D, which strongly resembles curve C. This suggests that curve C represents two events, i.e.
H₂O evolution due to participation of alumina hydroxyl groups in the NOₓ storage process, and H₂O desorption with no relation to the NOₓ storage process. The last-mentioned H₂O desorption is probably attributed to desorption of weakly bounded OH species, which can form during H₂O production in the rich phase as a result of the RWGS reaction. Furthermore, less NOₓ is stored in the fifth lean phase compared to the first cycle (Table 3.3), indicating that BaCO₃ sites are active in the NOₓ storage process. Complete NOₓ storage is seen for 6.2 min, as against 7.1 min for the first lean phase. The N balance is closed for the fifth lean/rich cycle and the reduction efficiency is 83 %. As lean/rich cycling continues, the same NOₓ storage and reduction performance is observed and a cyclic steady state has been reached.

Table 3.3. Barium utilization for lean and rich phases in the presence of CO₂.

<table>
<thead>
<tr>
<th>Cycle no</th>
<th>1</th>
<th>5</th>
<th>10</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lean</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stored NOₓ (μmol/gcat)</td>
<td>828</td>
<td>567</td>
<td>562</td>
<td>564</td>
</tr>
<tr>
<td>Released H₂O (μmol/gcat)</td>
<td>196</td>
<td>216</td>
<td>218</td>
<td>219</td>
</tr>
<tr>
<td><strong>Rich</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moles NOₓ released and reduced (μmol/gcat)</td>
<td>824</td>
<td>564</td>
<td>568</td>
<td>565</td>
</tr>
<tr>
<td>Reduction efficiency (%)</td>
<td>79</td>
<td>83</td>
<td>83</td>
<td>83</td>
</tr>
</tbody>
</table>

Lean: 0.2 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂ and 1 vol. % Ar in He, 30 min.  
Rich: 0.8 vol. % H₂, 10 vol. % CO₂ and 1 vol. % Ar in He, 120 min. T=300 °C.  
Pretreated catalyst. See also Figures 3.4 and 3.5.

After 9 h of lean exposure, 1395 μmol/g catalyst NOₓ is stored, indicating that only 30 % of the barium sites present are participating in NOₓ storage. In a preceding paper [25] we have reported that in the absence of CO₂ 100 % barium utilization is possible. Bulk barium sites are inactive in the NOₓ storage process in the presence of CO₂, which is confirmed by XRD measurements (Figure 3.7). After lean exposure in the presence of CO₂, only peaks characteristic for bulk BaCO₃ can be seen and crystalline Ba(NO₃)₂ is not observed.
Without the participation of bulk barium sites in the NO\textsubscript{x} storage process, the BET surface area, pore volume and Pt dispersion show no changes compared to a pretreated catalyst (Table 3.1). During NO\textsubscript{x} storage, Ba(NO\textsubscript{3})\textsubscript{2} is formed which has a molar volume twice that of BaCO\textsubscript{3} [28, 29], and covering of Pt sites can occur. As 70\% of the total barium sites is present as bulk barium sites [30], their participation in the NO\textsubscript{x} storage process can lead to a substantial increase in Pt coverage and reduction in the BET surface area and pore volume. Furthermore, storage of NO\textsubscript{x} on bulk barium sites can lead to formation of more stable bulk nitrates that cannot be regenerated at the used conditions and the Pt sites stay covered.
3.3.3. Presence of CO$_2$ and H$_2$O

The data obtained with the pretreated catalyst at 30 min lean/120 min rich cycling conditions at 300 °C with both CO$_2$ and H$_2$O in the gas feed, are shown in Figure 3.8. The H$_2$O and CO$_2$ signals are not shown, as H$_2$O and CO$_2$ produced during NO$_x$ storage can hardly be distinguished from the noise in the MS signals because of the high inlet concentrations. The first lean phase shows complete NO$_x$ storage for 3.5 min. After 30 min, 474 $\mu$mol NO$_x$/g catalyst is stored, as against 828 $\mu$mol NO$_x$/g catalyst without H$_2$O present (Table 3.4). Possible explanations for the observed decrease in the NO$_x$ trapping capability will be discussed in section 4. The reduction of stored NO$_x$ in the rich phase is highly selective towards N$_2$ since NH$_3$ is not observed while only minor amounts of NO$_x$ are found (Figure 3.9). The reduction efficiency is 93 %. The N balance is closed (Table 3.4) for the first lean/rich cycle. The RWGS reaction does not take place since CO formation is not observed. The fifth lean phase shows NO$_x$ breakthrough after 3 min, as

![Figure 3.7: XRD patterns of (A) fresh catalyst, (B) after lean/rich cycling, ending with lean exposure. Lean: 0.2 vol. % NO, 4 vol. % O$_2$ and 1 vol. % Ar, 30 min. (C) after lean/rich cycling, ending with lean exposure. Lean: 0.2 vol. % NO, 4 vol. % O$_2$, 10 vol. % CO$_2$ and 1 vol. % Ar, 9 h.](image)
against 3.5 min for the first lean exposure. Additionally, 392 μmol NO\textsubscript{x}/g catalyst is stored, as against 474 μmol NO\textsubscript{x}/g catalyst in the first cycle.

![Graph showing NO\textsubscript{x} concentration over time](image)

*Figure 3.8: Lean outlet concentration of NO\textsubscript{x} during lean/rich cycling experiments. Lean phase: 0.2 vol. % NO, 4 vol. % O\textsubscript{2}, 10 vol. % CO\textsubscript{2}, 10 vol. % H\textsubscript{2}O and 1 vol. % Ar, 30 min. Rich phase: 0.8 vol. % H\textsubscript{2}, 10 vol. % CO\textsubscript{2}, 10 vol. % H\textsubscript{2}O and 1 vol. % Ar, 120 min.*

Ba(OH)\textsubscript{2} is formed during the pre-treatment of the catalyst with H\textsubscript{2}. As a result, Ba(OH)\textsubscript{2} will participate in the NO\textsubscript{x} storage process in the first lean phase. However, with excess CO\textsubscript{2} present in the gas feed, it is expected that BaCO\textsubscript{3} forms during the rich phase, even in the presence of H\textsubscript{2}O. In the next lean phase, only the less reactive BaCO\textsubscript{3} is active in NO\textsubscript{x} trapping and less NO\textsubscript{x} is stored. This is supported by results obtained during a lean phase without CO\textsubscript{2} and with H\textsubscript{2}O present (not shown), as these results only show CO\textsubscript{2} evolution. The N balance is closed for the fifth lean/rich cycle and the reduction efficiency is 95 %. The NO\textsubscript{x} storage and reduction performance is the same for the following lean/rich cycles and the cyclic steady state has been reached. The BET surface area, pore volume, and Pt dispersion show no changes compared to a pretreated catalyst (Table 3.1).
Figure 3.9: Rich outlet concentrations of NO\(_x\), N\(_2\) and NH\(_3\) during lean/rich cycling experiments. Lean phase: 0.2 vol. % NO, 4 vol. % O\(_2\), 10 vol. % CO\(_2\), 10 vol. % H\(_2\)O and 1 vol. % Ar, 30 min. Rich phase: 0.8 vol. % H\(_2\), 10 vol. % CO\(_2\), 10 vol. % H\(_2\)O and 1 vol. % Ar, 120 min.

Table 3.4
Barium utilization for lean and rich phases in the presence of CO\(_2\) and H\(_2\)O.

<table>
<thead>
<tr>
<th>Cycle no</th>
<th>Lean Stored NO(_x) (μmol/gcat)</th>
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<th>25</th>
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<tr>
<td></td>
<td></td>
<td>474</td>
<td>392</td>
<td>398</td>
<td>391</td>
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</table>

<table>
<thead>
<tr>
<th>Cycle no</th>
<th>Rich Moles NO(_x) released and reduced (μmol/gcat)</th>
<th>480</th>
<th>389</th>
<th>399</th>
<th>394</th>
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<tbody>
<tr>
<td></td>
<td>Reduction efficiency (%)</td>
<td>93</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
</tbody>
</table>

Lean: 0.2 vol. % NO, 4 vol. % O\(_2\), 10 vol. % CO\(_2\), 10 vol. % H\(_2\)O and 1 vol. % Ar in He, 30 min. Rich: 0.8 vol. % H\(_2\), 10 vol. % CO\(_2\), 10 vol. % H\(_2\)O and 1 vol. % Ar in He, 120 min. T=300°C. Pretreated catalyst. See also Figures 3.7 and 3.8.

3.4. **Effect of H\(_2\)O and CO\(_2\) on NO\(_x\) storage**

NO\(_x\) storage results obtained during a series of lean/rich cycling experiments with 9 h lean and 15 h rich flow at 300 °C are presented in Figure 3.10a. The data shown are collected when the cyclic steady state had been reached. In this series, excess CO\(_2\) was always present in the gas mixture in
order to prevent changes of the catalyst properties like BET surface area and Pt dispersion. The NO\textsubscript{x} breakthrough profile in the presence of CO\textsubscript{2} can be divided in four time periods. In the first period of the lean phase, complete NO\textsubscript{x} storage is seen. The second period starts after 6.2 min as NO breakthrough is observed. Meanwhile, during the first 30 min, NO\textsubscript{2} is completely consumed. After about 30 min, the NO\textsubscript{2} concentration increases with time. During the first 65 min of the lean phase, there is still considerable NO\textsubscript{x} storage. The third period (after 65 min) is characterized by a slow but still measurable uptake of NO\textsubscript{x} until 200 min. After 200 min, the NO\textsubscript{x} outlet concentration is constant and equals the inlet concentration. The detected 0.14 vol. % NO and 0.06 vol. % NO\textsubscript{2} concentrations can be ascribed to the NO oxidation reaction.

Recently, we have developed a global reaction kinetic model based on a multiple barium storage sites mechanism [30]. Model results show that the initial complete NO\textsubscript{x} uptake can be mainly ascribed to NO storage on barium surface sites in the form of nitrites. As the barium surface sites fill, NO breakthrough is seen. The NO storage process continues at semi-bulk barium sites but at a lower rate due to diffusion limitation. Meanwhile NO\textsubscript{2} is consumed in oxidizing surface nitrites into nitrates and by getting stored as nitrates on semi-bulk barium sites. As a result, delay in NO\textsubscript{2} breakthrough can be seen.

In the presence of H\textsubscript{2}O, no NO\textsubscript{2} formation is detected. Olsson et al. [31] reported that H\textsubscript{2}O inhibits the NO oxidation activity of Pt/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts. Increasing the concentration of H\textsubscript{2}O in the feed gas from 0 to 5 %, leads to a decrease of NO oxidation activity of 33 %. They also found that H\textsubscript{2}O is able to replace NO\textsubscript{x} from the catalyst surface and that this process is reversible. Indeed, after the H\textsubscript{2}O supply is shut-off in our experiments, NO\textsubscript{2} formation is seen in the lean phase. The presence of H\textsubscript{2}O causes NO\textsubscript{x} adsorption on \gamma-Al\textsubscript{2}O\textsubscript{3} sites to be negligible [22,26] and complete NO uptake is observed for 3 min with H\textsubscript{2}O present, as against 6.2 min for experiments without H\textsubscript{2}O present (Figure 3.10b).
Figure 3.10a: Lean NO\textsubscript{x}, NO and NO\textsubscript{2} outlet concentration at cyclic steady state. Lean phase: 0.2 vol. % NO, 4 vol. % O\textsubscript{2}, 10 vol. % CO\textsubscript{2}, (10 vol. % H\textsubscript{2}O) and 1 vol. % Ar, 9 h. Rich phase: 0.8 vol. % H\textsubscript{2}, 10 vol. % CO\textsubscript{2}, (10 vol. % H\textsubscript{2}O) and 1 vol. % Ar, 15 h.

Figure 3.10b: Close-up of Figure 3.10a.

The NO breakthrough curve with H\textsubscript{2}O and the NO\textsubscript{x} breakthrough curve without H\textsubscript{2}O show a similar overall shape for the first 25 min, as NO\textsubscript{x} uptake in
this period can be mainly ascribed to NO storage. Already after 80 min, there is no NO\textsubscript{x} storage in the presence of H\textsubscript{2}O. Additionally, 698 \(\mu\)mol/g NO is stored after 9 h lean exposure in the presence of H\textsubscript{2}O, as against 1395 \(\mu\)mol/g without H\textsubscript{2}O. Results obtained during rich exposure point out that, for all experiments, NO is stored in the form of nitrates. The nitrites formed at the early stage of the lean phase, can be oxidized into nitrates. As no NO\textsubscript{2} is present, dissociative adsorption of O\textsubscript{2} on Pt could serve as a source of oxygen atoms for this oxidation step. Epling et al. [22] suggest that only barium sites in close contact with Pt sites demonstrate this reaction pathway. This may explain the observed lower NO\textsubscript{x} trapping capability in the presence of H\textsubscript{2}O.

3.5. Conclusions

In this paper, we have investigated the effect of CO\textsubscript{2} and H\textsubscript{2}O on NO\textsubscript{x} storage and reduction over a Pt-Ba/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} (1 wt. % Pt and 30 wt. % Ba) catalyst. The main conclusions are:

1. In the presence of H\textsubscript{2}O and CO\textsubscript{2}, NO\textsubscript{x} is stored only at BaCO\textsubscript{3} sites. Moreover, H\textsubscript{2}O inhibits NO oxidation and no NO\textsubscript{2} formation is observed. Even after 9 h lean exposure only 16 % of total barium sites is utilized in NO storage.

2. Predominantly \(N_2\) formation with minor amounts of NO are seen during rich operation in the presence of H\textsubscript{2}O and CO\textsubscript{2}, resulting in a selectivity towards \(N_2\) of 95 %. NO stored in the preceding lean phase is always completely regenerated.

3. In the presence of CO\textsubscript{2} only, NO\textsubscript{x} is stored on \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} and BaCO\textsubscript{3} sites. Bulk barium sites are inactive in NO\textsubscript{x} trapping in the presence of CO\textsubscript{2} and only 30 % of total barium participates in NO\textsubscript{x} storage. The fact that H\textsubscript{2}O inhibits NO oxidation and less NO is stored in the presence of H\textsubscript{2}O, supports the higher storage capacity towards NO\textsubscript{2} than towards NO.

4. Besides \(N_2\) formation and NO release, \(NH_3\) production is observed during rich exposure in the presence of CO\textsubscript{2}. However, the selectivity towards \(N_2\) is still 83 %. Ba(NO\textsubscript{3})\textsubscript{2} is always completely regenerated during the subsequent rich phase.
5. In the absence of H₂O and CO₂, NOₓ is trapped on γ-Al₂O₃ and barium sites. As lean/rich cycling proceeds, the NOₓ trapping capability of the catalyst increases at first, as BaCO₃ sites are exchanged for the more reactive Ba(OH)₂ sites. During NOₓ storage, both surface and bulk barium sites are active, and 100 % barium utilization is possible.

6. As lean/rich cycling continues, more NH₃ is formed during rich exposure and the selectivity towards N₂ decreases from 82 % to 47 %. Simultaneously, the N balance for successive lean/rich cycles shows incomplete regeneration, demonstrating inactive barium sites for further NOₓ storage and reduction. This incomplete regeneration along with a 40 % decrease in the Pt dispersion and BET surface area, leads to a reduced NOₓ trapping capability and thus less NOₓ is stored.

7. In the presence of CO₂, the Pt dispersion, BET surface area, and pore volume remain the same as for the pretreated catalyst.

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References

4

Model for NO$_x$ storage/reduction in the presence of CO$_2$

This chapter has been published as:

Abstract

In this paper a global reaction kinetic model is constructed to understand and describe the NO$_x$ storage/reduction process in the presence of CO$_2$. Experiments have been performed in a packed bed reactor with a Pt-Ba/$\gamma$-Al$_2$O$_3$ powder catalyst (1 wt. % Pt and 30 wt. % Ba) with different lean/rich cycle timings. The model is based on a multiple storage sites mechanism and considers that fast NO$_x$ storage occurs at surface barium sites, which is determined by the reaction kinetics. Slow NO$_x$ storage occurs at the semi-bulk and bulk barium sites, where diffusion plays a major role. It is assumed that surface, bulk and semi-bulk sites not only differ in physical appearance but also in chemical reactivity. The distribution of these sites is obtained from 9 h lean phase and 15 h rich phase cycling experiments and thermogravimetric analysis of fresh catalyst. The model adequately describes the NO and NO$_2$ breakthrough profiles during 9 h lean exposure as well as the subsequent release and reduction of the stored NO$_x$. Further, the model is
also capable of simulating transient reactor experiments with 240 s lean and 60 s rich cycle timings.

4.1. Introduction

The popularity of diesel and lean-burn engines is increasing as they have higher fuel efficiency and less emission of the greenhouse gas CO₂ compared to conventional gasoline engines. However, achieving oxidation of CO and hydrocarbons simultaneously with NOₓ reduction in the exhaust is challenging for lean-burn engines where excess of O₂ in the exhaust gas hinders the reduction of NOₓ. One promising solution to reduce NOₓ during lean exhaust operation is the use of a NOₓ storage reduction (NSR) catalyst [1]. The NSR catalytic systems usually investigated are Pt-based oxidation catalysts, which contain barium as a storage component. Under fuel lean conditions with excess O₂, NOₓ is stored onto the barium as nitrites/nitrates. As the storage capacity of barium gets saturated, the catalyst has to be regenerated. For regeneration, extra fuel is injected resulting in a fuel rich period where NOₓ is released and reduced into N₂. Understanding the NSR mechanism is crucial for reducing catalyst regeneration times and preventing catalyst deactivation. Unfortunately, the NSR catalysts have shown serious deactivation in the presence of SO₂ [2].

The NSR process has been the focus of several kinetic studies [see 3 and references herein]. However, there is no clear agreement on the steps through which NOₓ storage occurs. It is generally believed that first NO is oxidized to NO₂ over Pt sites. NO₂ is stored in the form of barium nitrate [4-7]. NO₂ storage can also proceed via a disproportionation route resulting in nitrate formation and NO release in the gas phase [4,5,8]. There is growing evidence that in the presence of O₂, NO can be stored directly as barium nitrites [4,9]. Additionally, the contribution of direct NO storage increases with increase in barium loading [10]. Nitrites can be further oxidized into nitrates with NO₂ as oxidizing agent [11-13]. Furthermore, several studies have been performed to understand the effect of different reductants in the rich phase. James et al. found that CO facilitates Ba(NO₃)₂ decomposition, but not NOₓ reduction [14]. However, H₂ enables both to take place, with high conversion to N₂.
In general three different time periods can be distinguished during lean exposure. In the first period, complete NO\textsubscript{x} storage is seen. During the second period, NO\textsubscript{x} breakthrough with considerable NO\textsubscript{x} storage is observed. The third period is characterized by a slow NO\textsubscript{x} storage and is active for a longer time as the other two periods. The three different time periods indicate the presence of multiple types of barium sites with different reactivity towards NO\textsubscript{x} storage [15]. Barium sites that are located close to Pt sites are considered to be more reactive than barium sites located further away [16]. Barium can be present in the catalyst as BaO, Ba(OH)\textsubscript{2}, and BaCO\textsubscript{3}, depending on the reaction conditions [7]. NO\textsubscript{x} storage occurs preferentially at BaO, then at Ba(OH)\textsubscript{2}, followed by BaCO\textsubscript{3} sites. Recently, low temperature (LT) and high temperature (HT) barium containing species have been distinguished [17,18]. The crystalline, bulk-like HT-barium sites are thermally more stable in comparison to the well-dispersed LT barium phase. The LT-barium sites show a higher activity towards NO\textsubscript{x} storage and reduction than the HT sites [19,20]. Upon increasing the total barium loading, the number of LT sites initially increases but reaches a constant maximum value at a barium loading of about 17 % (w/w) [18,19]. The HT phase also increases with barium loading, without saturation.

Although there is clear evidence in the literature that multiple types of barium sites exist, models of the NSR process are mostly based on a single type of reaction site. Olsson et al. [21] developed an elementary kinetic model, but the model could not describe the observed decreasing NO\textsubscript{x} trapping activity as the lean phase proceeds. Global models based on shrinking core mechanisms have been used to describe the NO\textsubscript{x} storage process [22-25]. In general, these models assume that NO\textsubscript{x} diffusion inside the barium clusters or NO\textsubscript{x} transfer to the barium sites is the rate controlling step in the NO\textsubscript{x} storage process. The presence of an inactive barium core has been assumed to describe the observed incomplete barium utilization [23]. In all these models no distinction is made between reactivity of surface and bulk barium sites towards NO\textsubscript{x} storage.

Furthermore, the vehicle exhaust gas always contains CO\textsubscript{2} and H\textsubscript{2}O. However, most studies do not take into account the presence of this species. It is reported that CO\textsubscript{2} negatively affects the NO\textsubscript{x} storage process [15,26,27].
while NO$_x$ release studies show that CO$_2$ has a promoting effect on the NO$_x$ release in the rich phase [26,28,29]. The H$_2$O effect is limited to the NO$_x$ storage process mainly at low temperatures (< 300 °C) [26].

The goal of this work is to develop a global reaction kinetic model based on a multiple storage sites mechanism for the NSR process in the presence of CO$_2$. In addition the model provides better understanding of reaction steps and barium utilization during the NSR process, at different time scales. Experiments have been performed in a packed bed reactor with a Pt-Ba/γ-Al$_2$O$_3$ powder catalyst (1 wt. % Pt and 30 wt. % Ba) with different lean/rich cycle timings. The contribution of the different barium sites and the model parameters have been deduced from 9 h lean/15 h rich cycling experiments. The model was validated for other conditions including different NO concentrations and different H$_2$ concentrations. Additionally, cycle times of 240 s lean and 60 s rich have been used to demonstrate the applicability of the developed model for lean/rich timings more closely to realistic automotive exhaust conditions. NO is used as NO$_x$ source, while H$_2$ is used as reducing agent. Catalyst characterization using thermogravimetric analysis (TGA) combined with mass spectrometry (MS), XRD, BET analysis, and Pt dispersion measurement has been done to support the model results.

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<tr>
<th>Temperature (K)</th>
<th>Inlet lean</th>
<th>Inlet rich</th>
</tr>
</thead>
<tbody>
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<td>513, 573, 643</td>
<td>0.2 vol. % NO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 vol. % O$_2$</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
<td></td>
<td>1 vol. % Ar</td>
</tr>
</tbody>
</table>

* He is carrier gas
4.2. Experimental
4.2.1. Alternation of lean and rich flows

Lean/rich cycling experiments are performed in a packed bed reactor, which is described in detail elsewhere [30]. The gas composition of reactants and products is measured with an online quadrupole mass spectrometer (ESS). A fixed amount of argon is fed as an internal standard during experiments to compensate for any intensity loss of the mass spectrometer. Gas analysis is performed on m/e 2 (H₂), 17 (NH₃ + H₂O), 18 (H₂O), 28 (N₂ + CO₂ + CO), 30 (NO + NO₂), 32 (O₂), 40 (Ar), 44 (CO₂ + N₂O), and 46 (NO₂). A high resolution magnetic sector mass spectrometer (Jeol JMS GCmate) is also used for the analysis of N₂ + CO and CO₂ + N₂O. It is verified that external and internal diffusion limitations are absent at the scale of the catalyst pellet. A NOₓ storage catalyst, Pt-Ba/Al₂O₃ (1/30/100, w/w/w), is used in powder form as provided by Engelhard. Typically 1.9 gram of catalyst with an average pellet diameter of 180 μm is used in the NOₓ storage/reduction experiments. The fresh catalyst is pre-treated at 773 K with 1 vol. % of oxygen in helium during 1 h, followed by 0.5 h in helium, and finally by reduction with 2 vol. % of hydrogen in helium for 2 h. The total gas flow during the experiments is kept constant at 0.743 mmol/s, resulting in a gas space velocity (GHSV) of 29,000 h⁻¹ (standard conditions 298 K, 1 bar). Table 4.1 shows the experimental conditions, for the lean/rich cycling experiments. Actually, in practice CO and hydrocarbons make up a significant portion of the reductant in the rich phase. However, quantification of the data with H₂ as reductant is less complicated as H₂ shows no mass overlap at m/e 28 and therefore H₂ is used in this study. H₂ is fed at higher concentrations as typically present in a real exhaust gas to ensure complete catalyst regeneration. NO is also fed at higher concentrations to guarantee enough sensitivity of the mass spectrometer for the gas phase component NO₂. The other experimental conditions are representative for conditions in diesel and lean-burn exhaust gases.
4.2.2. Catalyst characterization

Surface area, pore volume and pore size distribution are determined of fresh catalyst samples and catalyst samples used in the lean/rich cycling experiments. Samples used in the lean/rich cycling experiments are obtained after the cyclic steady state has been reached. The surface area is determined with the BET method at 77 K with N₂ as the adsorbent using a Tristar instrument (Micromeritics). The BJH pore size distribution and pore volume are calculated from the N₂ desorption isotherm. Pt dispersion is obtained from CO chemisorption at 298 K using an ASAP-2000 instrument (Micromeritics) and is determined for pretreated catalyst samples and catalyst samples used in lean/rich cycling experiments. The BET surface area, pore volume and Pt dispersion are listed in Table 4.2.

Table 4.2. BET surface area, pore volume and Pt dispersion.

<table>
<thead>
<tr>
<th></th>
<th>BET (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pt dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>71</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>Pretreated</td>
<td>70</td>
<td>0.22</td>
<td>20 ± 1</td>
</tr>
<tr>
<td>After lean, with CO₂</td>
<td>70</td>
<td>0.22</td>
<td>20 ± 1</td>
</tr>
<tr>
<td>After rich, with CO₂</td>
<td>70</td>
<td>0.22</td>
<td>20 ± 1</td>
</tr>
</tbody>
</table>

Lean exposure: 9 h, 0.2 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂ and 1 vol. % Ar. T = 573 K. Rich exposure: 15 h, 0.8 vol. % H₂, 10 vol. % CO₂ and 1 vol. % Ar. T = 573 K.

Powder X-ray diffraction is measured with a Rigaku Geigerflex diffractometer. Typically, an XRD spectrum is recorded in the range 15⁰ < 2θ < 75⁰ using Cu-Kα radiation. Thermogravimetric analysis (TGA) is carried out using a TGA/DSC (Mettler-Toledo) set-up combined with mass spectrometry (Quadrupole MS, Pfeiffer Vacuum). A catalyst sample of 50 mg and 30 ml/min flow of pure He were used with a heating rate of 10 K/min.

4.3. Experimental results

Typical results obtained during lean/rich cycling experiments with 9 h lean flow and 15 h rich flow at 573 K are presented in Figure 4.1. The data shown are collected after three storage/reduction cycles when the cyclic steady state had been reached. The NOₓ breakthrough profile shown in Figure 4.1a can be divided in three time periods. In the first period of the lean phase, complete NOₓ storage is seen. The second period starts after 6.2 min as NO
breakthrough is observed. The NO outlet concentration reaches a maximum value after 42.5 min and then the NO concentration begins to decrease. Meanwhile, during the first 33.3 min, NO$_2$ is completely consumed.

Figure 4.1a) Lean outlet concentrations of NO, NO$_2$ and NO$_x$ at cyclic steady state. Lean phase: 0.2 vol. % NO, 4 vol. % O$_2$, 10 vol. % CO$_2$ and 1 vol. % Ar, 9 h. Three different time periods can be distinguished. (4.1b) Rich outlet concentrations of N$_2$, NH$_3$, NO and CO at cyclic steady state. Rich phase: 0.8 vol. % H$_2$, 10 vol. % CO$_2$ and 1 vol. % Ar, 15 h. $T=573 \text{ K}$. 
After 33.3 min, the NO\textsubscript{2} concentration increases with time. During the first 65 min of the lean phase, there is still considerable NO\textsubscript{x} storage. The third period (> 65 min) is characterized by a slow but still measurable uptake of NO\textsubscript{x} until 200 min. After 200 min, the NO\textsubscript{x} concentration is constant and equal to the inlet concentration. As there is no NO\textsubscript{x} storage, the detected outlet 0.14 vol. % NO and outlet 0.06 vol. % NO\textsubscript{2} concentrations can be ascribed to the NO oxidation reaction.

If NO\textsubscript{x} is stored through the disproportionation route only, the disproportionation stoichiometry should be observed. This stoichiometry implies that for every three molecules of NO\textsubscript{2} removed from the gas phase, two molecules of NO\textsubscript{x} are stored on the barium and one molecule is released in the form of NO. It is assumed that the NO oxidation reaction is very fast and that the NO and NO\textsubscript{2} concentrations in the gas phase correspond to the oxidation reaction. Figure 4.2 shows the measured NO concentration and the calculated NO concentration as accounted for by the disproportionation mechanism; calculated NO concentration = 1/3 * stored NO\textsubscript{2} + 0.14 vol. %. As shown in Figure 4.2, according to the disproportionation mechanism, immediate NO formation should be observed. However, no NO is seen during
the first 6.2 min. This indicates that initial NO\textsubscript{x} storage occurs mainly through NO storage, i.e. through nitrites. After 36 min, more NO is observed as calculated through the disproportionation route. It is thus unlikely that NO\textsubscript{x} is stored through the disproportionation route only. Nitrites will also be oxidized into nitrates with NO\textsubscript{2} as oxidizing agent [11-13]. As a result mainly nitrates will be present after 9 h lean exposure. In parallel, NO\textsubscript{2} can also be stored directly into nitrates without NO release [4-7].

<table>
<thead>
<tr>
<th>Table 4.3. Barium utilization for lean and rich phases.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle no</td>
</tr>
<tr>
<td>Lean phase % Ba active</td>
</tr>
<tr>
<td>1           32</td>
</tr>
<tr>
<td>2           31</td>
</tr>
<tr>
<td>3           32</td>
</tr>
<tr>
<td>Rich phase % reduced</td>
</tr>
<tr>
<td>Lean phase: 9 h, 0.2 vol. % NO, 4 vol. % O\textsubscript{2}, 10 vol. % CO\textsubscript{2} and 1 vol. % Ar. Rich phase: 15 h, 0.8 vol. % H\textsubscript{2}, 10 vol. % CO\textsubscript{2} and 1 vol. % Ar. T = 573 K. See also Figure 4.1.</td>
</tr>
</tbody>
</table>

The barium utilization after 9 h of lean exposure corresponds with 32 % of the total barium present assuming that two moles of NO\textsubscript{x} are stored per mole barium and negligible capacity of \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} for NO\textsubscript{x} storage at 573 K [9]. The barium utilization of the previous lean/rich cycles is presented in Table 3, where the same fraction of barium active in NO\textsubscript{x} storage can be seen. Additionally, lean/rich cycling experiments in the presence of CO\textsubscript{2} at temperatures of 513 K and 643 K also show that about 30 % of total barium is involved in the NO\textsubscript{x} storage and reduction process. In a preceding paper [30] we have reported that in the absence of CO\textsubscript{2}, almost 100 % of barium is involved in NO\textsubscript{x} storage when the pretreated catalyst is exposed to 9 h lean conditions. It is reported that NO\textsubscript{x} cannot be stored on bulk barium sites with CO\textsubscript{2} present [31,32]. Additionally, CO\textsubscript{2} competes with NO\textsubscript{2} for the same barium sites inhibiting the NO\textsubscript{x} storage [15,26,27].

In Figure 4.3 the XRD pattern of the fresh catalyst is compared with the patterns of the catalyst exposed to lean/rich cycling experiments with and without CO\textsubscript{2} present in the gas feed. The XRD analysis of the fresh catalyst, pattern (A), shows the presence of crystalline BaCO\textsubscript{3}. Finely dispersed
barium sites are invisible for XRD while the bulk-barium phase is crystalline and detectable with XRD [18]. This suggests that the observed crystalline phase of the fresh catalyst corresponds with bulk-BaCO$_3$. After 9h lean exposure in the absence of CO$_2$, pattern (B), only peaks characteristic for crystalline Ba(NO$_3$)$_2$ can be seen, suggesting transformation of bulk-BaCO$_3$ to bulk-Ba(NO$_3$)$_2$. However after 9h lean exposure in the presence CO$_2$, pattern (C), only peaks characteristic for crystalline BaCO$_3$ can be seen and crystalline Ba(NO$_3$)$_2$ is not observed. This indicates that bulk-BaCO$_3$ sites are inactive in the NO$_x$ storage process in the presence of CO$_2$.

![XRD patterns](image)

**Figure 4.3** XRD patterns of (A) fresh catalyst, (B) after lean/rich cycling, ending with lean exposure. Lean: 0.2 vol. % NO, 4 vol. % O$_2$ and 1 vol. % Ar, 9 h, (C) after lean/rich cycling, ending with lean exposure. Lean: 0.2 vol. % NO, 4 vol. % O$_2$, 10 vol. % CO$_2$ and 1 vol. % Ar, 9 h. In the presence of CO$_2$, even after 9 h lean exposure, no crystalline bulk Ba(NO$_3$)$_2$ is formed contrary to the results in the absence of CO$_2$.

Figure 4.4 shows the TG and DTG curves of the fresh catalyst. Three distinct thermal decomposition events are shown in the DTG curve, with peaks located at 1040 K, 1110 K and 1273 K, respectively. This indicates the presence of three thermally different species. Piacentini et al. [18] found two thermal decomposition events for calcined catalysts. The low temperature
decomposition event is ascribed to the decomposition of LT-BaCO$_3$ to BaO. The high temperature event is associated with the decomposition of the HT-BaCO$_3$ sites. Nevertheless, three different barium species are distinguished: amorphous BaO, amorphous LT-BaCO$_3$, and crystalline HT-BaCO$_3$. The thermal stability of these species depends on their interaction with the alumina support and Pt sites. As the catalyst is exposed to the atmosphere, BaO will react with atmospheric CO$_2$ to form BaCO$_3$ with low thermal stability [18]. The catalyst in the present study has been stored for three years under ambient atmosphere and most of the barium will be present as BaCO$_3$. This might explain why the DTG curve shows three weight loss events. The first two events are ascribed to the decomposition of a dispersed LT phase. The high temperature event is ascribed to the decomposition of crystalline, bulk HT barium sites. The evolving gases during this TG experiment were analyzed by mass spectrometry. The MS signal (not shown) shows three evolution events, with peaks located at the same temperatures as for the TG measurement.

Figure 4.4) TG-DTG curve for the thermal decomposition of fresh catalyst.

The evolving gas above 600 K for all three events is CO$_2$. We used a curve fitting procedure for the CO$_2$ MS signal to calculate the integrals of the peaks. This shows that the relative LT weight loss is 35 %, while the HT weight loss is 65 %. This distribution of amorphous LT sites and crystalline HT sites corresponds well with the results of the lean/rich cycling experiments (LT sites: 30 %, HT sites: 70 %) and is in line with observations in literature [19].
The rich phase is shown in Figure 4.1b. Upon switching from lean to rich conditions, immediate $N_2$ formation and NO release can be seen. Minor amounts of NO$_2$ are detected. NO$_x$ is formed through nitrite/nitrate decomposition, as mentioned by Lietti et al. [7]. The released NO$_x$ is reduced to $N_2$ on the Pt sites. During $N_2$ formation, $H_2$ is completely consumed (not shown). Mahzoul et al. [16] concluded that two reduction processes proceed in parallel: reduction of stored NO$_x$ and reduction of oxidized Pt sites. This agrees with our experimental data. In the beginning of the rich phase, part of the fed hydrogen is used for the reduction of the oxidized Pt sites. This leads to less available hydrogen for the reduction of the released NO$_x$, resulting in a lower $N_2$ concentration. When the oxidized Pt sites are reduced, more hydrogen and Pt sites are available for the reduction of the stored NO$_x$. At that time the $N_2$ concentration increases to 0.15 vol. % corresponding to that expected from nitrate reduction. $NH_3$ and CO formation is observed once the $N_2$ production declines. The CO formation is accompanied by the parallel consumption of $H_2$ and CO$_2$ and by the parallel production of H$_2$O (not shown). This suggests that the reverse water gas shift (WGS) reaction takes place. The $NH_3$ formation indicates that the selectivity towards $N_2$ decreases with time, which seems to be coinciding with the diminishing quantity of NO. The N balance shows that the NO$_x$ stored during the lean phase is completely regenerated during the rich phase. Closed N balances are also observed in the preceding lean/rich cycles (Table 4.3) and there are no signs of incomplete regeneration.

![Figure 4.5](image-url) Pictorial representation of surface, semi-bulk and bulk barium sites. Surface and semi-bulk sites are amorphous LT-sites. Bulk sites are crystalline HT-sites.
4.4. Modeling

4.4.1. Kinetic model construction

The experimental results show that initially in the lean phase fast NO\textsubscript{x} storage occurs on Ba-sites, followed by slow storage. Not all of the Ba-sites participate in the NO\textsubscript{x} storage process and approximately 70 % of Ba remains inactive. As discussed above in the presence of excess CO\textsubscript{2}, barium is present mainly in the carbonate form. The three thermal events seen in the TG analysis, as discussed in the previous section, confirm the presence of three types of storage sites. The first thermal event is associated with surface Ba-sites where fast NO\textsubscript{x} storage occurs. The storage process is determined by the reaction kinetics. The second and the third event are associated with the semi-bulk and bulk Ba-sites respectively. At these sites slow NO\textsubscript{x} storage takes place, which is limited by NO\textsubscript{x} diffusion inside the barium cluster. The surface, semi-bulk and bulk sites not only differ in physical appearance (as shown in Figure 4.5), but also in chemical reactivity; surface sites are being the most reactive, whereas bulk sites are the least reactive. This is in line with Piacentini et al. [18] who suggested that depending on the Ba-loading three types of Ba-species exist on the support, which differ in reactivity and particle size. The surface sites are also present as highly dispersed barium carbonate species (not shown) along with Pt sites. The total amount of the surface barium and Pt sites affects the model results. The global reaction steps and rate equations used for modeling NO\textsubscript{x} storage and reduction with surface, semi-bulk and bulk barium sites are presented in Table 4.4.

An important reaction step in the NO\textsubscript{x} storage mechanism is the oxidation of NO into NO\textsubscript{2} on the Pt sites. We use the same form for the corresponding global reaction rate as the one published by Olsson et al. [23] (reaction (I), Table 4.4). The experimental results show that the NO\textsubscript{x} storage process is quite complex and different routes are possible. In this modeling, it is considered that NO\textsubscript{x} storage occurs through nitrates and nitrites formation. At first, NO will adsorb on the catalyst in the form of barium nitrites [4,9], as presented in reaction (II). These nitrites can be further oxidized to nitrates by NO\textsubscript{2}, resulting in NO release (reaction (III)) [11-13]. NO\textsubscript{2} can be stored directly as barium nitrates (reaction (IV)) [4-6]. With these two steps (III+IV), the experimentally observed stoichiometry of NO released and NO\textsubscript{2} stored can be
described well. As described before, the disproportionation route is not able to explain the measured NO concentration, and this step is therefore not included.

Table 4.4. The global reaction steps and rate equations used for modeling NOx storage and reduction.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Rate equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean phase</td>
<td></td>
</tr>
<tr>
<td>NO + ½ O₂ ⇌ NO₂</td>
<td>( R_{\text{ox}} = k_{\text{ox},i} C_{\text{NO}} C_{\text{O}<em>2}^{0.5} - k</em>{\text{ox},j} C_{\text{NO}_2} ) (I)</td>
</tr>
<tr>
<td>Ba(NO₂)₂ + 2 NO + 0.5 O₂ →</td>
<td>( R_{\text{st,NO}} = k_{\text{st,NO},i} \theta_{\text{BaCO}<em>3} C</em>{\text{NO}} C_{\text{O}_2}^{0.5} ) (II)</td>
</tr>
<tr>
<td>Ba(NO₂)₂ + 2 NO₂ → Ba(NO₃)₂ + 2 NO</td>
<td>( R_{\text{st,oxi}} = k_{\text{st,oxi},i} \theta_{\text{Ba(NO₂)₂},i} C_{\text{NO}_2} ) (III)</td>
</tr>
<tr>
<td>Ba(NO₃)₂ + 2 NO₂ + 0.5 O₂ →</td>
<td>( R_{\text{st,NO}<em>2} = k</em>{\text{st,NO}<em>2,i} \theta</em>{\text{BaCO}<em>3} C</em>{\text{NO}<em>2} C</em>{\text{O}_2}^{0.5} ) (IV)</td>
</tr>
<tr>
<td>Ba(NO₂)₂ + CO₂</td>
<td></td>
</tr>
<tr>
<td>Rich phase</td>
<td></td>
</tr>
<tr>
<td>Ba(NO₂)₂ + H₂ + CO₂ →</td>
<td>( R_{\text{reg,nitrite}} = k_{\text{reg,nitrite},i} \theta_{\text{Ba(NO₂)₂},i} C_{\text{H}_2} ) (V)</td>
</tr>
<tr>
<td>BaCO₃ + 2NO + H₂O</td>
<td></td>
</tr>
<tr>
<td>Ba(NO₃)₂ + 3 H₂ + CO₂ →</td>
<td>( R_{\text{reg,nitrate}} = k_{\text{reg,nitrate},i} \theta_{\text{Ba(NO₃)₂},i} C_{\text{H}_2} ) (VI)</td>
</tr>
<tr>
<td>BaCO₃ + 2NO + 3H₂O</td>
<td></td>
</tr>
<tr>
<td>NO + H₂ → ½ N₂ + H₂O</td>
<td>( R_{\text{red}} = k_{\text{red},i} C_{\text{NO}} C_{\text{H}_2} ) (VII)</td>
</tr>
</tbody>
</table>

The reaction rate parameters \( k_{\text{s,NO},i} \), \( k_{\text{s,dis},i} \), \( k_{\text{s,NO}_2,i} \), \( k_{\text{reg,nitrite},i} \), and \( k_{\text{reg,nitrate},i} \) have different units and values for the surface, semi-bulk and bulk barium sites with \( i = \) surface, semi-bulk or bulk. See also Table 4.5.

In the rich phase, it is considered that regeneration of barium sites takes place through nitrite/nitrate decomposition, as mentioned by Lietti et al. [7], and as presented in reactions (V) and (VI). The released NOₓ is reduced on the Pt sites into N₂ with the help of a reductant, described by reaction (VII). NH₃ formation is not taken into account, as no NH₃ is observed in the experiments with lean/rich cycling times close to automotive conditions. For the same reason, the reverse WGS reaction is not included. The activation energy for NO oxidation (reaction (I)) is taken from Olsson et al. [23]. The pre-exponential factor for the NO oxidation and the storage and reduction kinetic parameters are obtained by manually fitting the results of the model to the results of the 9 h/15 h lean/rich cycling experiments. The distribution of surface, semi-bulk and bulk sites is also acquired from the 9 h/15 h lean/rich cycling experiment supported by the results of the TGA experiment: 73 % of the total barium sites corresponds with bulk barium sites, 7 % with surface barium sites, and 20 % with semi-bulk barium sites. The diffusion coefficient of
the gas phase components in the semi-bulk and bulk barium is taken as 3.6×10^{-15} \text{ m}^2/\text{s}. Dong et al. suggested that the diffusion coefficient in case of diffusion through the bulk of oxides is in the order of 10^{-16} \text{ m}^2/\text{s} [33].

Table 4.5. Model parameters and constants.

<table>
<thead>
<tr>
<th>Catalyst parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>L_{Pt}</td>
<td>9.67 moles of Pt surface sites / m^3 reactor, (mol m^{-3}_{reactor})</td>
</tr>
<tr>
<td>L_Ba, total</td>
<td>2.06×10^3 moles of total Ba sites / m^3 reactor, (mol m^{-3}_{reactor})</td>
</tr>
<tr>
<td>L_Ba, surface</td>
<td>1.34×10^2 moles of Ba surface sites / m^3 reactor, (mol m^{-3}_{reactor})</td>
</tr>
<tr>
<td>L_Ba, semi-bulk</td>
<td>4.01×10^2 moles of Ba semi-bulk sites / m^3 reactor, (mol m^{-3}_{reactor})</td>
</tr>
<tr>
<td>L_Ba, bulk</td>
<td>1.53×10^3 moles of Ba bulk sites / m^3 reactor, (mol m^{-3}_{reactor})</td>
</tr>
<tr>
<td>A_{Ba}</td>
<td>2.20×10^7 specific barium surface, (m^2_{Ba} m^{-3}_{reactor})</td>
</tr>
<tr>
<td>d_{Ba}</td>
<td>10×10^{-9} diameter semi-bulk barium cluster, (m_{Ba})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reactor parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ε_b</td>
<td>0.35 bed porosity, (m^3_{gas} m^{-3}_{reactor})</td>
</tr>
<tr>
<td>A_r</td>
<td>1.40×10^{-4} surface area of the reactor, (m^2_{reactor})</td>
</tr>
<tr>
<td>F_v</td>
<td>3.54×10^{-5} volumetric flow rate, (m^3_{gas} s^{-1})</td>
</tr>
<tr>
<td>L_{reactor}</td>
<td>1.50×10^{-2} reactor length, (m_{reactor})</td>
</tr>
<tr>
<td>D_{eff}</td>
<td>3.64×10^{-15} [33] diffusion coefficient, (m^3_{gas} m^{-1}_{Ba} s^{-1})</td>
</tr>
<tr>
<td>ε_cluster</td>
<td>0.5 cluster porosity, (m^3_{Ba} m^{-3}_{reactor})</td>
</tr>
<tr>
<td>f</td>
<td>0.055 volume fraction, (m^3_{Ba} m^{-3}_{reactor})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NO oxidation parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>K_{oxi_equilibrium}</td>
<td>2.05×10^{-1}[23] NO oxidation equilibrium</td>
</tr>
<tr>
<td>K_{ox,f}</td>
<td>6.90×10^{-1}[23] forward NO oxidation, (m^{4.5}<em>{gas} mol^{0.5}</em>{i} mol^{-1}_{Pt} s^{-1})</td>
</tr>
<tr>
<td>K_{ox,b}</td>
<td>3.30×10^{-2}[23] backward NO oxidation, (m^{3}<em>{gas} mol^{1}</em>{i} s^{-1})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Storage parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface barium sites</td>
<td></td>
</tr>
<tr>
<td>k_{s, NO2, surface}</td>
<td>1.60×10^5 NO_2 storage, (m^{7.5}<em>{gas} mol^{-2.5}</em>{i} s^{-1})</td>
</tr>
<tr>
<td>k_{s, NO, surface}</td>
<td>5.09×10^2 NO storage, (m^{7.5}<em>{gas} mol^{-2.5}</em>{i} s^{-1})</td>
</tr>
<tr>
<td>k_{s, dis, surface}</td>
<td>3.74×10^{-1} nitrite oxidation, (m^{6}<em>{gas} mol^{2}</em>{i} s^{-1})</td>
</tr>
<tr>
<td>Semi-bulk barium sites</td>
<td></td>
</tr>
<tr>
<td>k_{s, NO2, semibulk}</td>
<td>5.36×10^4 NO_2 storage, (m^{7.5}<em>{gas} mol^{-2.5}</em>{i} s^{-1} mol_{Ba} m^{-3}_{Ba})</td>
</tr>
<tr>
<td>k_{s, NO, semibulk}</td>
<td>2.68×10^{-1} NO storage, (m^{7.5}<em>{gas} mol^{-2.5}</em>{i} s^{-1} mol_{Ba} m^{-3}_{Ba})</td>
</tr>
<tr>
<td>k_{s, dis, semibulk}</td>
<td>1.25×10^{-1} nitrite oxidation, (m^{6}<em>{gas} mol^{2}</em>{i} s^{-1} mol_{Ba} m^{-3}_{Ba})</td>
</tr>
<tr>
<td>Bulk barium sites</td>
<td></td>
</tr>
<tr>
<td>k_{s, NO2, bulk}</td>
<td>7.54×10^{-3} NO_2 storage, (m^{7.5}<em>{gas} mol^{-2.5}</em>{i} s^{-1} mol_{Ba} m^{-3}_{Ba})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Regeneration parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface barium sites</td>
<td></td>
</tr>
<tr>
<td>k_{reg, nitrite, surface}</td>
<td>5.96×10^{-2} Ba(NO_2)<em>2 regeneration, (m^{3}</em>{gas} mol^{-1}_{i} s^{-1})</td>
</tr>
<tr>
<td>k_{reg, nitrate, surface}</td>
<td>2.24×10^{-1} Ba(NO_3)<em>2 regeneration, (m^{3}</em>{gas} mol^{-1}_{i} s^{-1})</td>
</tr>
<tr>
<td>Semi-bulk barium sites</td>
<td></td>
</tr>
<tr>
<td>k_{reg, nitrite, semibulk}</td>
<td>1.99×10^{-2} Ba(NO_2)<em>2 regeneration, (m^{3}</em>{gas} mol^{-1}<em>{i} s^{-1} mol</em>{Ba} m^{-3}_{Ba})</td>
</tr>
<tr>
<td>k_{reg, nitrate, semibulk}</td>
<td>7.48×10^{-1} Ba(NO_3)<em>2 regeneration, (m^{3}</em>{gas} mol^{-1}<em>{i} s^{-1} mol</em>{Ba} m^{-3}_{Ba})</td>
</tr>
<tr>
<td>Bulk barium sites</td>
<td></td>
</tr>
<tr>
<td>k_{reg, nitrate, bulk}</td>
<td>1.96×10^{-1} Ba(NO_3)<em>2 regeneration, (m^{3}</em>{gas} mol^{-1}<em>{i} s^{-1} mol</em>{Ba} m^{-3}_{Ba})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reduction parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>k_{red}</td>
<td>2.9×10^{-4} NO_x reduction, (m^{6}<em>{gas} mol^{2}</em>{i} s^{-1})</td>
</tr>
</tbody>
</table>

** calculated with TGA result and 9 h lean/15 h rich cycling experiments
A semi-bulk barium cluster size of about 10 nm is obtained via CO₂ chemisorption. Calculations based on this value and on the fitted model parameters lead to a bulk barium cluster size of about 40 nm. This is in agreement with XRD results, which give a particle size range of 10 to 40 nm. Further a free alumina of 50.7 m²/gm of catalyst can be estimated. We expect that at 300 °C this alumina shows less than 1.5 % storage capacity for NOₓ. This was verified by performing NO desorption experiments with pure γ-alumina (BET: 200 m²/gm). The model parameters and constants can be found in Table 4.5.

4.4.2. Reactor model

The packed bed reactor is regarded as an ideal plug flow reactor, under isothermal conditions, as experimental data show a maximum increase in temperature of 5 K. The model is constructed to describe NOₓ storage and reduction at a temperature of 573 K. The pressure is taken uniform and equal to ambient throughout the packed bed. External and internal diffusion limitations are absent. Diffusion of the gas phase components is considered only from the external surface of the barium clusters to the interior of the barium clusters. The gas bulk in the packed bed reactor is discretized in axial direction \( z \) and the gas in the spherical barium clusters with the partial coordinate \( \xi \). Both parts are connected with diffusion from the bulk gas to the inner side of the barium clusters. The change in the concentration of the different components as a function of time at each axial position can be described as follows:

\[
\frac{\partial C_i}{\partial t} = -F_v \frac{\partial C_i}{A_r \partial z} - D_{eff} A_{Ba} \frac{\partial C_i}{\partial \xi} \bigg|_{\xi=R} +L_{Pt} \sum_j v_{ij} R_{Pt,j} +L_{Ba, surf} \sum_k u_{jk} R_{Ba, surf,k} \quad (1)
\]

where \( \epsilon_b \) [m³ gas m⁻³ reactor] is the bed porosity, \( C_i \) [mol m⁻³ gas] is the gas phase concentration of component \( i \) (NO, NO₂, O₂, H₂ and N₂), \( t \) [s] is time, \( F_v \) [m³ gas s⁻¹] is the volumetric flow rate, \( A_r \) [m² reactor] is the surface area of the reactor, \( z \) [m reactor] is the axial length, \( D_{eff} \) [m³ gas m⁻¹ Ba s⁻¹] is the effective gas diffusion coefficient, \( A_{Ba} \) [m² Ba m⁻³ reactor] is the specific barium surface, \( \xi \) [mBa] is the
radial direction in the barium clusters, \(L_{Pt} \text{ [mol\(Pt\) m\(^{-3}\text{reactor}\}]\) is the specific number of moles of active Pt surface sites, \(R_{Pt,j} \text{ [mol\(i\) mol\(^{-1}\text{Pt\ s}\^{-1}\)]}\) is the NO oxidation and reduction rate described in equations (I) and (VII) in Table 4.4, \(L_{Ba,\ surf} \text{ [mol\(Ba\) m\(^{-3}\text{reactor}\)]}\) is the specific number of moles of active barium surface sites. \(R_{Ba,\surf,k} \text{ [mol\(i\) mol\(^{-1}\text{Ba\ s}\^{-1}\)]}\) is the NO\(x\) storage and regeneration rate at barium surface sites and can be determined from the reaction equations (II) – (VI) mentioned in Table 4.4. Equation (2) calculates the time-dependent change of the different species on the surface barium sites:

\[
\frac{\partial \theta_{m,\surf}}{\partial t} = \sum_{k} v_{ij,k} R_{Ba,\surf,k} \tag{2}
\]

where \(\theta_{m,\surf} \text{ [-]}\) is the coverage of the surface barium sites and \(m\) denotes either Ba(NO\(_2\))\(_2\), Ba(NO\(_3\))\(_2\), or BaCO\(_3\). The site balance for the surface barium sites is shown in Equation (3):

\[
\theta_{BaCO_3,\surf} = 1 - \theta_{Ba(NO_2)_2,\surf} - \theta_{Ba(NO_3)_2,\surf} \tag{3}
\]

Equation 4 represents the change in the concentration of the different gas phase components as a function of time at each radial position for the semi-bulk and bulk barium sites:

\[
\frac{\partial C_i}{\partial t} = \frac{1}{\varepsilon_{\text{cluster}}} \frac{\partial}{\partial \xi} \left( D_{\text{eff}} \xi \frac{\partial C_i}{\partial \xi} \right) + \sum_{k} v_{ij,k} R_{Ba, X,k} \tag{4}
\]

Accumulation of moles in gas phase in the Ba clusters
Diffusion in Ba clusters
Reactions involved on semi-bulk and bulk Ba sites

where \(\varepsilon_{\text{cluster}} \text{ [m}^3\text{ gas m}^{-3}\text{Ba}]\) is the porosity of the barium clusters, \(X\) is semi-bulk or bulk barium sites, and \(R_{Ba,X,k} \text{ [mol\(i\) m}^3\text{Ba s}^{-1}]\) is the NO\(x\) storage and regeneration rate for the semi-bulk and bulk sites and can be determined from the rate equations (II) – (VI) mentioned in Table 4. Equations (5) and (6) describe the time-dependent change of the different species on the semi-bulk and bulk barium sites, respectively:

\[
\frac{L_{Ba,\text{semibulk}}}{f} \frac{\partial \theta_{m,\text{semibulk}}}{\partial t} = \sum_{k} v_{ij,k} R_{Ba,\text{semi-bulk},k} \tag{5}
\]

\[
\frac{L_{Ba,\text{bulk}}}{f} \frac{\partial \theta_{m,\text{bulk}}}{\partial t} = \sum_{k} v_{ij,k} R_{Ba,\text{bulk},k} \tag{6}
\]

where \(L_{Ba,\text{semibulk}}\) and \(L_{Ba,\text{bulk}} \text{ [mol\(Ba\) m}^3\text{reactor}]\) are the specific number of moles of active semi-bulk and bulk barium sites, \(f \text{ [m}^3\text{Ba m}^{-3}\text{reactor}]\) is the volume
fraction, $\theta_{m,\text{semi-bulk}}$ [-] is the coverage of the semi-bulk barium sites, and $\theta_{m,\text{bulk}}$ [-] is the coverage of the bulk barium sites. The site balance for the semi-bulk and bulk barium sites is shown in equations (7) and (8). In accordance with literature, NO$_x$ is only stored as nitrates on bulk barium sites [31,32].

$$\theta_{\text{BaCO}_3,\text{semi-bulk}} = 1 - \theta_{\text{Ba(NO}_2)_2,\text{semi-bulk}} - \theta_{\text{Ba(NO}_3)_2,\text{semi-bulk}} \quad (7)$$

$$\theta_{\text{BaCO}_3,\text{bulk}} = 1 - \theta_{\text{Ba(NO}_3)_2,\text{bulk}} \quad (8)$$

The initial and boundary conditions are shown below:

$C_0 = 0$, $\theta_{\text{Ba(NO}_3)_2,y = 0}$, and $\theta_{\text{Ba(NO}_2)_2,y = 0}$ at $t = 0$ with $y$ is surface, semi-bulk or bulk barium sites;

$C_0 = C_{\text{in}}$ at $t > 0$ and $z = 0$;

$$\frac{\partial C_0(z,\xi)}{\partial \xi} = 0 \text{ at } \xi = 0 \text{ at any } t.$$

The system of equations is solved using gPROMS (Process Systems Enterprise) software.

Figure 4.6) Simulated and measured lean NO and NO$_2$ outlet concentrations. For experimental conditions, see Figure 4.1.
Model for NSR in the presence of CO₂

Figure 4.7) Simulated coverages during lean exposure. A) coverage of surface barium sites (B) Ba(NO₃)₂ coverage of semi-bulk barium sites (C) Ba(NO₃)₂ coverage of semi-bulk barium sites (D) BaCO₃ coverage of semi-bulk barium sites (E) Ba(NO₃)₂ and BaCO₃ coverage of bulk barium sites after 9 h lean exposure. For experimental conditions, see Figure 4.1.
4.5. Modeling results and discussion

4.5.1. Lean/rich cycling in the order of hours

Figure 4.6 shows the results from the model (dashed lines) together with the measured outlet NO and NO\textsubscript{2} concentrations (solid lines) for the 9 h lean phase with 0.2 vol. % inlet NO. The model is well able to describe the three different time periods in the lean phase. The first period shows complete NO\textsubscript{x} uptake during the first 6.2 min. Figures 4.7a – e show that during this period mainly NO storage occurs on the surface barium sites, in the form of nitrites. As the storage process proceeds the surface coverage of nitrite and nitrates increases (Figure 4.7a) and NO breakthrough in the gas phase is seen. This is the start of the second period. The formation of surface barium nitrites continues showing a maximum coverage at 8.4 min (Figure 4.7a). At this stage all the surface BaCO\textsubscript{3} sites have been converted to nitrites and nitrates. After 8.4 min the surface nitrites coverage starts declining, while at the same time the surface barium nitrate coverage increases. This indicates that nitrites are oxidized into nitrates with NO\textsubscript{2} as oxidizing agent. As a result, delay in NO\textsubscript{2} breakthrough and increase in NO concentration can be seen in Figure 4.6. This point onwards semi-bulk barium sites start participating in the NO and NO\textsubscript{2} storage process (Figures 4.7b - d), showing barium nitrite and nitrate coverages. The third period begins after 65 min, where the surface barium sites are entirely occupied with Ba(NO\textsubscript{3})\textsubscript{2} (Figure 4.7a). The NO\textsubscript{x} storage rate decreases as only semi-bulk and bulk barium sites are available and diffusion starts playing a major role. After 67 min, all semi-bulk BaCO\textsubscript{3} sites have been replaced by Ba(NO\textsubscript{2})\textsubscript{2} and Ba(NO\textsubscript{3})\textsubscript{2} (Figures 4.7b – d). However, as the lean phase proceeds, the barium nitrate coverage of the semi-bulk sites increases, coinciding with a decrease of the barium nitrite coverage. After 200 min, the semi-bulk sites are fully covered with nitrates (Figures 4.7b – d). Only a fraction of the bulk barium sites still participates in NO\textsubscript{x} storage showing negligible reactivity (Figure 4.7e). Even after 9 h lean exposure, the bulk coverage consists mainly of BaCO\textsubscript{3}. As a result, the NO\textsubscript{x} storage process ends as the surface and semi-bulk sites have been fully converted to nitrates.
Upon rich conditions, $N_2$ formation and NO desorption are experimentally observed (Figure 4.8). The model adequately describes the NO desorption. The measured $N_2$ concentration shows initially a lower concentration before it increases to 0.16 vol. %. A possible reason might be that part of the $H_2$ is used for reduction of the Pt sites, resulting in less $H_2$ available for NO$_x$ reduction. This is not taken into account in the model. As a
result, the simulation shows immediately a N$_2$ concentration of 0.16 vol. %. Consequently, more nitrate will be reduced in the same time span in the model as compared to the experimental results. Therefore, the simulation results show a decrease in the N$_2$ concentration after 8 min compared to 11 min for the experimental data. Simulations show that at first all H$_2$ is completely consumed. As the rich phase proceeds, incomplete consumption of H$_2$ is seen. This results in the presence of excess H$_2$. It can be observed experimentally that this leads to NH$_3$ formation after 11 min. The NH$_3$ concentration slowly decreases with time. NH$_3$ production is not modeled as NH$_3$ is not observed at cycle timings close to automotive conditions. However, the simulated N$_2$ concentration shows the same characteristics as the experimentally observed N$_2 + 2$ NH$_3$ signal.

Figure 4.9) Simulated coverages during rich exposure (a) coverage of surface barium sites (b) Ba(NO$_3$)$_2$ coverage of semi-bulk barium sites (c) BaCO$_3$ coverage of semi-bulk barium sites (d) Ba(NO$_3$)$_2$ and BaCO$_3$ coverage of bulk barium sites. For experimental conditions, see Figure 4.1.
Figures 4.9 a – d show the coverages of the surface, semi-bulk and bulk barium sites. At first, the surface nitrates are reduced and surface BaCO$_3$ is formed (Figure 4.9a). After 5 min, the semi-bulk sites participate in the regeneration process (Figures 4.9 b – c). The surface sites are completely regenerated after 17 min. Complete regeneration for the semi-bulk sites can be seen after 27 min.

Figure 4.10a) Simulated and measured lean NO and NO$_2$ outlet concentrations at cyclic steady state. Lean phase: 0.3 vol. % NO, 4 vol. % O$_2$, 10 vol. % CO$_2$ and 1 vol. % Ar, 9 h. (4.10b) Simulated and measured rich NO, H$_2$ and N$_2$ outlet concentrations at cyclic steady state. Rich phase: 1.2 vol. % H$_2$, 10 vol. % CO$_2$ and 1 vol. % Ar, 15 h. $T=573$ K.
Figure 4.10a shows the lean NO and NO\textsubscript{2} concentrations for the higher inlet NO concentration (0.3 vol. %). The model is able to simulate the complete NO\textsubscript{x} uptake, and the NO and NO\textsubscript{2} breakthrough timings. There is a small discrepancy between the model and the experimental results for the NO profile. It is reported in literature that the NO oxidation rate shows a negative first order with respect to NO\textsubscript{2} concentration [34]. This inhibiting effect is not incorporated in the model and this can lead to the observed small discrepancy. Figure 4.10b shows that the model can also capture the NO\textsubscript{x} desorption during rich exposure with higher H\textsubscript{2} concentration (1.2 vol. %). The simulated N\textsubscript{2} profile corresponds well with the measured N\textsubscript{2} + 2 NH\textsubscript{3} signal.

![Figure 4.10a](image)

**Figure 4.10a** Simulated and measured NO, NO\textsubscript{2} and N\textsubscript{2} profiles at T = 573 K. Lean phase: 240 s, 0.2 vol. % NO, 4 vol. % O\textsubscript{2}, 10 vol. % CO\textsubscript{2} and 1 vol. % Ar. Rich phase: 60 s, 0.8 vol. % H\textsubscript{2}, 10 vol. % CO\textsubscript{2} and 1 vol. % Ar. For modeling purpose 0.6 vol. % H\textsubscript{2} was used in the rich phase. See text for explanation.

4.5.2. Lean/rich cycling in the order of seconds

Figure 4.11 shows the model prediction and experimental results of transient reactor operation for 20 lean/rich cycles with 240 s lean and 60 s rich phase. As mentioned before, during the first few minutes of rich exposure, part of the H\textsubscript{2} is probably used for the reduction of Pt sites. This leads to less
available H\textsubscript{2} for NO\textsubscript{x} reduction. Therefore, simulation results show initially a higher N\textsubscript{2} concentration as experimentally observed. For this reason, the inlet H\textsubscript{2} concentration used in the modeling of the transient experiments was set to 0.6 vol. %. The first two storage/reduction cycles show complete NO\textsubscript{x} uptake.

![Simulated coverages during transient reactor operation](image)

Figure 4.12) Simulated coverages during transient reactor operation (a) coverage of surface barium sites (b) Ba(NO\textsubscript{2})\textsubscript{2} coverage of semi-bulk barium sites (c) Ba(NO\textsubscript{3})\textsubscript{2} coverage of semi-bulk barium sites (d) BaCO\textsubscript{3} coverage of semi-bulk barium sites (e) Ba(NO\textsubscript{3})\textsubscript{2} and BaCO\textsubscript{3} coverage of bulk barium sites. For experimental conditions, see Figure 4.11.
Figure 4.12a shows that NO\textsubscript{x} is initially stored on surface barium sites in the form of nitrites. During the catalyst regeneration period, N\textsubscript{2} formation and NO desorption are observed. No NH\textsubscript{3} formation is seen and the reverse WGS reaction does not take place. NO\textsubscript{x} stored during lean exposure is not completely reduced during the subsequent rich period as can be seen in Figure 4.12a. As a result nitrites and nitrates accumulate on the barium sites and part of the barium will be inactive for NO\textsubscript{x} storage and reduction. After two lean/rich cycles, NO breakthrough during lean exposure can be seen. The NO storage continues with the involvement of semi-bulk barium sites (Figures 4.12 b – d). Meanwhile NO\textsubscript{2} is consumed in oxidizing surface nitrites into nitrates and by getting stored on semi-bulk barium sites. After a number of lean/rich cycles, NO\textsubscript{2} breakthrough can be seen. The experimental results show that the cyclic steady state is not reached. Simulation results (Figures 4.12 a – e) illustrate that as lean/rich cycling proceeds, more nitrate accumulates in the catalyst until all semi-bulk barium sites have been filled. At that moment, the cyclic steady state has been reached. At the cyclic steady state, only surface barium sites participate in the NO\textsubscript{x} storage/reduction process. Bulk barium sites show negligible activity towards NO\textsubscript{x} storage (Figure 4.12 e).

At real-life application, fast alternation of NO\textsubscript{x} storage and reduction phases takes place in the order of seconds. Above-mentioned model results suggest that in this case surface barium sites are decisive, and only a fraction of the total barium sites is active in NO\textsubscript{x} storage. As a result, NO\textsubscript{x} breakthrough in the lean phase is observed. Restoring the maximum NO\textsubscript{x} storage capacity implies regeneration of both surface and semi-bulk barium sites. Consequently, considerable breakthrough of the reducing agent can occur. The present model can be used to simulate and optimize the transient operating conditions.

4.6. Conclusions

A global reaction kinetic model is developed based on a multiple storage sites mechanism for the NO\textsubscript{x} storage/reduction process in the presence of CO\textsubscript{2}. The model considers that fast NO\textsubscript{x} storage occurs at surface barium sites, which is determined by the reaction kinetics. Slow NO\textsubscript{x}
storage occurs at semi-bulk sites, where diffusion plays a major role. Bulk barium sites show negligible reactivity towards NO\textsubscript{x} storage. It is assumed that surface, bulk and semi-bulk sites not only differ in physical appearance but also in chemical reactivity. It is considered that surface and semi-bulk sites correspond with a dispersed LT barium phase and bulk barium sites with crystalline HT-BaCO\textsubscript{3} sites. The distribution of these sites is obtained from a TGA experiment with a fresh catalyst, which shows that around 35 % (w/w) of total barium is present as LT barium sites and 65 % as HT-BaCO\textsubscript{3}. This agrees well with results obtained from 9 h/15 h lean/rich cycling experiments in combination with XRD measurements. The barium utilization after 9 h lean exposure is about 32 % of the total barium present. XRD measurements show that HT-BaCO\textsubscript{3} is inactive in the NO\textsubscript{x} storage process in the presence of CO\textsubscript{2}.

The model elucidates that the initial complete NO\textsubscript{x} uptake can be mainly ascribed to NO storage on surface barium sites in the form of nitrites. As the surface coverage increases, NO breakthrough can be seen. The NO storage process continues with the involvement of semi-bulk barium sites but at a lower rate due to diffusion limitation. Meanwhile NO\textsubscript{2} is consumed in oxidizing surface nitrites into nitrates and by getting stored on semi-bulk barium sites. As a result, delay in NO\textsubscript{2} breakthrough can be seen. It appears that the bulk barium sites show negligible activity towards NO\textsubscript{x} storage. The model is also able to describe the NO\textsubscript{x} desorption during rich exposure. Experimental results show at first N\textsubscript{2} formation followed by NH\textsubscript{3} production. NH\textsubscript{3} formation is not seen for cycle timings close to automotive conditions. For this reason, NH\textsubscript{3} formation was not modeled. The simulated N\textsubscript{2} signal describes the measured N\textsubscript{2} + 2 NH\textsubscript{3} characteristics. The model is able to describe experiments with higher NO and H\textsubscript{2} inlet concentration as well as transient reactor experiments with 240 s lean and 60 s rich cycle timings.

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References
Influence of reducing agent (CO, H₂, C₂H₄) and of H₂O on NOₓ reduction

This chapter has been submitted as:

Abstract
In this paper, a comparative study on the NOₓ reduction/regeneration capabilities at 300 °C of a Pt-Ba/γ-Al₂O₃ catalyst is presented. Different reductants (H₂, CO, and C₂H₄) are used in the absence and presence of H₂O in the rich phase. Lean/rich cycling experiments show that in the absence of H₂O both H₂ and C₂H₄ are capable of reducing all the stored NOₓ, although C₂H₄ poisons the Pt sites by carbon decomposition. CO not only poisons the catalyst through carbon decomposition but also through formation of strongly bound isocyanates on alumina and barium sites. These isocyanates are removed by O₂ in the lean phase. The type of reducing agent also affects the NOₓ storage route in the lean phase. H₂O in the rich phase prevents poisoning of the catalyst by CO and C₂H₄, and all three reducing agents show comparable reduction efficiencies.
5.1. Introduction

Diesel and lean-burn engines operate under net oxidizing conditions and exhibit a better fuel efficiency and lower CO₂ emission than conventional gasoline engines, which operate at stoichiometric air to fuel ratios. However, due to the excess oxygen in the exhaust gas, the traditional three-way catalyst is ineffective in NOₓ reduction as all of the reducing agents present are oxidized. One promising solution to reduce NOₓ during lean exhaust operation is the use of a NOₓ storage reduction (NSR) catalyst [1]. The NSR catalysts usually investigated contain Pt and the NOₓ storage material barium on an alumina support. These catalytic systems operate under cyclic conditions, during which NOₓ is stored under lean conditions as barium nitrites/nitrates and subsequent catalyst regeneration takes place during periodic, brief fuel-rich excursions of the engine. For real-life application, it is important to understand the NSR mechanism in order to minimize both fuel penalty and emissions.

The NSR process has been the focus of numerous studies ([2] and references herein). Most of these studies have focused on the NOₓ storage process with the reduction step receiving considerably less attention. However, some studies have been performed to understand the effect of different reductants in the rich phase. At temperatures above 250 °C, both H₂ and CO appear to be highly efficient towards NOₓ reduction compared to hydrocarbons [3-5]. At lower temperatures, CO is noticeably less effective in NOₓ reduction than H₂ [4,6]. CO appears to facilitate Ba(NO₃)₂ decomposition, but not NO₂ reduction, while H₂ enables both to occur, with excellent conversion to N₂ [7]. The difference in reactivity can be explained with poisoning of the Pt sites by adsorbed CO species [4,7-10]. This inhibition effect also occurs with hydrocarbons [8,9,11]. CO may also inhibit the regeneration process through the formation of isocyanates, which strongly adsorb on the alumina and barium oxide components of the catalyst [12,13].

Poisoning of the Pt sites during rich exposure may influence the NOₓ storage route at lean conditions, as it is generally believed that the first step is the NO oxidation to NO₂ over Pt sites. NO₂ can be stored on barium via a disproportionation route resulting in nitrate formation and NO release [14-16], or via a direct route without NO release [15,17]. Pt sites also catalyze another
pathway for NO\textsubscript{x} storage, which implies the direct uptake of NO in the presence of O\textsubscript{2} in the form of nitrites [14,15].

In practice, the vehicle exhaust gas always contains CO\textsubscript{2} and H\textsubscript{2}O. However, very few studies have reported the effect of CO\textsubscript{2} and H\textsubscript{2}O on NO\textsubscript{x} reduction. NO\textsubscript{x} release studies show that CO\textsubscript{2} promotes NO\textsubscript{x} release at rich conditions [18-20] while H\textsubscript{2}O hinders NO\textsubscript{2} and NO release during temperature-programmed decomposition of stored NO\textsubscript{x} [21].

The focus of this work is the NO\textsubscript{x} reduction step and its influence on the NO\textsubscript{x} storage process. Lean/rich cycling experiments at 300 °C have been carried out over a Pt-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3} (1 wt.% Pt and 30 wt.% Ba) catalyst. CO\textsubscript{2} was always present in the gas mixture in order to prevent changes of the catalyst properties, like BET surface area and Pt dispersion [22]. Rich conditions contain either CO, H\textsubscript{2}, or C\textsubscript{2}H\textsubscript{4} as reducing agent in the absence and presence of H\textsubscript{2}O. NO is used as NO\textsubscript{x} source. Cycle times of 200 min lean and 100 min rich have been used to monitor the complete NO\textsubscript{x} breakthrough profile during lean exposure and to ensure complete catalyst regeneration at rich conditions.

5.2. Experimental

Lean/rich cycling experiments at 300 °C are performed in a packed bed reactor, which is described in detail elsewhere [23]. The gas composition of reactants and products is measured with an online mass spectrometer (ESS EcoSys). A fixed amount of argon is fed as an internal standard during experiments to compensate for any intensity loss of the mass spectrometer. Gas analysis is performed on m/e 2 (H\textsubscript{2}), 17 (NH\textsubscript{3} + H\textsubscript{2}O), 18 (H\textsubscript{2}O), 27 (C\textsubscript{2}H\textsubscript{4}), 28 (C\textsubscript{2}H\textsubscript{4} + N\textsubscript{2} + CO\textsubscript{2} + CO), 30 (NO + NO\textsubscript{2}), 32 (O\textsubscript{2}), 40 (Ar), 44 (CO\textsubscript{2} + N\textsubscript{2}O), and 46 (NO\textsubscript{2}). The MS data are analyzed using the fragmentation patterns determined experimentally from calibration gases. A high resolution magnetic sector mass spectrometer (Jeol JMS GCmate) is also used for the analysis of C\textsubscript{2}H\textsubscript{4} + N\textsubscript{2} + CO and CO\textsubscript{2} + N\textsubscript{2}O. A NO\textsubscript{x} storage catalyst, Pt-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3} (1 wt. % Pt and 30 wt .% Ba), is used in powder form as provided by Engelhard. Typically, 1.9 gram of catalyst with an average pellet diameter of 180 \textmu m is used. The fresh catalyst is pre-treated at 500 °C with 1 vol. % O\textsubscript{2} in
He during 1 h, followed by 0.5 h in He, and finally by reduction with 2 vol. % of H₂ in He for 2 h. The total gas flow during the experiments is kept constant at 0.743 mmol/s, resulting in a gas space velocity (GHSV) of 29,000 h⁻¹ (298 K, 1 bar). The lean phase of the cycle contains 0.2 vol. % NO, 4 vol. % O₂, 1 vol. % Ar, 10 vol. % CO₂, and a balance of He. The rich phase includes 1 vol. % Ar, 10 vol. % CO₂, 0 or 10 vol. % H₂O, and either 0.8 vol. % H₂, 0.8 vol. % CO or 0.15 vol. % C₂H₄, balanced with He. NO is fed at higher concentrations as typically present in a real exhaust gas to guarantee enough sensitivity of the mass spectrometer for the gas phase component NO₂. H₂ is also fed at higher concentrations for better comparison of reduction performance between H₂, CO, and C₂H₄. The other gas concentrations are representative for conditions in diesel and lean-burn exhaust gases. The experimental data shown are collected after performing several lean/rich cycles and the cyclic steady state has been reached.

![Figure 5.1](image)

**Figure 5.1** (A) Rich outlet concentrations of NO, NO₂, N₂, and NH₃ during lean/rich cycling experiments. Rich phase: 0.8 vol. % H₂, 1 vol. % Ar, and 10 vol. % CO₂, 100 min. (B) Lean outlet concentrations of NO, NO₂, and NOₓ. Lean phase: 0.2 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂, and 1 vol. % Ar, 200 min.

### 5.3. NOₓ storage-reduction performance

#### 5.3.1. Influence of H₂

Figure 5.1 shows the catalyst outlet gas concentrations for a lean/rich cycling experiment with H₂ as the reducing agent. The NOₓ breakthrough profile in the lean phase (Figure 5.1a) shows complete NOₓ storage for 6.2
Influence of reducing agent and of H₂O on NOₓ reduction

After 6.2 min, NO breakthrough is observed. The NO signal reaches a maximum value after 42.5 min followed by a decrease in NO concentration. NO₂ is completely consumed for about 30 minutes, after which its concentration increases gradually with time. After 200 min, the NOₓ concentration is constant and equal to the inlet concentration. As no NOₓ storage is ongoing, the detected outlet 0.14 vol. % NO and the outlet 0.06 vol. % NO₂ can be ascribed to the NO oxidation reaction taking place on the Pt sites. Recently, we have found that the initial complete NOₓ uptake mainly occurs through NO adsorption as nitrites on the surface barium sites (reaction (I)) [24].

\[
\begin{align*}
\text{BaCO}_3 + 2 \text{NO} + 0.5 \text{O}_2 & \rightarrow \text{Ba(NO}_2)_2 + \text{CO}_2 \\
\text{Ba(NO}_2)_2 + 2 \text{NO}_2 & \rightarrow \text{Ba(NO}_3)_2 + 2\text{NO} \\
\text{BaCO}_3 + 2 \text{NO}_2 + 0.5 \text{O}_2 & \rightarrow \text{Ba(NO}_3)_2 + \text{CO}_2
\end{align*}
\]

It is considered that in the presence of CO₂, barium is present in the carbonate form. BaCO₃ is present as surface, semi-bulk and bulk sites. These sites not only differ in physical appearance but also in chemical reactivity. As the surface sites fill, NO breakthrough can be seen. The NO storage process continues at the semi-bulk sites, but at a lower rate due to diffusion limitation. Meanwhile, NO₂ is consumed in oxidizing nitrites into nitrates (reaction (II)) and by getting stored directly as nitrates on the semi-bulk sites (reaction (III)). As a result, a delay in NO₂ breakthrough can be seen in Figure 5.1b. Reaction (II) produces NO, resulting in a maximum in the NO concentration. Bulk BaCO₃ sites are inactive in NOₓ storage in the presence of CO₂, and after 200 minutes only surface and semi-bulk barium sites are filled with nitrates.

Figure 5.1b shows the rich outlet NO, NO₂, NH₃, and N₂ signals. Upon switching from lean to rich conditions with H₂, immediate N₂ formation and NOₓ release can be seen. Switching from lean conditions to pure He, results in only negligible NO desorption (not shown), which indicates that release of stored NOₓ is triggered by the reducing agent. NH₃ formation is observed once the N₂ production declines. At the same time, CO formation (not shown) is observed, accompanied by the parallel consumption of H₂ and CO₂ and by the parallel production of H₂O. This suggests that the reverse water gas shift reaction (RWGS) takes place.
Table 5.1. Proposed reaction mechanism

<table>
<thead>
<tr>
<th>NOx reduction on Pt sites</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂ + ( )* ↔ NO₂*</td>
<td>(1)</td>
</tr>
<tr>
<td>NO + ( )* ↔ NO*</td>
<td>(2)</td>
</tr>
<tr>
<td>NO* + O* ↔ NO₂* + ( )*</td>
<td>(3)</td>
</tr>
<tr>
<td>NO* + ( )* ↔ N* + O*</td>
<td>(4)</td>
</tr>
<tr>
<td>2N* → N₂ + 2 ( )*</td>
<td>(5)</td>
</tr>
</tbody>
</table>

H₂ interaction with Pt
2 ( )* + H₂ ↔ 2H*          | (6)      |
O* + 2H* → 3( )* + H₂O     | (7)      |
N* + H* ↔ NH* + ( )*       | (8)      |
NH* + H* ↔ NH₂* + ( )*    | (9)      |
NH₂* + H* ↔ NH₃ + ( )*     | (10)     |

RWGS reaction
2 H* + CO₂ ↔ H₂O* + CO*    | (11)     |

CO interaction with Pt
( )* + CO ↔ CO*            | (12)     |
O* + CO* → CO₂ + 2( )*     | (13)     |
CO* + ( )* ↔ C* + O*       | (14)     |
N* + CO* → NCO* + ( )*     | (15)     |
NCO* + Ba ↔ BaNCO + *      | (16)     |
NCO* + 20* → N* + CO₂ + 2* | (17)     |

C₂H₄ interaction with Pt
C₂H₄ + 2* ↔ C₂H₄**         | (18)     |
C₂H₄** ↔ C₂H₄* + *         | (19)     |
C₂H₄* + 60* → 2CO₂ + 2H₂O + 8* | (20)   |
C₂H₄* + 60* → 2CO₂ + 2H₂O + 7* | (21)   |
C₂H₄* + 40* → CO₂ + 2H₂O + C* | (22)   |

Accordingly with our observations and in line with indications in literature, the reaction mechanism shown in Table 5.1 can be considered to explain the NOₓ reduction process on the Pt sites. The first two reactions show the reversible NO and NO₂ adsorption on the Pt sites. The third reaction is the reversible NO oxidation. The next two reactions show the formation of N₂. Reactions 6-10 show the interaction of H₂ with the Pt sites. As the rich phase starts, most of the Pt sites throughout the reactor are oxidized with O₂. Subsequently, as the reductant front passes through the reactor, H₂ will reduce the Pt sites scavenging the O₂. The reduced Pt sites can interact with NOₓ for reduction to N₂. However, as the reductant front passes, not all the stored NOₓ on barium will be released, due to diffusion limitation. As a result, part of the NOₓ is not yet released after the reduction front has passed.
Meanwhile, the Pt sites upstream of the reduction front will be highly covered with \( \text{H}_2 \) (reaction 6). As the remaining \( \text{NO}_x \) in the upstream front is released, it encounters the highly reduced Pt sites, which results in \( \text{NH}_3 \) formation (reactions 8-10).

**Table 5.2. The amount of \( \text{NO}_x \) stored, released and reduced in a lean/rich cycle per gram of catalyst.**

<table>
<thead>
<tr>
<th></th>
<th>( \text{H}_2 )</th>
<th>( \text{CO} )</th>
<th>( \text{C}_2\text{H}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lean</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{NO}_x ) stored (mmol/g)</td>
<td>1.39</td>
<td>1.27</td>
<td>1.36</td>
</tr>
<tr>
<td>( \text{N}_2 ) formation (mmol/g)</td>
<td>-</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>N-balance, lean (mmol/g)</td>
<td>1.39</td>
<td>0.97</td>
<td>1.36</td>
</tr>
<tr>
<td><strong>Rich</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{N}_2 ) formation (mmol/g)</td>
<td>0.56</td>
<td>0.42</td>
<td>0.62</td>
</tr>
<tr>
<td>( \text{NO}_x ) release (mmol/g)</td>
<td>0.09</td>
<td>0.10</td>
<td>0.12</td>
</tr>
<tr>
<td>( \text{NH}_3 ) formation (mmol/g)</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-balance, rich (mmol/g)</td>
<td>1.39</td>
<td>0.98</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Lean phase: 0.2 vol. % NO, 4 vol. % \( \text{O}_2 \), 10 vol. % \( \text{CO}_2 \), and 1 vol. % \( \text{Ar} \), 200 min.

Rich phase: 0.8 vol. % \( \text{H}_2 \) or 0.8 vol. % \( \text{CO} \) or 0.15 vol. % \( \text{C}_2\text{H}_4 \), 1 vol. % \( \text{Ar} \), and 10 vol. % \( \text{CO}_2 \), 100 min.

The results of the N balance during the lean/rich cycle are shown in Table 5.2. During the lean phase 1.39 mmol \( \text{NO}_x \)/g catalyst is stored. Upon rich conditions, the \( \text{N}_2 \) formation, \( \text{NO}_x \) release and \( \text{NH}_3 \) formation result in an N-balance of 1.39 mmol/g catalyst, which indicates that all the \( \text{NO}_x \) stored in the lean phase is completely released and reduced in the next rich phase.

**5.3.2. Influence of CO**

Figure 5.2 shows the results of the corresponding experiment with CO as the reducing agent. The \( \text{NO}_x \) storage behavior in the lean phase (Figure 5.2a) shows some remarkable differences compared to the storage behavior in lean/rich cycles with \( \text{H}_2 \) in the rich phase. Upon lean exposure the NO and \( \text{NO}_2 \) outlet concentrations show a dead time of 3.4 min after which they both gradually increase in time. Furthermore, a small \( \text{NO}_2 \) peak (0.05 vol. %) is observed after 9.2 min lean phase. Results reported by Abdulhamid et al. [3] also show a peak in the \( \text{NO}_x \) breakthrough profile for experiments with CO as reducing agent. This peak is not observed when \( \text{H}_2 \) is used, similar with our results. These findings seem to indicate that \( \text{NO}_x \) can be stored through
different routes and that the followed storage route may depend on the preceding rich phase.

Figure 5.2) (A) Rich outlet concentrations of NO, NO₂, and N₂ during lean/rich cycling experiments. Rich phase: 0.8 vol. % CO, 1 vol. % Ar, and 10 vol. % CO₂, 100 min. (B) Lean outlet concentrations of NO, NO₂, and NOₓ. Lean phase: 0.2 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂, and 1 vol. % Ar, 200 min.

The rich characteristics with CO show differences with the rich phase observed in lean/rich cycles with H₂ (Figure 2b). Upon switching to the rich conditions with CO, immediate N₂ formation, NO and NO₂ release can be seen. Compared to the results with H₂, more NO₂ release is observed. Recently, Cant et al. [25] reported that in a sequential catalytic system with Pt/SiO₂ ahead of the BaO/Al₂O₃, the initial product of the thermal decomposition of stored NOₓ in He is NO₂, followed by NO. However, the Pt present in our Pt-Ba/γ-Al₂O₃ catalyst can decompose NO₂ and NO into N₂ (Table 5.1, reactions (1)-(5)). The overall release and reduction reactions for both CO and H₂ as reducing agent are:

\[
\begin{align*}
\text{Ba(NO}_3\text{)}_2 + 3\text{H}_2 / \text{CO + CO}_2 & \rightarrow \text{BaCO}_3 + 2\text{NO} + 3\text{CO}_2 / \text{H}_2\text{O} \quad \text{(IV)} \\
\text{Ba(NO}_3\text{)}_2 + \text{H}_2 / \text{CO + CO}_2 & \rightarrow \text{BaCO}_3 + 2\text{NO}_2 + \text{CO}_2 / \text{H}_2\text{O} \quad \text{(V)} \\
2\text{NO} + 2\text{CO} / \text{H}_2 & \rightarrow \text{N}_2 + 2\text{CO}_2 / \text{H}_2\text{O} \quad \text{(VI)} \\
2\text{NO}_2 + 4\text{CO} / \text{H}_2 & \rightarrow \text{N}_2 + 4\text{CO}_2 / \text{H}_2\text{O} \quad \text{(VII)}
\end{align*}
\]

In the presence of CO, Pt sites can be poisoned due to carbon decomposition (see Table 5.1, reaction (14)) what results in less efficient decomposition of
NO₂. Consequently, NO₂ is observed during the rich phase with CO, contrary to rich conditions with H₂. Furthermore, the N₂ outlet concentration decreases after 60 s to 0.14 vol. % which can also be related to poisoning of the Pt sites.

Table 5.3. The amount of CO consumption during the rich phase per gram of catalyst.

| (CO_{in})-(CO_{out}) in rich phase, (mmol/g) | 2.74 |
| CO consumption based on NO, NO₂ and N₂ concentration, (mmol/g) | 2.25 |
| CO used for formation of isocyanates, (mmol/g) | 0.30 |
| CO used for carbon decomposition, (mmol/g) | 0.21 |

Lean phase: 0.2 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂, and 1 vol. % Ar, 200 min.
Rich phase: 0.8 vol. % CO, 1 vol. % Ar, and 10 vol. % CO₂, 100 min.

Based on the measured N₂, NO and NO₂ concentrations and reactions (IV)-(VII), the CO consumption can be calculated. The results are shown in Table 5.3. With the measured CO breakthrough profile (not shown), the real CO consumption is known. Table 5.3 shows that more CO is consumed as expected based on the outlet N₂, NO and NO₂ concentrations. Furthermore, Table 5.2 shows that in the lean phase 1.28 mmol NOₓ/g catalyst is stored. However, based on the N balance of the rich phase, only 0.99 mmol NOₓ/g catalyst is released and reduced at rich conditions. As mentioned before, CO may inhibit the regeneration process through the formation of isocyanates on the alumina and barium oxide components of the catalyst [12,13]. Nevertheless, alumina shows only negligible storage capacity for NOₓ at this temperature [22] and probably only barium isocyanates can form (see reaction (15)). These isocyanates can react with O₂ according to reactions (16+17) in Table 5.1. Indeed, upon switching to lean conditions, N₂ and CO₂ are observed. To distinguish between CO₂ formed during NOₓ storage (reactions (I) and (III)) and CO₂ produced through reaction (17), the catalyst is exposed to 4 vol. % O₂ in He flow without CO₂ present after a rich phase. As shown in Figure 5.3, immediate N₂ formation is observed followed by CO₂ evolution. The CO₂ formation shows a delay of 2 s, probably due to adsorption of CO₂ on barium sites. The N₂ production decreases to zero after 0.3 min and corresponds with 0.15 mmol N₂ per gram catalyst. A tail is observed in the concentration of CO₂ and the CO₂ concentration decreases to zero only after
9 min. The CO$_2$/N$_2$ molar ratio equals 3.4, which is not in agreement with the value 2 obtained from the stoichiometry of reaction (17). However, O$_2$ can also react with adsorbed carbon on Pt sites, according to reaction (14), which explains the observed CO$_2$/N$_2$ molar ratio. With the measured CO$_2$ and N$_2$ signals as shown in Figure 5.3, the amounts of formed isocyanates and carbon decomposition can be calculated. Table 5.3 shows that the formation of isocyanates and carbon decomposition closes the CO balance.

![Figure 5.3: CO$_2$ and N$_2$ formation with 4 vol. % O$_2$ in He flow after the rich phase with CO as reducing agent.](image)

Thus, CO present as reductant in the rich phase leads to poisoning of the Pt sites and formation of barium isocyanates. This provides a likely explanation for the difference in NO$_x$ breakthrough profile compared with lean/rich cycles with H$_2$. Upon switching from rich with CO to lean conditions, initially the activity of Pt will be less to oxidize NO into NO$_2$ (reaction (3)). Consequently, less NO$_2$ will be available to oxidize barium nitrites into nitrates (reaction (II)). However, the stored NO$_x$ can be further oxidized into nitrates with O$_2$ (reaction (VIII)) [17].

$$\text{Ba(NO}_2\text{)}_2 + \text{O}_2 \rightarrow \text{Ba(NO}_3\text{)}_2 \quad \text{(VIII)}$$

With reaction (VIII), no NO is released and as a result the NO concentration increases gradually in time (Figure 5.2b) without showing a maximum value as observed for experiments with H$_2$ (Figure 5.1b). As no NO$_2$ is consumed in oxidizing surface nitrites, NO and NO$_2$ will break through at the same time.
As mentioned before, the RWGS reaction occurs with H₂ in the rich phase resulting in CO and H₂O formation. However, no NCO species will form as CO formation is only seen after the catalyst has been completely regenerated. It is also unlikely that poisoning of Pt sites will occur due to adsorbed carbon species as H₂O has a positive effect on carbon decomposition [26,27]. Indeed, no CO₂ and N₂ formation peaks are seen in the beginning of the lean phase for experiments with H₂ as reducing agent.

### 5.3.3. Influence of C₂H₄

The effect of C₂H₄ on the NOₓ storage/reduction is presented in Figure 5.4. The rich phase shows immediate formation of N₂ and NO release (Figure 5.4a). Only minor amounts of NO₂ are observed. Reaction (IX) shows the overall regeneration reaction of Ba(NO₃)₂ with C₂H₄ as reducing agent.

\[
\text{Ba(NO₃)₂ + } \frac{5}{6} \text{C}_2\text{H}_₄ \rightarrow \text{BaCO}_3 + \text{N}_₂ + \frac{2}{3}\text{CO}_₂ + \frac{5}{3}\text{H}_₂\text{O} \tag{IX}
\]

Figure 5.4) (A) Rich outlet concentrations of NO, NO₂, and N₂ during lean/rich cycling experiments. Rich phase: 0.15 vol. % C₂H₄, 1 vol. % Ar, and 10 vol. % CO₂, 100 min. (B) Lean outlet concentrations of NO, NO₂, and NOₓ. Lean phase: 0.2 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂, and 1 vol. % Ar, 200 min.

The inlet C₂H₄ concentration is 0.15 vol. %, which according to reaction (IX) can result in a maximum N₂ concentration of 0.18 vol. %. It is reported that the reversible adsorption of C₂H₄ on Pt sites at first leads to di-σ ethylene (reaction (18)), followed by conversion of di-σ ethylene to π ethylene (reaction (19)) [28]. Both di-σ and π ethylene can react with O₂ on Pt sites (reactions...
(20) and (21)). Ethylene is less capable as H\textsubscript{2} and CO to adsorb on Pt sites with a high coverage of O\textsubscript{2}. This is supported by the initially lower N\textsubscript{2} concentration and C\textsubscript{2}H\textsubscript{4} breakthrough (not shown). After 2 min, the N\textsubscript{2} concentration increases to 0.18 vol. % after which it remains constant for 5.3 min. After 5.3 min, the N\textsubscript{2} outlet concentration decreases and a tail is observed. Only after 34 min, the N\textsubscript{2} concentration decreases to zero. It is reported that strong adsorption of the species derived from hydrocarbons can poison Pt sites (reaction (22)) [8, 11]. This might explain why the NO\textsubscript{x} reduction into N\textsubscript{2} becomes less effective in time. Table 5.2 shows that at the end of the rich phase 1.36 mmol NO\textsubscript{x}/g catalyst is released and reduced which indicates that all of the stored NO\textsubscript{x} in the preceding lean phase has been removed.

The CO\textsubscript{2} peak formed at the start of the lean phase (not shown) supports the presence of adsorbed molecules derived from C\textsubscript{2}H\textsubscript{4} on Pt sites. The lean phase shows complete NO\textsubscript{x} storage for 5 min, after which NO breaks through. The NO concentration shows a maximum value of 0.16 vol. % after 20 min before it decreases to 0.14 vol. %. The NO concentration is equal to 0.14 vol. % after 80 min, as against 156 min for experiments with H\textsubscript{2} and 16 min for experiments with CO. NO\textsubscript{2} breaks through after 6.7 min, in contrast to 30 min for experiments with H\textsubscript{2} and 3.4 min for experiments with CO. This seems to indicate that the NO\textsubscript{x} storage route for experiments with C\textsubscript{2}H\textsubscript{4} as reducing agent is a combination of routes followed for experiments with CO and H\textsubscript{2}.

### 5.4. Effect of H\textsubscript{2}O on NO\textsubscript{x} reduction

Catalyst regeneration in the presence of H\textsubscript{2}O shows no NH\textsubscript{3} formation, even with H\textsubscript{2} as the reducing agent (Figure 5.5). At a temperature of 300 °C, H\textsubscript{2}O coverage on Pt sites is of the same magnitude as NO and NO\textsubscript{2} [29]. This might explain the absence of NH\textsubscript{3} as H\textsubscript{2}O Pt species might compete with H\textsubscript{2}, resulting in reduced H coverage and deceleration of NH\textsubscript{3} formation. Upon switching from lean to rich immediate formation of N\textsubscript{2} can be seen, as well as NO release. Only minor amounts of NO\textsubscript{2} are observed. During the rich phase, the catalyst is completely regenerated. In contrast to experimental results obtained with CO without H\textsubscript{2}O present (Figure 5.2), only minor amounts of
Figure 5.5) Rich outlet concentrations of NO, NO₂, and N₂ during lean/rich cycling experiments. Lean phase: 0.2 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂ and 1 vol. % Ar, 200 min. (A) Rich phase: 0.8 vol. % H₂, 1 vol. % Ar, 10 vol. % CO₂, and 10 vol. % H₂O, 100 min. (B) Rich phase: 0.8 vol. % CO, 1 vol. % Ar, 10 vol. % CO₂, and 10 vol. % H₂O, 100 min. (C) Rich phase: 0.15 vol. % C₂H₄, 1 vol. % Ar, 10 vol. % CO₂, and 10 vol. % H₂O, 100 min.
NO$_2$ are observed (Figure 5.5). Interestingly, in the presence of H$_2$O, the same NO release, N$_2$ formation profile, and selectivity towards N$_2$ are seen for the experiments with CO and H$_2$. This observed similarity between H$_2$ and CO can possibly be ascribed to the WGS reaction (reaction 11) [4,30,31]. In fact, after catalyst regeneration, 0.8 vol. % H$_2$ is observed and no CO is detected (not shown), indicating that H$_2$ is produced from CO + H$_2$O. No H$_2$ or CO is detected during N$_2$ formation, but it is reasonable to assume that H$_2$ acts as reductant. This is supported by the fact that there are no signs of Pt poisoning by CO or isocyanates formation. Immediate N$_2$ formation and NO release are also seen for experiments with C$_2$H$_4$ (Figure 5.5). As 0.15 vol. % C$_2$H$_4$ has a higher molar reduction capacity as 0.8 vol. % H$_2$ or CO, the N$_2$ concentration formed is 0.18 vol. %, as against 0.16 vol. % for CO and H$_2$. As a consequence, the N$_2$ concentration drops to zero for C$_2$H$_4$ after 8.9 min, as against 10 min for CO and H$_2$ experiments. However, the N$_2$ signal for C$_2$H$_4$ shows a more pronounced tail while decreasing to zero compared to the N$_2$ signals for CO and H$_2$. The N balance shows that the barium nitrates stored in the previous lean phase are completely removed.

![Figure 5.6](image-url) Lean outlet concentrations of NO, NO$_2$ and NO$_x$ during lean/rich cycling experiments. Lean phase: 0.2 vol. % NO, 4 vol. % O$_2$, 10 vol. % CO$_2$, 10 vol. % H$_2$O and 1 vol. % Ar, 200 min.
For all the used reducing agents, the lean phase shows the same NO and NO\textsubscript{2} breakthrough profiles (Figure 5.6). These breakthrough profiles are about the same as the observed NO and NO\textsubscript{2} breakthrough curves with H\textsubscript{2} in the absence of H\textsubscript{2}O. This confirms that no isocyanates form on the catalyst and indicates that almost no poisoning of Pt sites occurs in the presence of H\textsubscript{2}O.

5.5. Conclusions

The reduction of stored NO\textsubscript{x} by H\textsubscript{2} has been shown to produce mainly N\textsubscript{2} with smaller quantities of NO and NH\textsubscript{3}. Only minor amounts of NO\textsubscript{2} are observed. During the rich phase with H\textsubscript{2}, the catalyst is able to completely remove the stored NO\textsubscript{x}. At rich periods with CO, poisoning of the catalyst is observed through carbon decomposition on the Pt sites and formation of strongly bound isocyanates on alumina and barium sites. Under these conditions, stored NO\textsubscript{x} is not fully removed in the rich phase. However, upon switching to lean conditions, O\textsubscript{2} removes the isocyanates. Both O\textsubscript{2} and NO\textsubscript{2} can participate in regeneration of the carbon-poisoned Pt sites. Reduction of C\textsubscript{2}H\textsubscript{4} shows the highest selectivity towards N\textsubscript{2} of the three reductants investigated. During the rich phase, poisoning of the Pt sites occurs. The type of reducing agent also affects the NO\textsubscript{x} storage route followed in the lean phase. For lean/rich cycling experiments with H\textsubscript{2} as reductant, the NO\textsubscript{x} breakthrough profile shows a dead time followed by NO breakthrough. The NO concentration passes through a maximum. NO\textsubscript{2} breaks through with a delay compared to NO. This can be explained with the participation of NO\textsubscript{2} in the oxidation of nitrites into nitrates, with release of NO. The lean phase after catalyst regeneration with CO, shows simultaneous NO and NO\textsubscript{2} breakthrough. Both NO and NO\textsubscript{2} concentrations increase gradually in time. Poisoning of the Pt sites by carbon can affect the NO oxidation into NO\textsubscript{2}. Furthermore, NO\textsubscript{2} can participate in the carbon oxidation. Consequently, less NO\textsubscript{2} is available for nitrite oxidation and nitrites can be oxidized with O\textsubscript{2}. The results for C\textsubscript{2}H\textsubscript{4} as reductant, show that the NO\textsubscript{x} storage route is a combination of the routes observed for experiments with H\textsubscript{2} and CO as reducing agent. H\textsubscript{2}O in the rich phase does not affect the amount of NO\textsubscript{x} stored in the lean phase. H\textsubscript{2}O prevents poisoning of the catalyst by CO and
C$_2$H$_4$ and as a result the followed NO$_x$ storage route is the same for all three reductants. With CO and H$_2$O the reverse water gas shift reaction takes place and H$_2$ acts as reducing agent.

Acknowledgements
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Reference List
Model for NO\textsubscript{x} storage/reduction in the presence of CO\textsubscript{2} and H\textsubscript{2}O

This chapter has been submitted as:
C.M.L. Scholz, K.M. Nauta, M.H.J.M. de Croon, J.C. Schouten, Kinetic modeling of NO\textsubscript{x} storage and reduction with different reducing agents (CO, H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}) on a Pt-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst in the presence of CO\textsubscript{2} and H\textsubscript{2}O, Journal of Catalysis

Abstract

In this paper a global reaction kinetic model is used to understand and describe the NO\textsubscript{x} storage/reduction process in the presence of CO\textsubscript{2} and H\textsubscript{2}O. Experiments have been performed in a packed bed reactor with a Pt-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3} powder catalyst (1 wt. % Pt and 30 wt. % Ba) with different lean/rich cycle timings at different temperatures (200, 250, and 300 °C) and using different reductants (H\textsubscript{2}, CO, and C\textsubscript{2}H\textsubscript{4}). Model simulations and experimental results are compared. H\textsubscript{2}O inhibits the NO oxidation capability of the catalyst and no NO\textsubscript{2} formation is observed. The rate of NO storage increases with temperature. The reduction of stored NO with H\textsubscript{2} is complete for all investigated temperatures. At temperatures above 250 °C, the WGS reaction takes place and H\textsubscript{2} acts as reductant instead of CO. At 200 °C, CO and C\textsubscript{2}H\textsubscript{4} are not able to completely regenerate the catalyst. At the higher temperatures,
C\textsubscript{2}H\textsubscript{4} is capable of reducing all the stored NO, although C\textsubscript{2}H\textsubscript{4} poisons the Pt sites by carbon decomposition at 250 \textdegree C. The model adequately describes the NO breakthrough profile during 100 min lean exposure as well as the subsequent release and reduction of the stored NO. Further, the model is capable of simulating transient reactor experiments with 240 s lean and 60 s rich cycle timings.

6.1. Introduction

Diesel and lean-burn gasoline engines have the benefit of improved fuel economy and consequently reduced emission of the greenhouse gas CO\textsubscript{2} compared to conventional gasoline engines. However, due to the high air-to-fuel ratio, excess O\textsubscript{2} is present in their exhaust gas and the control of NO\textsubscript{x} emissions remains a challenge. One promising solution to reduce NO\textsubscript{x} in the exhaust gas of passenger cars is the use of a NO\textsubscript{x} storage reduction (NSR) catalyst along with mixed lean operation, where the air-to-fuel ratio is altered between fuel lean conditions with excess O\textsubscript{2} and fuel rich conditions [1,2]. The NSR catalytic systems usually investigated are Pt-based oxidation catalysts, which contain barium as a storage component. In real-life application, NO\textsubscript{x} is stored onto barium as nitrites/nitrates during the relatively long lean periods. As the storage capacity of barium gets saturated, NO\textsubscript{x} breaks through and the catalyst needs to be regenerated. Regeneration takes place during short rich periods and the stored NO\textsubscript{x} is released and reduced by the hydrocarbons, CO, and H\textsubscript{2}, typically present in an automotive exhaust gas. To optimize the operating conditions and consequently the overall NO\textsubscript{x} reduction efficiency and fuel consumption, a good understanding of the NSR mechanism is necessary. This mechanism can be used as input for a model of the NSR process to predict the NO\textsubscript{x} emissions and fuel consumption as a function of time and varying operating conditions.

Extensive research has been done in the past decade to understand the NSR process [see 3 and references herein]. In general, the oxidation of NO into NO\textsubscript{2} over Pt sites is seen as an important step in the NO\textsubscript{x} storage process [4-7]. It is believed that barium has a higher storage capacity for NO\textsubscript{2} than for NO [8]. NO\textsubscript{2} can be stored on barium via a disproportionation route resulting in nitrate formation and NO release [4,5,9], or via a direct route
without NO release [4,7]. Additionally, Pt sites also catalyze the direct uptake of NO in the presence of O\textsubscript{2} in the form of nitrites [4,5]. However, as nitrites are further oxidized into nitrates, the final state of the stored NO\textsubscript{x} is in the form of barium nitrate [10-12]. Studies focusing on the rich phase show that at temperatures above 250 °C, both H\textsubscript{2} and CO are highly efficient towards NO\textsubscript{x} reduction compared to hydrocarbons [13-15]. At lower temperatures, CO facilitates Ba(NO\textsubscript{3})\textsubscript{2} decomposition, but not NO\textsubscript{x} reduction, while H\textsubscript{2} enables both to occur [16]. Detailed kinetic models [17,18] and global models based on the shrinking core mechanism [19-22] have been used to describe the NSR process. In all these models no distinction is made between e.g. the reactivity of the surface and bulk barium sites, although there is growing evidence that NO\textsubscript{x} storage occurs through multiple storage sites [23-26]. Furthermore, most of these studies do not consider the influence of CO\textsubscript{2} and/or water, which are known to effect the NSR process [23, 27-29] and are always present in vehicle exhaust gas.

It is reported that CO\textsubscript{2} negatively affects the NO\textsubscript{x} storage capacity [23,30,31]. The significant decrease of NO\textsubscript{x} storage in the presence of CO\textsubscript{2} suggests that there is a competition between NO\textsubscript{2} and CO\textsubscript{2} for the same barium sites [27]. Interestingly, NO\textsubscript{2} shows inactivity for carbonate replacement, while NO is able to replace carbonate by nitrites with the release of CO\textsubscript{2} [12]. This is in agreement with recent results, showing that in the presence of CO\textsubscript{2}, initial NO\textsubscript{x} storage mainly occurs through NO adsorption as nitrites and the role of NO\textsubscript{2} is mostly to oxidize nitrites into nitrates [26]. Furthermore, with CO\textsubscript{2} present, only the well-dispersed barium sites are active in NO\textsubscript{x} trapping while the bulk, crystalline barium sites are inactive [28,32]. NO\textsubscript{x} release studies show that CO\textsubscript{2} has a promoting effect on the NO\textsubscript{x} release in the rich phase [27,29,31], while H\textsubscript{2}O hinders NO\textsubscript{x} release [33]. Moreover, H\textsubscript{2}O inhibits the NO oxidation capability of the Pt sites [34] and no NO\textsubscript{2} formation is seen in the lean phase in the presence of H\textsubscript{2}O [32], resulting in decreased NO\textsubscript{x} storage capacity.

The focus of this work is to understand and describe the NSR mechanism in the presence of both CO\textsubscript{2} and H\textsubscript{2}O for different temperatures and reducing agents. For this purpose, a recently developed global reaction kinetic model based on a multiple storage sites mechanism has been used
Lean/rich cycling experiments at three different temperatures (200, 250, and 300 °C) have been carried out over a Pt-Ba/γ-Al₂O₃ catalyst (1 wt. % Pt and 30 wt. % Ba) catalyst. Rich conditions contain either CO, H₂, or C₂H₄ as reducing agent. NO is used as NOₓ source. Cycle times of 100 min lean and 80 min rich have been used to monitor the complete NOₓ breakthrough profile during lean exposure and to ensure complete catalyst regeneration at rich conditions. Additionally, cycle times of 240 s lean and 60 s rich have been used to demonstrate the applicability of the developed model for lean/rich timings more closely to realistic automotive exhaust conditions.

6.2. Experimental

Lean/rich cycling experiments at 200, 250, and 300 °C are performed in a packed bed reactor, which is described in detail elsewhere [35]. The gas composition of reactants and products is measured with an online mass spectrometer (ESS EcoSys). A fixed amount of argon is fed as an internal standard during experiments to compensate for any intensity loss of the mass spectrometer over time. Gas analysis is performed on m/e 2 (H₂), 17 (NH₃ + H₂O), 18 (H₂O), 27 (C₂H₄), 28 (C₂H₄ + N₂ + CO₂ + CO), 30 (NO + NO₂), 32 (O₂), 40 (Ar), 44 (CO₂ + N₂O), and 46 (NO₂). The MS data are analyzed using the fragmentation patterns determined experimentally from calibration gases. A high resolution magnetic sector mass spectrometer (Jeol JMS GCmate) is also used for the analysis of C₂H₄ + N₂ + CO and CO₂ + N₂O. A NOₓ storage catalyst, Pt-Ba/γ-Al₂O₃ (1 wt. % Pt and 30 wt.% Ba), is used in powder form as provided by Engelhard. Typically, 1.9 gram of catalyst with an average pellet diameter of 180 µm is used. The fresh catalyst is pre-treated at 500 °C with 1 vol. % O₂ in He during 1 h, followed by 0.5 h in He, and finally by reduction with 2 vol. % of H₂ in He for 2 h. The total gas flow during the experiments is kept constant at 0.743 mmol/s, resulting in a gas space velocity (GHSV) of 29,000 h⁻¹ (298 K, 1 bar). Table 6.1 shows the experimental conditions, for the lean/rich cycling experiments. NO is fed at higher concentrations as typically present in a real exhaust gas to guarantee enough sensitivity of the mass spectrometer for the gas phase component NO₂. H₂ is also fed at higher concentrations for better comparison of the
reduction performance between $\text{H}_2$, $\text{CO}$, and $\text{C}_2\text{H}_4$. The other gas concentrations are representative for conditions in diesel and lean-burn exhaust gases. The experimental data shown are collected after performing several lean/rich cycles and the cyclic steady state has been reached. As will be discussed in sections 6.4.4 and 6.4.5, $\text{CO}$ and $\text{C}_2\text{H}_4$ are not capable of completely regenerating the catalyst at a temperature of 200 °C. Therefore, at the end of the rich phase, $\text{H}_2$ is also fed to ensure that all the NO$_x$ stored in the preceding lean phase is released and reduced.

Table 6.1. Experimental conditions for the lean/rich cycling experiments.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Inlet lean*</th>
<th>Inlet rich*</th>
</tr>
</thead>
<tbody>
<tr>
<td>473, 523, 573</td>
<td>0.14 vol. % NO</td>
<td>1.2 vol. % H$_2$ or</td>
</tr>
<tr>
<td></td>
<td>4 vol. % O$_2$</td>
<td>1.2 vol. % CO or</td>
</tr>
<tr>
<td></td>
<td>10 vol. % CO$_2$</td>
<td>0.2 vol. % $\text{C}_2\text{H}_4$</td>
</tr>
<tr>
<td></td>
<td>10 vol. % H$_2$O</td>
<td>10 vol. % CO$_2$</td>
</tr>
<tr>
<td></td>
<td>1 vol. % Ar</td>
<td>10 vol. % H$_2$O</td>
</tr>
</tbody>
</table>

* He is carrier gas

6.3. Modeling

6.3.1. Reactor model

The plug flow reactor model uses a global reaction kinetic model, which considers that NO$_x$ storage occurs on three different types of barium sites: surface, semi-bulk, and bulk sites [26].

![Figure 6.1. Pictorial representation of surface, semi-bulk, and bulk barium sites. Surface and semi-bulk sites are amorphous and bulk sites are crystalline [26].](image-url)
These sites not only differ in physical appearance (as shown in Figure 6.1), but also in chemical reactivity. Surface sites are being the most reactive, followed by semi-bulk sites whereas bulk sites are not active in NO\textsubscript{x} trapping. Fast NO\textsubscript{x} storage, which is determined by the kinetics, occurs at the surface sites while slow NO\textsubscript{x} storage occurs at the semi-bulk sites, where diffusion plays a major role. Diffusion of the gas phase components is considered only from the external surface of the barium clusters to the interior of the barium clusters. The gas bulk in the packed bed reactor is discretized in the axial direction \( z \) and the gas in the spherical barium clusters with the partial coordinate \( \xi \). Both parts are connected through diffusion from the bulk gas to the inner part of the barium clusters. It is considered that barium is only present in the carbonate form. The global reaction steps with the rate equations are presented in Table 6.2.

The change in the concentration of the different components as a function of time at each axial position in the reactor can be described as follows:

\[
\varepsilon_b \frac{\partial C_i}{\partial t} = - \frac{F_v}{A_r} \frac{\partial C_i}{\partial z} - D_{\text{eff}}A_{\text{Ba}} \frac{\partial^2 C_i}{\partial \xi^2} |_{\xi=R} + L_{\text{Pt}} \sum_j \nu_{ij} R_{\text{Pt},ij} + L_{\text{Ba, surf}} \sum_k \nu_{ik} R_{\text{Ba, surf},k} \tag{1}
\]

where \( \varepsilon_b \) [m\textsuperscript{3} gas m\textsuperscript{-3} reactor] is the bed porosity, \( C_i \) [mol m\textsuperscript{-3} gas] is the gas phase concentration of component \( i \) (NO, O\textsubscript{2}, H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, CO, and N\textsubscript{2}), \( t \) [s] is time, \( F_v \) [m\textsuperscript{3} gas s\textsuperscript{-1}] is the volumetric flow rate, \( A_r \) [m\textsuperscript{2} reactor] is the surface area of the reactor, \( z \) [m reactor] is the axial reactor coordinate, \( D_{\text{eff}} \) [m\textsuperscript{3} gas m\textsuperscript{-1} Ba s\textsuperscript{-1}] is the effective gas diffusion coefficient, \( A_{\text{Ba}} \) [m\textsuperscript{2} Ba m\textsuperscript{-3} reactor] is the specific barium surface, \( \xi \) [m Ba] is the radial coordinate in the barium clusters, \( L_{\text{Pt}} \) [mol Pt m\textsuperscript{-3} reactor] is the specific number of moles of active Pt surface sites, and \( L_{\text{Ba, surf}} \) [mol Ba m\textsuperscript{-3} reactor] is the specific number of moles of active barium surface sites.

As will be discussed in more detail in section 6.4.1, no NO\textsubscript{2} formation is seen in the lean phase. As such, only NO storage can take place and consequently \( R_{\text{Ba, surf},k} \) [mol mol\textsuperscript{-1} Ba s\textsuperscript{-1}] is the NO storage and regeneration rate at the barium surface sites and can be determined from the reaction equations (I) – (V) mentioned in Table 6.2. During the lean phase, Pt will be
covered with O₂, which can react with the reducing agent in the rich phase. Furthermore, the water gas shift (WGS) reaction can take place (section 6.4.3) and at temperatures lower than 250 °C, the Pt sites are poisoned by C₂H₄ (section 6.4.4). Therefore, Rₚₜ,j [mol·mol⁻¹·Pt·s⁻¹] not only represents the NO reduction rate, as described in equations (VI) - (VIII) in Table 6.2, but also the rate of adsorption of O₂ on the Pt sites (equation (IX)), the rate of combustion of H₂, CO and C₂H₄ (equations (X) – (XII)), the deposition of carbonaceous and hydrocarbon fragments from C₂H₄ (equation (XIII)), and the water gas shift (WGS) reaction (equation (XIV)). Reaction equations (X) – (XII) show Eley-Rideal type of reaction paths, what is necessary to initiate adsorption onto a surface fully covered by O₂. Only Pt coverage by O₂ and C₂H₄ is used in the parameter fitting procedure, as adsorption of other species is not crucial for simulating the experiments.

Equation (2) describes the time-dependent change of the species on the Pt sites:

\[
\frac{\partial \theta_{l,Pt}}{\partial t} = \sum_{n} v_{i,n} R_{Pt,n} \tag{2}
\]

where \( \theta_{l,Pt} \) [-] is the coverage of the Pt sites and \( l \) denotes Pt-O, Pt-C₂H₄, or Pt. \( R_{Pt,n} \) [mol·mol⁻¹·Pt·s⁻¹] is the rate of adsorption of O₂ on Pt sites, the rate of combustion of H₂, CO and C₂H₄, and the poisoning of Pt sites by C₂H₄. Equation (3) calculates the time-dependent change of the nitrite/nitrate species on the surface barium sites:

\[
\frac{\partial \theta_{m,surf}}{\partial t} = \sum_{k} v_{i,k} R_{Ba\_surf,k} \tag{3}
\]

where \( \theta_{m,surf} \) [-] is the coverage of the surface barium sites and \( m \) denotes either Ba(NO₂)₂, Ba(NO₃)₂, or BaCO₃. The site balance for the surface barium sites is shown in Equation (4):

\[
\theta_{BaCO_3,surface} = 1 - \theta_{Ba(NO_2)_2,surface} - \theta_{Ba(NO_3)_2,surface} \tag{4}
\]

The NO storage and reduction at the semi-bulk sites is limited by the diffusion of gas components inside the barium clusters. Equation 5 represents the change in the concentration of the different gas phase components as a function of time at each radial position for the semi-bulk barium sites at a specific location in the reactor:
\[
\varepsilon_{\text{cluster}} \frac{\partial C_i}{\partial t} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( D_{\text{eff}} \frac{\partial C_i}{\partial \xi} \right) + \sum_k v_{i,k} R_{\text{Ba},k} \tag{5}
\]

Accumulation of moles in gas phase in the Ba clusters
Diffusion in Ba clusters
Reactions involved on semi-bulk Ba sites

where \( \varepsilon_{\text{cluster}} \) [m\(^3\) gas m\(^3\) Ba] is the porosity of the barium clusters, and \( R_{\text{Ba},k} \) [mol m\(^3\) Ba s\(^{-1}\)] is the NO\(_x\) storage and regeneration rate for the semi-bulk barium and can be determined from the rate equations (I) – (IV) mentioned in Table 1.

Equation (6) describes the time-dependent change of the different species on the semi-bulk barium:

\[
\frac{L_{\text{Ba,semibulk}}}{f} \frac{\partial \theta_{m,\text{semibulk}}}{\partial t} = \sum_k v_{i,k} R_{\text{Ba,semi-bulk},k} \tag{6}
\]

where \( L_{\text{Ba,semibulk}} \) [mol\(_{\text{Ba}}\) m\(^3\) reactor\] is the specific number of moles of active semi-bulk barium sites, \( f \) [m\(^3\) Ba m\(^{-3}\) reactor\] is the volume fraction, and \( \theta_{m,\text{semi-bulk}} \) [-] is the coverage of the semi-bulk barium sites. The site balance for the semi-bulk barium is shown in equation (7):

\[
\theta_{\text{BaCO}_3,\text{semi-bulk}} = 1 - \theta_{\text{Ba(NO}_2)_2,\text{semi-bulk}} - \theta_{\text{Ba(NO}_3)_2,\text{semi-bulk}} \tag{7}
\]

The initial and boundary conditions are given as:

\( C_i = 0, \ \theta_{\text{Ba(NO}_2)_2,y} = 0, \ \text{and} \ \theta_{\text{Ba(NO}_3)_2,y} = 0 \) at \( t = 0 \) with \( y \) is surface, or semi-bulk barium sites;

\( C_i = C_{\text{in}} \) at \( t > 0 \) and \( z = 0 \);

\[
\frac{\partial C_i}{\partial \xi} = 0 \text{ at } \xi = 0 \text{ at any } t.
\]

The system of equations is solved using gPROMS (Process Systems Enterprise) software.

### 6.3.2. Model parameters

The model parameters can be found in Table 6.3. The distribution of surface, semi-bulk, and bulk sites are taken from Scholz et al. [26], where the distribution is acquired from 9h/15h lean/rich cycling experiments in the presence of CO\(_2\) supported by the results of a TGA experiment. In the presence of CO\(_2\), a small amount of NO\(_x\) can be stored on \( \gamma\)-Al\(_2\)O\(_3\) [32], which corresponds at 300 °C of about 1.5 % of the total NO\(_x\) storage capacity. However, in the presence of H\(_2\)O, NO\(_x\) storage on \( \gamma\)-Al\(_2\)O\(_3\) is even less,
resulting in faster NO\textsubscript{x} breakthrough. This difference is incorporated by adjusting the amount of surface sites from 134 to 67 mol m\textsuperscript{-3} reactor. The diffusion coefficient of the gas phase components in the semi-bulk and bulk barium is taken as 3.6×10\textsuperscript{-15} m\textsuperscript{2}/s [26]. A semi-bulk barium cluster size of about 10 nm is obtained via CO\textsubscript{2} chemisorption. Calculations based on this value and on the fitted model parameters lead to a bulk barium cluster size of about 40 nm. This is in agreement with XRD results, which give a particle size range of 10 to 40 nm. Furthermore, the same NO storage parameters have been used, as the ones published by Scholz et al. [26] and Gangwal et al. [41]. The temperature dependence for NO storage on semi-bulk sites is included. The regeneration and reduction parameters for H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, and CO are obtained by fitting the results of the model to the results of the 100 min/80 min lean/rich cycling experiments.

Table 6.2. The global reaction steps and rate equations used for kinetic modeling of NO storage and reduction.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Rate equation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lean phase</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Storage</strong></td>
<td></td>
</tr>
<tr>
<td>BaCO\textsubscript{3} + 2NO + 0.5O\textsubscript{2} → Ba(NO\textsubscript{2})\textsubscript{2} + CO\textsubscript{2}</td>
<td>( R_{\text{st_NO}} = k_{s_NO,i} \theta_{\text{BaCO3,i}} \theta_{\text{NO},2} \text{C}_{\text{CO2},0.5} ) (I)</td>
</tr>
<tr>
<td>Ba(NO\textsubscript{2})\textsubscript{2} + O\textsubscript{2} → Ba(NO\textsubscript{3})\textsubscript{2}</td>
<td>( R_{\text{st_oxi}} = k_{\text{dis}<em>i} \theta</em>{\text{Ba(NO2)2,i}} \text{C}_{\text{O2}} ) (II)</td>
</tr>
<tr>
<td><strong>Rich phase</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Release</strong></td>
<td></td>
</tr>
<tr>
<td>Ba(NO\textsubscript{3})\textsubscript{2} + 3H\textsubscript{2} + CO\textsubscript{2} → BaCO\textsubscript{3} + 2NO + 3H\textsubscript{2}O</td>
<td>( R_{\text{reg,H2}} = k_{\text{reg,H2,nitrate,i}} \theta_{\text{Ba(NO3)2,i}} \text{C}_{\text{H2}} ) (III)</td>
</tr>
<tr>
<td>Ba(NO\textsubscript{3})\textsubscript{2} + 3CO + CO\textsubscript{2} → BaCO\textsubscript{3} + 2NO + 3CO\textsubscript{2}</td>
<td>( R_{\text{reg,CO}} = k_{\text{reg,CO,nitrate,i}} \theta_{\text{Ba(NO3)2,i}} \text{C}_{\text{CO}} ) (IV)</td>
</tr>
<tr>
<td>Ba(NO\textsubscript{3})\textsubscript{2} + 0.5C\textsubscript{2}H\textsubscript{4} + CO\textsubscript{2} → BaCO\textsubscript{3} + 2NO + H\textsubscript{2}O + CO\textsubscript{2}</td>
<td>( R_{\text{reg,C2H4}} = k_{\text{reg,C2H4,nitrate,i}} \theta_{\text{Ba(NO3)2,i}} \text{C}_{\text{C2H4}} ) (V)</td>
</tr>
<tr>
<td><strong>Reduction</strong></td>
<td></td>
</tr>
<tr>
<td>NO + H\textsubscript{2} → 1/2N\textsubscript{2} + H\textsubscript{2}O</td>
<td>( R_{\text{red,H2}} = k_{\text{red,H2,CNO,H2}} ) (VI)</td>
</tr>
<tr>
<td>NO + CO → 1/2N\textsubscript{2} + CO\textsubscript{2}</td>
<td>( R_{\text{red,CO}} = k_{\text{red,CO,CNO,CO}} ) (VII)</td>
</tr>
<tr>
<td>NO + 1/6C\textsubscript{2}H\textsubscript{4} → 1/2N\textsubscript{2} + 1/3H\textsubscript{2}O + 1/3CO\textsubscript{2}</td>
<td>( R_{\text{red,C2H4}} = k_{\text{red,C2H4,CNO,C2H4}} ) (VIII)</td>
</tr>
<tr>
<td><strong>Pt sites</strong></td>
<td></td>
</tr>
<tr>
<td>Pt + O\textsubscript{2} → 2Pt-O</td>
<td>( R_{\text{O2,store}} = k_{\text{O2,store,CO2,0,Pt}} ) (IX)</td>
</tr>
<tr>
<td>Pt-O + H\textsubscript{2} → Pt + H\textsubscript{2}O</td>
<td>( R_{\text{H2,rel}} = k_{\text{H2,rel,CO2,0,Pt}} ) (X)</td>
</tr>
<tr>
<td>Pt-O + CO → Pt + CO\textsubscript{2}</td>
<td>( R_{\text{CO,rel}} = k_{\text{CO,rel,CO2,0,Pt}} ) (XI)</td>
</tr>
<tr>
<td>3Pt-O + 1/2C\textsubscript{2}H\textsubscript{4} → Pt + CO\textsubscript{2} + H\textsubscript{2}O</td>
<td>( R_{\text{C2H4,rel}} = k_{\text{C2H4,rel,C2H4,0,Pt}} ) (XII)</td>
</tr>
<tr>
<td>Pt + C\textsubscript{2}H\textsubscript{4} → Pt-C\textsubscript{2}H\textsubscript{4}</td>
<td>( R_{\text{carbon}} = k_{\text{carbon,C2H4,0,Pt}} ) (XIII)</td>
</tr>
<tr>
<td>CO + H\textsubscript{2}O → H\textsubscript{2} + CO\textsubscript{2}</td>
<td>( R_{\text{WGS}} = k_{\text{WGS,CO2,0,CO}} ) (XIV)</td>
</tr>
</tbody>
</table>

The reaction rate parameters \( k_{s\_NO,i} \), \( k_{s\_dis,i} \), and \( k_{\text{reg,nitrate,i}} \) have different units and values for the surface and semi-bulk barium sites with \( i = \text{surface, or semi-bulk}. \) Bulk sites are not participating in the NO\textsubscript{x} storage process. See also Table 6.3.
### Table 6.3: Model parameters.

<table>
<thead>
<tr>
<th>Catalyst parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPt</td>
<td>moles of Pt surface sites / m³ reactor, (mol m⁻³ reactor)</td>
</tr>
<tr>
<td>LBa, surface</td>
<td>moles of Ba surface sites/m³ reactor, (mol m⁻³ reactor)</td>
</tr>
<tr>
<td>LBa, semi-bulk</td>
<td>moles of Ba semi-bulk sites/m³ reactor, (mol m⁻³ reactor)</td>
</tr>
<tr>
<td>LBa, bulk</td>
<td>moles of Ba bulk sites per m³ reactor, (mol m⁻³ reactor)</td>
</tr>
<tr>
<td>A_Ba</td>
<td>specific barium surface, (m² reactor)</td>
</tr>
<tr>
<td>d_Ba</td>
<td>diameter barium cluster, (m_Ba)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reactor parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε_b</td>
<td>bed porosity, (m³ gas m⁻³ reactor)</td>
</tr>
<tr>
<td>A_r</td>
<td>surface area of the reactor, (m² reactor)</td>
</tr>
<tr>
<td>F_v</td>
<td>volumetric flow rate, (m³ gas s⁻¹)</td>
</tr>
<tr>
<td>l_reactor</td>
<td>reactor length, (m_reactor)</td>
</tr>
<tr>
<td>D_eff</td>
<td>diffusion coefficient, (m³ gas m⁻¹ Ba s⁻¹)</td>
</tr>
<tr>
<td>ε_cluster</td>
<td>cluster porosity, (m³ gas m⁻³ Ba)</td>
</tr>
<tr>
<td>f</td>
<td>volume fraction, (m³ Ba m⁻³ reactor)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Storage parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ks_NO,surface</td>
<td>NO storage, (m⁷.5 gas mol⁻².⁵ i s⁻¹)</td>
</tr>
<tr>
<td>Ks_dis,surface</td>
<td>nitrite oxidation, (m³ gas mol⁻² Ba s⁻¹)</td>
</tr>
<tr>
<td>Ks_NO,semibulk</td>
<td>NO storage, (m⁷.5 gas mol⁻².⁵ i s⁻¹ mol⁻¹ Ba m⁻³ Ba)</td>
</tr>
<tr>
<td>Ks_dis,semibulk</td>
<td>nitrite oxidation, (m³ gas s⁻¹ mol⁻¹ Ba m⁻³ Ba)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Regeneration parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_regh₂, nitrate</td>
<td>Ba(NO₃)₂ regeneration, (m³ gas mol⁻¹ i s⁻¹)</td>
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<tr>
<td>K_WGS</td>
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### 6.4. Results and discussion

#### 6.4.1. Lean operation

The NO breakthrough profiles in the lean phase as a function of time, at temperatures of 200, 250, and 300 °C, respectively, are shown in Figures 6.2a to 6.2c. No NO₂ formation is detected during the lean phase.
Figure 6.2. Lean phase NO reactor outlet concentration at different temperatures: a) 200 °C, b) 250 °C, and c) 300 °C. Continuous lines show experimental data and dash lines show model predictions.
Figure 6.3. Lean phase simulated barium sites coverage: a) surface BaCO$_3$ coverage at 200 $^\circ$C, b) surface BaCO$_3$ coverage at 300 $^\circ$C, c) semi-bulk BaCO$_3$ coverage at 200 $^\circ$C at the outer part of the barium cluster, d) semi-bulk BaCO$_3$ coverage at 300 $^\circ$C at the outer part of the barium cluster, e) surface barium coverage at the reactor outlet at 200 $^\circ$C, f) semi-bulk Ba(NO$_3$)$_2$ coverage at the end of the lean phase at 200, 250, and 300 $^\circ$C.
The NO breakthrough profiles shown represent the maximum NO storage capacity for each temperature, as it is checked that during the rich phase all the stored NO in the preceding lean phase is released and reduced. Initially, NO is completely stored onto the catalyst and no NO is detected at the reactor outlet. Complete NO storage is seen for 3.6 min at 200 °C. This time increases with a raise in temperature to 6.1 min at 250 °C and 6.9 min at 300 °C. Immediately after NO breakthrough, the NO profile shows still considerable NO storage for all temperatures. This is followed by a period which is characterized by a slow but still measurable NO uptake until the outlet concentration is equal to the NO inlet concentration. The temperature has an effect on the total amount of NO stored at the end of the lean phase, and increases from 556 μmol NO/g catalyst at 200 °C to 698 μmol NO/g catalyst at 300 °C. Results obtained during rich phases indicate that, at the end of the lean phase, NO is stored in the form of nitrates. The nitrites formed at the early stage of the lean phase (equation (I), Table 2), can be oxidized into nitrates. As no NO₂ is present, dissociative adsorption of O₂ on Pt could serve as a source of oxygen atoms for this oxidation step (equation (II), Table 6.2). Epling et al. [8] suggest that only barium sites in close contact with Pt sites demonstrate this reaction pathway. This may explain the observed lower NOₓ trapping capability of 698 μmol NO/g catalyst at 300 °C in the presence of H₂O as against 1395 μmol NOₓ/g catalyst without H₂O [32].

As also shown in Figures 6.2a to 6.2c, the kinetic model is able to describe the NO breakthrough profile at different temperatures. The initial complete NO uptake occurs mainly at the surface BaCO₃ sites at a temperature of 200 °C (Figures 6.3a and 6.3c). However, at higher temperatures semi-bulk sites show a higher reactivity towards NO storage, and as the NO front passes through the reactor, NO is also stored on the semi-bulk sites (Figures 6.3b and 6.3d). This results in a delay in NO breakthrough with a raise in temperature. As soon as surface BaCO₃ at the outlet of the reactor starts converting, NO breakthrough can be seen (Figures 6.3a and 6.3b). At this stage, all the surface BaCO₃ sites have been converted to nitrites and nitrates (Figure 6.3e). As a result, the NO storage rate decreases as only semi-bulk sites are available for NO storage and diffusion.
starts playing a role. At the end of the lean phase, almost all semi-bulk sites have been replaced by Ba(NO$_3$)$_2$ at 300 °C. However, at lower temperatures, the semi-bulk sites are not yet fully covered with nitrates (Figure 6.3f).

### 6.4.2. Influence of H$_2$ on NO$_x$ release and reduction

Figures 6.4a to 6.4c show the experimental rich outlet NO and N$_2$ signals and the model NO, N$_2$, and H$_2$ concentrations as a function of time, at temperatures of 300, 250, and 200 °C. N$_2$ formation and NO release are seen, immediately after switching from lean to rich conditions. Neither NO$_2$ nor NH$_3$ is detected. H$_2$ is effectively able to fully regenerate the catalyst at all temperatures and at the end of the regeneration, the stored NO in the lean phase is completely released and reduced. Figures 6.4a and 6.4b show that the model adequately describes the NO desorption and its reduction into N$_2$. At 200 °C (Figure 6.4c) the model under predicts the NO release, while the model is well able to describe the N$_2$ formation. At temperatures above 300 °C, γ-Al$_2$O$_3$ shows negligible capacity for NO storage [36]. At lower temperatures, however, more NO can be stored on γ-Al$_2$O$_3$. Interestingly, switching from lean conditions to pure He at 200 °C, results in about the same NO release profile as observed for rich conditions with H$_2$ present (not shown). Additionally, Figure 6.5 shows the NO rich results of the lean/rich cycling experiments with γ-Al$_2$O$_3$ at 200 °C with the rich phase only containing He, 10 vol. % CO$_2$, and 10 vol. % H$_2$O. This NO release profile resembles the observed rich NO profile for the Pt-Ba/γ-Al$_2$O$_3$ catalyst at 200 °C. This suggests that some NO is stored on γ-Al$_2$O$_3$ and that this NO can be released at O$_2$ poor conditions without the assistance of H$_2$. This effect is not captured in the model, resulting in under prediction of NO release at 200 °C.

Figures 6.6a and 6.6b show the simulated coverage of the surface and semi-bulk barium sites at 200 °C. Stored nitrates are rapidly converted to carbonates and within 3.6 min all surface sites are regenerated, while complete regeneration of the semi-bulk sites takes 4.1 min. As more NO is stored in the lean phase as the temperature increases, the total regeneration period increases from 4.1 min to 5.2 min with a raise in temperature from 200 to 300 °C.
Figure 6.4. Rich phase NO, H$_2$ and N$_2$ reactor outlet concentrations at different temperatures: a) 300 °C, b) 250 °C, and c) 200°C. Continuous lines show experimental data and dashed-dotted lines (N$_2$), dashed lines (NO), and dotted lines (H$_2$) show model predictions.
Figure 6.5. NO desorption from γ-Al₂O₃ in He at 200 °C after a lean phase. Lean: 0.14 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂, 10 vol. % H₂O, and 1 vol. % Ar in He.

Figure 6.6. Rich phase simulated barium coverage at the outlet of the reactor: a) surface barium coverage, b) semi-bulk BaCO₃ coverage.
Figure 6.7. Rich phase NO, H2, CO and N2 reactor outlet concentrations at different temperatures: a) 300 °C, b) 250 °C, and c) 200 °C. Continuous lines show experimental data and dashed-dotted lines (N2), dashed lines (NO), and dotted lines (CO/H2) show model predictions.
6.4.3. Influence of CO on NO\textsubscript{x} release and reduction

Interestingly, the rich operation at 300 and 250 °C with CO show the same NO release and N\textsubscript{2} formation profiles as for experiments with H\textsubscript{2} (Figures 6.7a and 6.7b). This observed similarity between H\textsubscript{2} and CO can possibly be ascribed to the water gas shift (WGS) reaction (reaction (XIV), Table 6.2) [14]. In fact, Figure 6.7a shows that after catalyst regeneration 1.2 vol. % H\textsubscript{2} is observed and no CO is detected, indicating that H\textsubscript{2} is produced from CO + H\textsubscript{2}O. Although, neither H\textsubscript{2} nor CO is detected during N\textsubscript{2} formation, it is reasonable to assume that H\textsubscript{2} acts as reductant at 300 and 250 °C. Figure 6.7c shows the experimental rich results at 200 °C. Only minor NO release and N\textsubscript{2} formation are detected. Almost immediately after switching to rich conditions, CO breakthrough can be seen. This indicates that at 200 °C, the WGS reaction does not take place and that CO is not able to regenerate the catalyst. With the WGS reaction added to the model, it is able to capture all the above-mentioned characteristics (Figures 6.7a – c). Published WGS reaction rates at 300 °C for Pt and Pt-ceria formulations are too low to describe the observed H\textsubscript{2} formation [37,38]. It is possible, however, that barium promotes the reaction rate, but the investigation of the WGS reaction is not within the scope of this research work. Yet, the WGS reaction rate is chosen to be very fast at 300 and 250 °C, with a reaction rate parameter of infinite (Table 6.3).

6.4.4. Influence of C\textsubscript{2}H\textsubscript{4} on NO\textsubscript{x} release and reduction

Figure 6.8 presents the effect of C\textsubscript{2}H\textsubscript{4} on the NO reduction. At a temperature of 300 °C, the characteristics are similar as observed with H\textsubscript{2} in the rich phase. However, at a temperature of 250 °C, the NO reduction behavior with C\textsubscript{2}H\textsubscript{4} shows some remarkable differences. The NO release profile has a different shape and more NO release is seen. Furthermore, the N\textsubscript{2} outlet concentration increases initially from 0.14 vol. % to 0.20 vol. %. However, after 2.7 min the N\textsubscript{2} concentration decreases and a tail is observed. Based on the measured N\textsubscript{2} and NO concentrations and reactions (V) and (VIII), the C\textsubscript{2}H\textsubscript{4} consumption can be calculated. With the measured C\textsubscript{2}H\textsubscript{4} breakthrough profile, the actual C\textsubscript{2}H\textsubscript{4} consumption is known.
Figure 6.8. Rich phase NO, C2H4 and N2 reactor outlet concentrations at different temperatures: a) 300 °C, b) 250 °C, and c) 200°C. Continuous lines show experimental data and dashed-dotted lines (N2), dashed lines (NO), and dotted lines (C2H4) show model predictions.
It appears that during the first 100 sec, more C₂H₄ is consumed as expected based on the outlet N₂ and NO concentrations. It is reported that strong adsorption of the species derived from hydrocarbons can poison Pt sites (equation (XIII)) [39,40], what provides a likely explanation for the experimental results.

As the rich phase starts, most of the Pt sites throughout the reactor have been oxidized with O₂. Subsequently, as the reductant front passes through the reactor, C₂H₄ reduces the Pt sites scavenging the O₂. Additionally, C₂H₄ adsorbs on the reduced Pt sites. As a result, less C₂H₄ will be available for NO reduction into N₂, resulting in less N₂ formation. However, as the reduction front passes, not all the stored NO on the semi-bulk sites will be released, due to diffusion limitation. As a result, this NO is not yet released after the reduction front has passed. Meanwhile, C₂H₄ is no longer consumed in poisoning the Pt sites and more C₂H₄ is available for NO reduction. As the remaining NO in the upstream front is released, this results in a higher N₂ concentration (Figure 6.8b). However, due to the Pt poisoning, C₂H₄ is less efficient in catalyst regeneration as H₂, and a tail in N₂ formation is observed. This decreased regeneration efficiency with increased Pt poisoning is not captured adequately within the model. As a result, the tail in N₂ formation is overpredicted by the model. At a temperature of 200 °C, some N₂ formation and NO release are observed for the first 40 s. The model shows more NO release and N₂ formation as the experiments show, as the effect of Pt poisoning on the regeneration efficiency is not included. C₂H₄ is not capable of completely regenerating the catalyst, and the model shows that only surface barium sites are being regenerated.

6.4.5. Lean/rich cycling in the order of seconds

Figure 6.9 shows the model prediction and the experimental data at the cyclic steady state during transient reactor operation for lean/rich cycles with 240 s lean and 60 s rich phases. As the lean/rich cycling starts, NO is mainly stored on the surface barium sites. NO stored during the lean phase is not completely reduced during the subsequent short rich period. As the lean/rich cycling proceeds, nitrate accumulates on the barium sites until the cyclic steady state has been reached.
Figure 6.9. Periodic lean (240 s)/rich (60 s) reactor operation at 300 °C. Continuous lines show experimental data and discontinuous lines show model predictions.

Figure 6.10 shows that at the cyclic steady state, part of the barium is inactive for NO storage and reduction. For both 200 and 300 °C, only the surface barium sites in the first part of the reactor are involved in NO trapping (Figures 6.10a and 6.10b), as the other sites are already completely filled with Ba(NO₃)₂ as a result of the incomplete regeneration. Furthermore, part of the semi-bulk barium sites will be active in NO storage, as shown in Figures 6.10c and 6.10d. No nitrites are present at the end of the lean phase. With an increase in temperature from 200 to 300 °C, the NO storage rate on the semi-bulk barium sites increases and a higher fraction of the semi-bulk sites is participating in the NSR process. However, even at higher temperatures most of the NO is stored on the surface barium sites. At real-life application, fast alternation of lean and rich phases takes place in the order of seconds. Above-mentioned results suggest that in this case, mostly surface barium sites contribute significantly in NO trapping and only a small fraction of the total barium participates in NO storage. As a result, NO breakthrough in the
The lean phase is observed. With longer regeneration times, more surface and semi-bulk barium sites can be regenerated resulting in an increased NO storage capacity and consequently less NO breakthrough. However, this can lead to considerable breakthrough of the reducing agent, what is not desired. The present model can be used to simulate and optimize the catalyst storage capacity and the related transient operating conditions.

![Figure 6.10. Simulated coverages during transient reactor operation: a) coverage of surface Ba(NO₃)₂ at 200 °C at the end of the lean and rich phase, b) coverage of surface Ba(NO₃)₂ at 300 °C at the end of the lean and rich phase, c) Ba(NO₃)₂ coverage at the outside of the semi-bulk sites at 200 °C, d) Ba(NO₃)₂ coverage at the outside of the semi-bulk sites at 300 °C](image)

6.5. Conclusions

The influence of the temperature and the reducing agent on the NSR behavior in the presence of CO₂ and H₂O has been investigated both experimentally and by kinetic modeling. The experimental findings have been compared with the simulations of a recently developed dynamic plug flow reactor model using global reaction kinetics in the presence of CO₂. The
model is based on a multiple storage sites mechanism and considers that fast NO\textsubscript{x} storage, which is determined by the reaction kinetics, occurs at surface barium sites. Slow NO\textsubscript{x} storage occurs at semi-bulk sites where diffusion plays a major role. Bulk sites are not participating in the NO\textsubscript{x} trapping. As no NO\textsubscript{2} formation is seen in the lean phase in the presence of CO\textsubscript{2} and H\textsubscript{2}O, only NO storage can take place.

The model elucidates that at 200 °C, the initial complete NO uptake can be mainly ascribed to NO storage on surface barium sites. As the temperature increases, semi-bulk sites show a higher reactivity towards NO storage and as the NO front passes through the reactor, NO is also stored on semi-bulk sites. This results in a delay in NO breakthrough with a raise in temperature. The model is also able to describe the NO release and reduction during rich exposure. Experimental results show that H\textsubscript{2} is efficient in catalyst regeneration at all temperatures. Experiments with CO as reducing agent show that at temperatures above 250 °C, the WGS reaction takes place and H\textsubscript{2} acts as reductant instead of CO. At 200 °C, CO and C\textsubscript{2}H\textsubscript{4} are not able to fully regenerate the catalyst. At higher temperatures, C\textsubscript{2}H\textsubscript{4} is capable of reducing all the stored NO, although C\textsubscript{2}H\textsubscript{4} poisons the Pt sites by carbon decomposition at 250 °C. The model is able to capture all the experimental findings for 100 min lean and 80 min rich cycling experiments as well as transient reactor experiments with 240 s lean and 60 s rich cycle timings.

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**References**


Conclusions and outlook

7.1. Conclusions

In this thesis, the NO\textsubscript{x} storage/reduction mechanism on an automotive catalyst was investigated, using both experimental and modeling methods. Lean/rich cycling experiments were performed in a packed bed reactor using Pt-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3} (1 wt. % Pt and 30 wt. % Ba) catalyst. Emphasis was given in understanding the catalyst behavior, the role of multiple storage sites, the influence of CO\textsubscript{2} and H\textsubscript{2}O, and the influence of different reducing agents (CO, H\textsubscript{2}, and C\textsubscript{2}H\textsubscript{4}) on NO\textsubscript{x} storage and reduction.

It was found that in the absence of CO\textsubscript{2} and H\textsubscript{2}O, almost 100 % of barium is involved in NO\textsubscript{x} storage when the catalyst is exposed to 9 h lean conditions. The subsequent rich phase shows incomplete regeneration of stored NO\textsubscript{x} even after 15 h rich exposure with H\textsubscript{2}. Due to this incomplete regeneration of the catalyst, less barium participates in the following lean phase. At cyclic steady state, only maximum 60 % of barium is involved in NO\textsubscript{x} storage. The NO oxidation efficiency of the catalyst decreases upon lean exposure till steady cycling is achieved. Furthermore, the BET surface area, pore volume, and Pt dispersion decrease by about 40 %, which may be a result of masking of Pt sites or blocking of the pores of the barium clusters as BaCO\textsubscript{3} becomes Ba(NO\textsubscript{3})\textsubscript{2}.
Similar findings are seen for 30 min lean and 120 min rich cycling experiments in the absence of CO\textsubscript{2} and H\textsubscript{2}O. NO\textsubscript{x} is trapped on $\gamma$-Al\textsubscript{2}O\textsubscript{3} and barium sites. The pretreated, fresh catalyst contains mainly BaCO\textsubscript{3} sites. As lean/rich cycling proceeds, the NO\textsubscript{x} trapping capability of the catalyst increases at first, as BaCO\textsubscript{3} sites are exchanged for the more reactive Ba(OH)\textsubscript{2} sites. During NO\textsubscript{x} storage, both surface and bulk barium sites are active. The rich phase with H\textsubscript{2} shows more NH\textsubscript{3} formation as lean/rich cycling continues, and the selectivity towards N\textsubscript{2} decreases from 82 \% to 47 \%. Simultaneously, the N balance for successive lean/rich cycles shows incomplete regeneration, demonstrating inactive barium sites for further NO\textsubscript{x} storage and reduction. This incomplete regeneration along with a 40 \% decrease in the Pt dispersion and BET surface area, leads to a reduced NO\textsubscript{x} trapping capability and thus less NO\textsubscript{x} is stored.

In the presence of CO\textsubscript{2}, NO\textsubscript{x} is stored on $\gamma$-Al\textsubscript{2}O\textsubscript{3} and BaCO\textsubscript{3} sites. Bulk barium sites are inactive in NO\textsubscript{x} trapping in the presence of CO\textsubscript{2} and only 30 \% of total barium participates in NO\textsubscript{x} storage. Ba(NO\textsubscript{3})\textsubscript{2} is always completely regenerated during the subsequent rich phase and the selectivity towards N\textsubscript{2} is 83 \%. In the presence of CO\textsubscript{2}, the Pt dispersion, BET surface area, and pore volume remain the same as for the pretreated catalyst.

A global reaction kinetic model is developed to describe the NO\textsubscript{x} storage/reduction process in the presence of CO\textsubscript{2} with H\textsubscript{2} as reducing agent at a temperature of 300 \degree C. The model considers that NO\textsubscript{x} storage occurs on three types of barium sites, viz. surface, semi-bulk and bulk barium sites. Fast NO\textsubscript{x} storage, which is determined by the reaction kinetics, occurs at surface barium sites. Slow NO\textsubscript{x} storage occurs at semi-bulk sites, where diffusion plays a major role. Bulk barium sites show negligible reactivity towards NO\textsubscript{x} storage. It is assumed that surface, bulk and semi-bulk sites not only differ in physical appearance but also in chemical reactivity. It is considered that surface and semi-bulk sites correspond with a dispersed barium phase and bulk barium sites with crystalline BaCO\textsubscript{3} sites.

The model elucidates that the initial complete NO\textsubscript{x} uptake can be mainly ascribed to NO storage on surface barium sites in the form of nitrites. As the surface coverage increases, NO breakthrough can be seen. The NO
storage process continues with the involvement of semi-bulk barium sites but at a lower rate due to diffusion limitation. Meanwhile NO$_2$ is consumed in oxidizing surface nitrites into nitrates with release of NO and by getting stored on semi-bulk barium sites. As a result, delay in NO$_2$ breakthrough can be seen and the NO concentration passes through a maximum.

At rich periods with CO in the presence of CO$_2$ at 300 °C, poisoning of the catalyst is observed through carbon decomposition on the Pt sites and formation of strongly bound isocyanates on alumina and barium sites. Under these conditions, stored NO$_x$ is not fully removed in the rich phase. However, upon switching to lean conditions, O$_2$ removes the isocyanates. Both O$_2$ and NO$_2$ can participate in regeneration of the carbon-poisoned Pt sites. Reduction of C$_2$H$_4$ shows the highest selectivity towards N$_2$ compared to CO and H$_2$ at a temperature of 300 °C. During the rich phase, poisoning of the Pt sites occurs, but all the NO$_x$ stored in the preceding lean phase is released and reduced.

The type of reducing agent also affects the NO$_x$ storage route followed in the lean phase. The lean phase after catalyst regeneration with CO, shows simultaneous NO and NO$_2$ breakthrough. Both NO and NO$_2$ concentrations increase gradually in time. Poisoning of the Pt sites by carbon can affect the NO oxidation into NO$_2$. Furthermore, NO$_2$ can participate in the carbon oxidation. Consequently, less NO$_2$ is available for nitrite oxidation and nitrites can be oxidized with O$_2$. The results for C$_2$H$_4$ as reductant, show that the NO$_x$ storage route is a combination of the routes observed for experiments with H$_2$ and CO as reducing agent.

H$_2$O in the rich phase only, does not affect the amount of NO$_x$ stored in the lean phase. H$_2$O prevents poisoning of the catalyst at 300 °C by CO and C$_2$H$_4$ and as a result, the followed NO$_x$ storage route is the same for all three reductants. Moreover, H$_2$O in the lean phase inhibits NO oxidation and no NO$_2$ formation is observed. Less NO is stored in the presence of H$_2$O, which supports the higher storage capacity towards NO$_2$ than towards NO. Even after 9 h lean exposure only 16 % of total barium sites is utilized in NO storage. In the presence of H$_2$O and CO$_2$, NO is stored only at BaCO$_3$ sites.

The previous developed model is adapted to describe lean/rich cycling experiments in the presence of CO$_2$ and H$_2$O for temperatures between 200
and 300 °C and for different reductants (CO, H₂, and C₂H₄). At 200 °C, the initial NO uptake can be mainly ascribed to NO storage on surface barium sites. As the temperature increases, semi-bulk sites show a higher reactivity towards NO storage and as the NO front passes through the reactor, NO is also stored on semi-bulk sites. This results in a delay in NO breakthrough with a raise in temperature. The model is also able to describe the NO release and reduction during rich exposure. Experimental results show that H₂ is efficient in catalyst regeneration at all temperatures. Experiments with CO as reducing agent show that at temperatures above 250 °C, the water gas shift reaction takes place and H₂ acts as reductant instead of CO. At 200 °C, CO and C₂H₄ are not able to regenerate the catalyst. At higher temperatures, C₂H₄ is capable of reducing all the stored NO, although C₂H₄ poisons the Pt sites by carbon decomposition at 250 °C. The present model can be used to simulate and optimize the catalyst at transient operating conditions.

7.2. Outlook

Despite the fact that the NOₓ storage/reduction technology has been known for some years and is already in use, like e.g. in Europe implemented in the Toyota Avensis, there is still a lack of detailed knowledge about how the system works. However, for improving the catalyst activity and to meet the stricter emission standards in the future, this knowledge is important. The results of this study can be put in perspective for future research work.

Improving catalyst activity

As mentioned in this thesis, barium shows a higher storage capacity towards NO₂ than NO. However, the Pt-Ba/γ-Al₂O₃ catalyst used in this research work shows negligible NO oxidation activity in the presence of H₂O. It would be interesting to explore why H₂O has such a negative impact on the NO oxidation and to use this information to optimize the catalyst regarding the oxidative capacity.

It is found that H₂ is efficient in catalyst regeneration, even at 200 °C, while CO and C₂H₄ are not able to regenerate the catalyst at that temperature. Unfortunately, H₂ is not present in large quantity in exhaust gas. At
temperatures higher than 250 °C, however, it is shown that the water gas shift reaction takes place and H₂ is formed. Since especially diesel engines have a low exhaust temperature, it is motivating to investigate further possibilities to form H₂ or to look for other efficient reductants. Recently, more details are provided about a new NOₓ catalytic converter, which has a two-layered structure [1]. One layer adsorbs NOₓ during lean driving and converts a portion of it into ammonia, while the other layer adsorbs the resulting ammonia, and uses it later in a reaction to convert the remaining NOₓ in the exhaust into N₂. Ammonia is highly effective in NOₓ reduction, also at lower temperatures and this catalyst enhances the NOₓ reduction performance.

Simultaneous removal of NOₓ and soot

In fact, the present oxidizing catalytic systems, which are in general available for diesel engines, are not able to effectively eliminate NOₓ and particulate matter (PM). As diesel engines become predominant in Europe and even begin to gain increased interest in the USA, their contribution in the increase in NOₓ and PM will be significant. With respect to the reduction of PM emissions, diesel particulate (soot) filters are already commercially available. As soon as the exhaust gas passes through the filter, it begins to capture the soot particles. The particles remain trapped, until the catalyst needs to be regenerated. The regeneration process is performed by increasing the filter temperature to 700 °C or even higher by combustion of extra-fuel injected in the flue gases. Under these conditions, the trapped materials are oxidized and converted to CO₂ and H₂O. Aiming at low temperature oxidation of soot, the use of the powerful oxidant NO₂ has been proposed [2]. If both NOₓ and PM levels have to be decreased to the levels of forthcoming legislations, NOₓ storage/reduction catalyst and soot oxidation catalyst have to be integrated. In spite of the fact that many studies are available about NSR catalyst, investigation of the combined soot-NOₓ removal is scarce [3,4]. It would be interesting to expand our work and use our model to investigate simultaneous soot and NOₓ removal.
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**Conference proceedings**


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About the author

Karen Scholz was born in Sittard on 26th April, 1977. She obtained her ‘VWO Gymnasium’ high school certificate at Serviam R.K. Scholengemeenschap Lyceum in Sittard in 1995. She continued her education in Chemical Engineering at the Eindhoven University of Technology. In 2001 she obtained her M.Sc. degree on the topic of “The operating window of a pulsed sieve plate column for continuous emulsion polymerization” in the group of prof.dr.ir. A.A.H. Drinkenburg. After her M.Sc. degree, she worked as junior process engineer at Tebodin, The Hague. In March 2002, she started her Ph.D. Research at the Eindhoven University of Technology in the group of prof.dr.ir. J.C. Schouten. Since June 15th, 2006 she works as process/research engineer at Unilever Food and Health Research Institute in Vlaardingen in the department of Process and Supply Chain Design.