Influence of reducing agent (CO, H2 and C2H4) and H2O on NOx storage and reduction on a Pt-Ba/gamma-Al2O3 catalyst

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Graduation report

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Summary

Diesel and lean-burn engines have the benefit of improved fuel economy and consequently, reduced CO₂ emissions compared to conventional gasoline-burning engines. The diesel and lean-burn engines operate at net-oxidizing conditions and therefore the traditional three-way catalyst, which is used in gasoline engines, is ineffective in NOₓ reduction as all of the reducing agents present are oxidized. A promising solution for the reduced capability of NOₓ reduction is the use of a NOₓ storage and reduction (NSR) catalyst. The concept of the NSR catalyst (mostly Pt-Ba/γ-Al₂O₃) is based on a two step process in which the engine periodically switches between lean and rich conditions. During lean conditions, the NOₓ formed in the engine is stored on barium. At the same time, H₂, CO and hydrocarbons, also present in the exhaust gas, are converted into CO₂ and H₂O. Because NOₓ is stored during lean conditions, the barium will eventually become saturated with NOₓ and periodical regeneration of the catalyst is needed. This is accomplished by injecting extra fuel into or directly downstream the engine, which causes the release and subsequent reduction of NOₓ stored by the available reducing agents being CO, H₂ and hydrocarbons.

The aim of this research project is to investigate the influence of the type of reducing agent and H₂O on the NOₓ storage and reduction on a NSR catalyst and to develop a model for the NOₓ storage and reduction process in the presence of CO₂ and H₂O. Therefore, lean/rich cycling experiments have been performed using a fixed bed reactor. 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 composition has been measured with mass spectrometry. All experiments have been performed with CO₂ in the feed and with different reducing agents. The reducing agents used are C₂H₄ (as a representative for hydrocarbons), H₂ and CO. Experiments with and without H₂O in the gas feed have been performed.

Lean/rich cycling experiments at 300 °C without H₂O in the feed showed that H₂ and C₂H₄ are able to fully regenerate the catalyst during rich conditions. In the case of CO incomplete regeneration is observed, which is probably caused by the formation of isocyanates. Also deposition of carbon or C₂H₄ derived species on Pt sites has been observed. The poisoning of the catalyst effects the lean phase, resulting in different reaction routes during storage of NOₓ for the used reducing agents.

Experiments at 300 °C also showed that the presence of H₂O in the rich phase does not effect the amount of NOₓ stored on the catalyst. It does, however, influence the lean phase, resulting in the same NO and NO₂ outlet concentrations during lean phase for all reducing agents. This is in contrast with experiments without H₂O showing different lean phase behavior. Experiments with H₂O in both the lean and rich phase also showed the same lean phase behavior for the three reducing agents. Due to the presence of H₂O no NO oxidation takes place and therefore less NOₓ is stored during lean operation.

Experiments at various temperatures showed that H₂ is capable of regenerating the catalyst at all measured temperatures (200, 250 and 300 °C), whereas CO and C₂H₄ are only effective at 250 and 300 °C. The amount of NOₓ stored is also influenced by the temperature. Most storage occurs at 300 °C, whereas least storage takes place at a temperature of 200 °C. Experiments have also shown that NO adsorbs on γ-Al₂O₃ during lean conditions and desorbs from γ-Al₂O₃ during rich conditions.

To model the data of experiments with H₂O and CO₂ in both the lean and rich phase a global reaction kinetic model has been developed for the NOₓ storage/reduction process. The model considers that fast NOₓ storage occurs at surface barium sites, which is determined by the kinetics. Slow NOₓ storage occurs at the semi-bulk sites, where diffusion plays a major role. Bulk barium sites show no reactivity towards NOₓ storage. It is assumed that surface, bulk and semi-bulk sites not only differ in physical appearance but also in chemical reactivity. The model is able to adequately describe the NO and N₂ outlet concentration of experiments at 300 °C in the presence of CO₂ and H₂O.
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1 Introduction

1.1 General description

Diesel and lean-burn engines have the benefit of improved fuel economy and consequently, reduced CO₂ emissions compared to conventional gasoline-burning engines. However, there is also a major drawback. Because these diesel and lean-burn engines operate at an air-fuel ratio of 25 and above, they exhibit net-oxidizing conditions. Due to the excess O₂ in the exhaust gas, the traditional three-way catalyst, which is used in gasoline engines, is ineffective in NOₓ reduction as all of the reducing agents present are oxidized. With the ever stricter legislation on the emissions of gaseous pollutants, a solution for the reduced NOₓ reduction should be found. One promising solution is the use of a NOₓ storage and reduction (NSR) catalyst [1].

The NSR catalyst concept is based on a two step process in which the engine periodically switches between two different stages, the lean-burn stage and the rich-burn stage. 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. The lean-burn stage of the engine is when the engine operates at normal conditions. During this period excess O₂ is present in the exhaust gas. The NOₓ, which is formed from nitrogen and oxygen in the engine at net-oxidizing conditions, cannot be reduced, also due to the net-oxidizing conditions. Therefore it is stored on barium. At the same time, H₂, CO and hydrocarbons, also present in the exhaust gas, are converted into CO₂ and H₂O. As the lean-burn phase continues, the catalyst will become saturated with NOₓ and periodical regeneration of the catalyst is needed. This is accomplished with the second step in the process, the so-called rich-burn phase. By injecting extra fuel into or directly downstream the engine the stored NOₓ is released and subsequently reduced by the available reducing agents such as CO, H₂ and hydrocarbons.

1.2 Project goal

To fully utilize the potential of the NSR catalyst and to minimize fuel penalty, it is important to understand the NSR mechanism. In order to get a better understanding of the mechanism this graduation project aims at three objectives.

- In literature mostly H₂ is discussed as the reducing agent to regenerate the catalyst after NOₓ storage. Because of the presence of other reducing agents in engine exhaust also these components should be considered in order to get a proper understanding of the NSR mechanism. The reducing components available in engine exhaust are H₂, CO and hydrocarbons. As representative hydrocarbon for the engine exhaust, we use C₂H₄, because of its relative high concentration in engine exhaust compared to other nonmethane hydrocarbons [2]. The first objective is to investigate the influence of reducing agents (H₂, CO and C₂H₄) on the NOₓ storage and reduction.

- Few studies have reported the effect of H₂O on the NOₓ storage and reduction, although in practice the engine exhaust gas always contains H₂O. The second objective therefore is to investigate the influence of H₂O on the NOₓ storage and reduction.

- The last objective of this graduation project is to model the results of lean/rich cycling with the different reducing agents and H₂O. Starting point for the modeling is the model for NOₓ storage/reduction in the presence of CO₂ from Scholz et al. [3].

Experiments have been performed with a Pt-Ba/γ-Al₂O₃ catalyst (1 wt. % Pt and 30 wt. % Ba) with NO and O₂ in the lean phase and several reducing agents in the rich phase in the gas feed. These
experiments have been performed with and without H₂O in the lean and rich phase. Furthermore CO₂ was always fed at 10 vol. % during both phases, as previous research has shown that without CO₂ present the catalyst properties like BET surface area and Pt dispersion can change in time [4].

1.3 Outline

In chapter 2 a literature overview of the NSR catalyst will be given with respect to NOₓ storage and release/reduction, the influence of CO₂ and H₂O on the NSR catalyst mechanism and modeling the NSR catalyst mechanism. In chapter 3 the experimental setup will be shown, with details concerning reactor, analysis system and measurement procedures as well as experimental procedures. In chapter 4 results of experiments with lean/rich cycling will be shown and discussed. Results of these experiments will be used in modeling the NSR mechanism in chapter 5. In chapter 6 conclusions will be given as well as some recommendations for future research and work.
Chapter 2 - Literature overview

2 Literature overview

In this chapter the most important steps will be discussed, as well as the influence of other components commonly present in automotive exhaust gas. At the end of the chapter also a literature overview of modeling of the NSR catalyst is given.

2.1 NO\textsubscript{x} storage on barium

During lean operation NO\textsubscript{x} is stored on the barium component of the catalyst. A detailed understanding of the overall NO\textsubscript{x} storage mechanism on a NSR catalyst is one of the basic steps required to understand the overall working of the catalyst.

It is generally assumed that the first step in this NO\textsubscript{x} storage process is the NO oxidation to NO\textsubscript{2} over Pt sites, as in Equation 2-1 [5-7].

\[
    NO + \frac{1}{2}O_2 \xrightleftharpoons{m} NO_2
\]  

(2-1)

The formed NO\textsubscript{2} can subsequently be stored via a disproportionation reaction resulting in nitrate formation and NO release as in Equation 2-2 [5, 6, 8, 9].

\[
    3NO_2 + BaO \longrightarrow Ba(NO_3)_2 + NO
\]  

(2-2)

It is also possible to store NO\textsubscript{2} via a direct route without NO release [9-12], as shown in Equation 2-3. Another pathway for NO\textsubscript{x} storage is suggested, which implies the direct uptake of NO in the presence of O\textsubscript{2} in the form of nitrites at barium sites, catalyzed by Pt [10, 13], as shown in Equation 2-4.

\[
    2NO_2 + BaO + \frac{1}{2}O_2 \longrightarrow Ba(NO_3)_2
\]  

(2-3)

\[
    2NO + BaO + \frac{1}{2}O_2 \longrightarrow Ba(NO_3)_2
\]  

(2-4)

The nitrites formed by the storage of NO can be further oxidized into nitrates with NO\textsubscript{2} as oxidizing agent [5, 14, 15] as in Equation 2-5.

\[
    Ba(NO_3)_2 + 2NO_2 \longrightarrow Ba(NO_3)_2 + 2NO
\]  

(2-5)

During the lean-phase NO\textsubscript{x} is stored on the catalyst and thus the barium compound will gradually become saturated with NO\textsubscript{x}. After a certain period of lean operation not all NO\textsubscript{x} formed will be stored and consequently NO\textsubscript{x} will pass the catalyst (breakthrough). The complete NO\textsubscript{x} breakthrough profile during lean exposure can be divided into three periods of different length. In the first period, complete NO\textsubscript{x} storage is seen. During the second period, NO\textsubscript{x} breakthrough with still 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 than the other two periods. The three different time periods indicate the presence of multiple types of barium sites with different activity towards NO\textsubscript{x} storage. Besides storage of NO\textsubscript{x} on BaO as shown in Equations 2-2, 2-3 and 2-4 NO\textsubscript{x} storage can also take place on Ba(OH)\textsubscript{2} and BaCO\textsubscript{3} in a similar way as on BaO, but resulting in the formation of H\textsubscript{2}O and CO\textsubscript{2}, respectively. In literature differences in reactivity are described for these components and NO\textsubscript{x} storage preferentially occurs at BaO, then at Ba(OH)\textsubscript{2}, followed by BaCO\textsubscript{3} [12]. Mahzoul et al. [16] described a difference in Ba sites with respect to their position with respect to Pt. They say that Ba sites closer to Pt, where NO is oxidized, are able to store oxidized NO\textsubscript{x}, as opposed to Ba sites further away from the oxidizing Pt sites, which are less
reactive towards storage. 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 [17, 18]. Recent work of Piacentini et al. [18, 19] shows that, for instance, two BaCO$_3$ sites can be distinguished. They subjected calcined catalyst samples to temperature programmed desorption (TPD) resulting in a small peak around 700 °C. The sites associated with this TPD signal, are called low temperature (LT) BaCO$_3$ sites, which are well-dispersed particles of BaCO$_3$ on the γ-Al$_2$O$_3$ surface. These particles are amorphous and therefore cannot be detected with X-ray diffraction (XRD). A second peak was observed at 1000 °C, which they ascribe to high temperature (HT) BaCO$_3$ sites. These sites are bulk-like sites or clusters that are crystalline and therefore can be detected with XRD measurements. This provides the possibility to discriminate between the different sites that participate in the storage process. Chen et al. [17, 20] deposited Ba(NO$_3$)$_2$ on Pt/γ-Al$_2$O$_3$ and performed thermal gravimetric analysis, which shows three peaks: the first is observed below 100 °C, which is weight loss due to the release of physically adsorbed H$_2$O. The second one is observed around 400 °C which are LT sites. The third one is observed above 550 °C which can be ascribed to bulk-like Ba(NO$_3$)$_2$ or HT sites. The LT-barium sites show a higher activity towards NO$_x$ 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, 20]. The HT phase also increases with barium loading, without saturation.

2.2 NO$_x$ release and reduction

Because of the NO$_x$ storage on the barium, the catalyst should be regenerated periodically to prevent the catalyst from saturating. For the release and reduction towards nitrogen a reducing agent is necessary. The NSR process has been the focus of numerous studies [21 and references herein]. Most of these studies have focused on the NO$_x$ storage process with the reduction step receiving considerably less attention. However, several studies have been performed to understand the effect of different reductants in the rich phase. In literature various reducing agents are used, such as CO, H$_2$ and C$_3$H$_6$. At temperatures above 250 °C, both H$_2$ and CO appear to be highly efficient towards NO$_x$ reduction compared to hydrocarbons [22-24]. At lower temperatures, CO is noticeably less effective in NO$_x$ reduction than H$_2$ [23, 25]. CO appears to facilitate Ba(NO$_3$)$_2$ decomposition, but not NO$_x$ reduction, while H$_2$ enables both to occur, with excellent conversion to N$_2$ [26]. This difference in reactivity can be explained with poisoning of the Pt sites by adsorbed CO species [23, 26, 27, 28, 29]. The inhibition effect also occurs with hydrocarbons [27, 28, 30]. It is also reported that during reduction with CO, isocyanates form and strongly adsorb on the oxide components of the catalyst [31, 32]. These NCO species can be hydrolyzed in the presence of H$_2$O to form NH$_3$ and CO$_2$ or oxidized with O$_2$ to form N$_2$ and CO$_2$. When using H$_2$ as a reducing agent during NO$_x$ release and reduction, the formation of NH$_3$ has been reported at lower temperatures up to 300 °C [33]. During the release and reduction among others N$_2$, NO$_x$ and NH$_3$ is formed. Because N$_2$ is a non-toxic exhaust gas, its formation is favored above other nitrogen-components such as NO$_x$ and NH$_3$. Therefore the reduction efficiency or selectivity towards N$_2$ of the catalyst is important. It can be expressed as:

$$\text{Selectivity to } N_2 = \frac{2N_2}{2N_2 + NH_3 + NO + NO_2} \cdot 100\% \quad (2-6)$$

2.3 Effect of CO$_2$ and H$_2$O on NO$_x$ storage and reduction

In practice, the vehicle exhaust gas always contains CO$_2$ and H$_2$O. Therefore, it is obvious to also investigate the effect of these components on the NSR mechanism. However, very few studies have reported the effect of CO$_2$ and H$_2$O on the NO$_x$ storage and reduction mechanism.
CO₂ proves to have a negative effect on the amount of NOₓ stored [12, 35, 36]. Lietti et al. found that this negative effect is most significant at 200 °C and less at 300-400 °C [12]. Epling et al., however, found that CO₂ has a large inhibiting effect, especially at temperatures above 300 °C [36]. Further, Epling et al. found that, although CO₂ significantly influences the initial interval of NOₓ trapping, CO₂ has a smaller influence on the capture efficiency after NOₓ starts breaking through. The significant decrease of NOₓ storage in the presence of CO₂ suggests there is a competitive storage between NOₓ and CO₂ [35, 36]. CO₂ competes with NO₂ for the same barium sites, inhibiting NOₓ storage. Rodrigues et al. furthermore concluded that the well dispersed BaCO₃ sites probably form the NOₓ trapping sites [37]. NOₓ release studies show that CO₂ has a promoting effect on the NOₓ release in the rich phase [36, 38, 39]. By introducing CO₂ to the helium flow a significant increase in the NOₓ release rate is observed [38]. This observation has also been made by Amberntsson et al., who explained this on thermodynamic grounds [39]. With H₂ as reducing agent, CO₂ has an inhibiting effect on the reduction towards N₂ [12, 36]. Epling observed this effect especially at temperatures above 300 °C [36]. With the introduction of CO₂ in rich phases with H₂ as reducing agent, the reverse water gas shift (RWGS) reaction can take place as described in Equation 2.7 [35].

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} 
\] (2-7)

Furthermore, Lietti et al. [12] found that during reduction with H₂ the Ba sites are transformed into BaO and Ba(OH)₂, while in the presence of CO₂ all the Ba sites are transformed into BaCO₃. It is reported that NOₓ cannot be stored on bulk barium sites with CO₂ present [37, 40].

In the temperature range of 250 °C to 400 °C, the presence of 8 % H₂O shows an inhibiting effect on NOₓ storage [35]. A promoting effect, however, has been reported in the presence of 1 % H₂O at 200 °C [12]. H₂O hinders NO₂ and NO release during temperature-programmed decomposition of stored NOₓ [41]. Olsson et al. reported that H₂O inhibits the NO oxidation activity of Pt/γ-Al₂O₃ catalysts [42]. The presence of H₂O causes NOₓ adsorption on γ-Al₂O₃ sites to be negligible [35, 43].

### 2.4 Modeling the NSR mechanism

Being able to describe the NSR mechanism is crucial for reducing catalyst regeneration times and thus a model is needed. In literature the shrinking core mechanism has been used to describe the NOₓ storage process [44-47]. Olsson et al. [45], Tuttiles et al. [46] and Hepburn et al. [47] have developed global models based on this mechanism. In general they assume that NOₓ diffusion inside the barium clusters or NOₓ transfer to the barium sites is the rate controlling step in the NOₓ storage process. Although there is clear evidence in the literature that multiple types of barium sites exist, which differ in reactivity [14, 35], models of the NSR process are mostly based on a single type of reaction site. In these models no distinction is made between reactivity of surface and bulk barium sites towards NOₓ storage. Olsson et al. [48] developed an elementary kinetic model, but the model could not describe the observed decreasing NOₓ trapping activity as the lean phase proceeds. The presence of an inactive barium core has been assumed to describe the observed incomplete barium utilization [45]. Scholz et al. [3] developed a global kinetic reaction model based on a multiple storage sites mechanism for the NOₓ storage/reduction process in the presence of CO₂. The model considers that fast NOₓ storage occurs at surface barium sites, which is determined by the kinetics. Slow NOₓ storage occurs at the semi-bulk sites, where diffusion plays a major role. Bulk barium sites show negligible reactivity towards NOₓ storage. It is assumed that surface, bulk and semi-bulk sites not only differ in physical appearance but also in chemical reactivity.
Figure 3.1: Picture of the experimental setup showing the setup with the heater section closed (picture above) and the heater section open (picture below).
3. Experimental setup

3.1 Introduction

Lean/rich cycling experiments are performed with a reactor, containing a fixed bed of catalyst pellets. The experimental setup consists of a reactor section, two different feed streams and an analysis section (Figure 3.1). The reactor has been designed to approach plug flow behavior, as an axial mixing of gases would disturb the transient signal measured by the analysis equipment.

3.2 Inlet system

The feed section consists of 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. By means of four magnetic valves, the different feed lines are alternated to either the reactor or the vent during lean/rich measurements. One feed corresponds with the lean-burn phase, while the other corresponds with the rich-burn phase.

3.3 Reactor section

The reactor section consists of a titanium fixed bed reactor with a length of 15 mm and an internal diameter of 14 mm. As NO\textsubscript{x} storage catalyst, 1.9 gram of Pt-Ba/\gamma-Al\textsubscript{2}O\textsubscript{3}, is used in powder form as provided by Engelhard. 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 also used as input for a PID controller, which sets the reactor temperature. The catalyst bed in the reactor is retained by two titanium sinter plates placed on the top and bottom of the reactor. The reactor pressure is controlled by a back-pressure valve, set downstream of the reactor and kept at constant pressure during a measurement. Two sample points, immediately above and below the catalyst bed, are connected via capillaries to the online mass spectrometers for real-time analysis of inlet and outlet concentrations of all components.

3.4 Analysis section

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 frequently. 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}). 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.
Table 3.1: Lean/rich experiments performed with the Pt-Ba/γ-Al₂O₃ catalyst.

<table>
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<tr>
<th></th>
<th>Temp. (°C)</th>
<th>Lean (min)</th>
<th>NO conc. (vol. %)</th>
<th>Rich (min)</th>
<th>Reductant (vol. %)</th>
<th>H₂O lean</th>
<th>H₂O rich</th>
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3.5 Experimental conditions

3.5.1 Catalyst pretreatment
To remove impurities and prevent sintering of the Pt sites during experiments, the catalyst should be pre-treated. 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 H\textsubscript{2} in He for 2 h.

3.5.2 Experimental procedure
In order to investigate the influence of reducing agents and H\textsubscript{2}O on NO\textsubscript{x} reduction on the NSR catalyst the experiments as described in Table 3.1 have been done.

Lean/rich cycling experiments are performed at 200, 250 and 300 °C. 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\textsuperscript{-1} (standard conditions 25 °C, 1 bar). The lean phase of the cycle contains 0.2 or 0.14 vol. % NO, 4 vol. % O\textsubscript{2}, 1 vol. % Ar, 10 vol. % CO\textsubscript{2}, 0 or 10 vol. % H\textsubscript{2}O, and a balance of He. The rich phase contains 1 vol. % Ar, 10 vol. % CO\textsubscript{2}, 0 or 10 vol. % H\textsubscript{2}O, and either H\textsubscript{2}, CO or C\textsubscript{2}H\textsubscript{4} balanced with He. The concentration of reductants is chosen to approximately have the same reduction capacity for sake of comparable results. H\textsubscript{2} and CO have the same molar reduction capacity and are therefore fed at the same concentration. C\textsubscript{2}H\textsubscript{4} however has a six times higher molar reduction capacity and therefore is fed at lower concentrations. NO is fed at higher concentrations than actually in real exhaust gas to guarantee enough sensitivity of the mass spectrometer for the gas phase component NO\textsubscript{2}. The other experimental conditions are representative for conditions in diesel and lean-burn exhaust gases. The experimental data shown are collected after performing several lean/rich cycles and cyclic steady state is reached.

The experiments with both H\textsubscript{2}O and CO\textsubscript{2} in the gas feed are for model applications. A summary of the experiments performed is shown in Table 3.1.
Figure 4.1: (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.

Figure 4.2: (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.


# Chapter 4 - Results and discussion

## 4.1 Influence of H\textsubscript{2}

Figure 4.1 shows the outlet NO\textsubscript{x}, NO, NO\textsubscript{2}, N\textsubscript{2} and NH\textsubscript{3} signals obtained during 200 min lean and 100 min rich cycling experiments at 300 °C. Upon switching from lean to rich conditions, NO\textsubscript{x} can be formed through nitrate decomposition, as mentioned by Lietti et al. [12]. The released NO\textsubscript{x} is reduced to N\textsubscript{2} on the Pt sites. The experimental results during rich exposure show immediate N\textsubscript{2} formation and NO release. In the beginning of the rich phase, part of the fed H\textsubscript{2} is probably consumed for the reduction of the oxidized Pt sites, resulting in a lower N\textsubscript{2} concentration [16]. Only minor amounts of NO\textsubscript{2} are detected. It is possible that no NO\textsubscript{2} release occurs or that NO\textsubscript{2} reacts directly with H\textsubscript{2} into N\textsubscript{2}. NH\textsubscript{3} formation is observed once the N\textsubscript{2} production declines. At the same time, CO formation (not shown) is observed, accompanied by the parallel consumption of H\textsubscript{2} and CO\textsubscript{2} and by the parallel production of H\textsubscript{2}O. This suggests that the RWGS reaction takes place (Equation 2-7). As seen in the literature overview, the selectivity towards N\textsubscript{2} can be expressed as:

\[
\text{Selectivity to } \text{N}_2 = \frac{2N_2}{2N_2 + \text{NH}_3 + \text{NO} + \text{NO}_2} \cdot 100\% \quad (2-6)
\]

The rich phase shows a selectivity of 86 %. At the end of the rich phase 100 % of the formed nitrates in the preceding lean phase are removed.

The lean phase shows complete NO\textsubscript{x} storage for 6.2 min (Figure 4.1). 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. Meanwhile, NO\textsubscript{2} is still completely consumed. Only after about 30 min, the NO\textsubscript{2} concentration increases with time. After 200 min, the NO\textsubscript{x} concentration is constant and equal to the inlet concentration. As no NO\textsubscript{x} storage is ongoing, the detected outlet 0.14 vol. % NO and the outlet 0.06 vol. % NO\textsubscript{2} can be ascribed to the NO oxidation reaction. After 200 min of lean exposure the total amount of NO\textsubscript{x} stored is 1.39 mmol/g catalyst. Scholz et al. [3] reported results of a global reaction kinetic model based on a multiple storage sites mechanism. Model results show that the initial complete NO\textsubscript{x} uptake can be mainly ascribed to NO storage on surface sites in the form of nitrites (Equation 4-1).

\[
\text{BaCO}_3 + 2\text{NO} + 0.5\text{O}_2 \rightarrow \text{Ba(NO}_2)_2 + \text{CO}_2 \quad (4-1)
\]

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

\[
\text{BaCO}_3 + 2\text{NO}_2 + 0.5\text{O}_2 \rightarrow \text{Ba(NO}_3)_2 + \text{CO}_2 \quad (4-3)
\]

As the surface sites fill, NO breakthrough can be seen. The NO storage process continues at the semi-bulk barium sites but at a lower rate due to diffusion limitation. Meanwhile NO\textsubscript{2} is consumed in oxidizing nitrites into nitrates (Equation 4-2) and by getting stored directly as nitrates on the semi-bulk sites (Equation 4-3). As NO is produced in the oxidation reaction of nitrites into nitrates with NO\textsubscript{2} as oxidizing agent, the NO outlet concentration shows a maximum and delay in NO\textsubscript{2} breakthrough can be seen. The bulk BaCO\textsubscript{3} sites are inactive in NO\textsubscript{x} storage in the presence of CO\textsubscript{2}. After 200 min lean exposure, only barium nitrates will be present on the catalyst.

## 4.2 Influence of CO

Figure 4.2 shows the results of the corresponding experiment with CO as the reducing agent. The rich phase shows immediate N\textsubscript{2} formation and NO release. Contrary to the results with H\textsubscript{2}, NO\textsubscript{2} release is
Figure 4.3: CO$_2$ and N$_2$ formation with 4 vol. % O$_2$ in He flow after rich phase with CO as reducing agent.

Figure 4.4: (A) Rich outlet concentrations of NO, NO$_2$, and N$_2$ during lean/rich cycling experiments. Rich phase: 0.15 vol. % C$_2$H$_4$, 1 vol. % Ar, and 10 vol. % CO$_2$, 100 min. (B) Lean outlet concentrations of NO, NO$_2$ and NO$_x$. Lean phase: 0.2 vol. % NO, 4 vol. % O$_2$, 10 vol. % CO$_2$ and 1 vol. % Ar, 200 min.
also observed. At first, the N₂ outlet concentration is 0.16 vol. %. However, after 60 s the N₂ outlet concentration decreases to 0.14 vol. % which can probably be related to poisoning of the Pt sites by CO. Abdulhamid et al. [22] also reported that deactivation of the reduction function of CO is observed after a short time of the reduction period and also relate it to self poisoning of the Pt sites by CO. The self poisoning probably occurs through the Boudouard reaction (Equation 4-4) resulting in carbon deposition by CO dissociation on the Pt sites [49].

\[
2CO_{\text{Pt}} \rightarrow C + CO_2 \quad (4-4)
\]

The reduction with CO shows selectivity towards N₂ of 88 %, as against 86 % for experiments with H₂. At the end of the rich phase, only 77 % of the nitrates formed in the previous lean phase are removed, probably due to poisoning of the catalyst by formation of strongly bonded isocyanates coordinated with Al³⁺ and Ba²⁺ cations [31, 32].

Upon switching to lean conditions, N₂ and CO₂ peaks are observed. Isocyanates, formed in the rich phase, can react with O₂ according to Equation 4-5:

\[
2NCO + O_2 \rightarrow N_2 + 2CO_2 \quad (4-5)
\]

To distinguish between CO₂ formed during NOₓ storage (Equations 4-1 and 4-3) and CO₂ produced through Equation 4-5, the catalyst is exposed to 4 vol. % O₂ in He flow after a rich phase. As shown in Figure 4.3, 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. Both N₂ and CO₂ signals seem to exist of two peaks, possibly relating to isocyanates formed on Al³⁺ and Ba²⁺ cations, respectively. The N₂ concentration decreases to zero after 0.3 min. A tail is observed in the concentration of CO₂ and the CO₂ concentration decreases to zero only after 9 min. The CO₂/N₂ molar ratio equals 4.3, which is not in agreement with the value 2 obtained from the stoichiometry of Equation 4-5. However, O₂ and NO₂ can also react with the adsorbed carbon on Pt sites, according to Equation 4-6 and Equation 4-7, respectively [50, 51, 52]. This could explain the observed CO₂/N₂ molar ratio:

\[
C + O_2 \rightarrow CO_2 \quad (4-6)
\]

\[
C + 2NO_2 \rightarrow 2NO + CO_2 \quad (4-7)
\]

The stored amount of NOₓ after 200 min lean exposure is 1.28 mmol/g catalyst which is slightly lower than the 1.39 mmol/g catalyst stored in the experiment with H₂ as the reducing agent. Upon lean exposure the NO and NO₂ outlet concentrations show a dead time of 3.4 min after which they increase in time (Figure 4.2). The breakthrough timing is about the same for both NO and NO₂, contrary to the results seen with H₂ as the reducing agent. Furthermore, a small NO₂ peak (0.05 vol. %) is observed after 9.2 min lean phase. Results reported by Abdulhamid et al. [22] also show a peak in the NOₓ breakthrough profile for experiments with CO as reducing agent. This peak is not observed when H₂ is used, similar with our results. Also NO shows no maximum as in the experiments with H₂. All this seems to indicate that in the case of CO as reducing agent, the storage of NOₓ in the lean phase occurs through a different reaction route, than in the case of experiments with H₂ as a reducing agent. The NO₂ peak could be a result of the reaction of adsorbed species on the Pt sites with O₂ forming NO₂.

Upon lean conditions, NO is oxidized to NO₂, which in turn oxidizes carbon (Equation 4-7) or is stored on the barium sites (Equation 4-3). The NO released according to reaction (Equation 4-7) is oxidized again to NO₂ or is stored as nitrites on the BaCO₃ sites (Equation 4-1). Before NOₓ breakthrough, nitrites will be the most abundant species present on the barium sites. As NO₂ possibly participates in the carbon oxidation process, the stored nitrites can be oxidized into nitrates with O₂ (Equation 4-8) [12].

\[
Ba(NO_2)_2 + O_2 \rightarrow Ba(NO_3)_2 \quad (4-8)
\]
Figure 4.5: 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.
With Equation 4-8, no NO is released and as a result the NO concentration would increase in time without showing a maximum value as observed for experiments with H2 (Figure 4.1).

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 almost completely regenerated. It is also unlikely that poisoning of Pt sites will occur due to adsorbed carbon species as H2O inhibits carbon deposition [53, 54]. Indeed, no CO2 and N2 formation peaks are seen in the beginning of the lean phase for experiments with H2 as reducing agent.

### 4.3 Influence of C2H4

The effect of C2H4 on the NOx storage/reduction is presented in Figure 4.4. The rich phase shows immediate formation of N2 and NO release. Only minor amounts of NO2 are observed. The N2 concentration shows an initial value of 0.16 vol. % and increases after 2 min to 0.18 vol. % after which it remains constant for 5.3 min. Ethylene is unable to adsorb on oxygen covered Pt sites [55], resulting in an initial lower N2 concentration and observed C2H4 breakthrough (not shown). After 5.3 min, the N2 outlet concentration decreases and a tail is observed. Only after 34 min, the N2 concentration decreases to zero. It is reported that strong adsorption of the species derived from hydrocarbons can poison Pt sites [27, 30]. This might explain why the NOx reduction into N2 becomes less effective in time. Although more time is needed for complete catalyst regeneration with C2H4 as reducing agent, the selectivity towards N2 is 93 %, as against 86 % for experiments with H2 as reducing agent. At the end of the rich phase 100 % of the formed nitrates in the preceding lean phase are removed, indicating that no isocyanates are formed.

The CO2 peak formed at the start of the lean phase (not shown) supports the presence of adsorbed molecules derived from C2H4 on Pt sites. The lean phase shows complete NOx 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 H2 and 16 min for experiments with CO. NO2 breaks through after 6.7 min, in contrast to 30 min for experiments with H2 and 3.4 min for experiments with CO. This seems to indicate that only part of the formed NO2 is used for carbon oxidation (Equation 4-7) and that NOx storage occurs through Equations 4-1, 4-2, 4-3 and 4-8. The stored amount of NOx at the end of the lean phase is 1.36 mmol/g catalyst.

### 4.4 Effect of H2O on NOx reduction

Catalyst regeneration in the presence of H2O shows no NH3 formation, even with H2 as the reducing agent (Figure 4.5). Immediate formation of N2 can be seen, as well as NO release. Only minor amounts of NO2 are observed. During the rich phase, the catalyst is completely regenerated. The selectivity towards N2 is 90 %, compared to 86 % without H2O present in the rich phase. In contrast to experimental results obtained with CO without H2O present (Figure 4.2), only minor amounts of NO2 are observed (Figure 4.5). Interestingly, in the presence of H2O the same NO release, N2 formation profile and selectivity towards N2 is seen for the experiments with CO and H2. This observed similarity between H2 and CO can possibly be ascribed to the water gas shift (WGS) reaction [23, 56, 57]. In fact, after catalyst regeneration, 0.8 vol. % H2 is observed and no CO is detected (not shown), indicating that H2 is produced from CO + H2O. No H2 or CO is detected during catalyst regeneration, but it is reasonable to assume that H2 acts as reductant. This is supported by the fact that there are no signs of Pt poisoning by CO or isocyanates formation. Immediate N2 formation and NO release are also seen for experiments with C2H4 (Figure 4.5). As 0.15 vol. % C2H4 has a higher molar reduction capacity as 0.8 vol. % H2 or CO, the N2 concentration is 0.18 vol. %, as against 0.16 vol. % for CO and H2. As a consequence, the N2 concentration drops to zero for C2H4 after 8.9 min, as against 10 min
Figure 4.6: Lean outlet concentrations of NO, NO₂ and NOₓ during lean/rich cycling experiments. Lean phase: 0.2 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂, 10 vol. % H₂O and 1 vol. % Ar, 200 min.

Figure 4.7: Lean outlet concentrations of NO during lean/rich cycling experiments at 300 °C. Lean phase: 0.14 vol. % NO, 4 vol. % O₂, 10 vol. % CO₂, 10 vol. % H₂O and 1 vol. % Ar, 100 min.

Figure 4.8: Rich outlet concentrations of NO and N₂ during lean/rich cycling experiments at 300 °C. (A) Rich phase: 1.2 vol. % H₂, 1 vol. % Ar, 10 vol. % CO₂, and 10 vol. % H₂O, 80 min. (B) Rich phase: 1.2 vol. % CO, 1 vol. % Ar, 10 vol. % CO₂, and 10 vol. % H₂O, 80 min. (C) Rich phase: 0.2 vol. % C₂H₄, 1 vol. % Ar, 10 vol. % CO₂, and 10 vol. % H₂O, 80 min.
for CO and H\textsubscript{2} experiments. The N\textsubscript{2} signal decreases to zero after 12 min. The selectivity towards N\textsubscript{2} is 88 \%, and the N balance shows that the nitrates stored in the previous lean phase are completely removed.

For all the used reducing agents, the lean phase shows the same NO and NO\textsubscript{2} breakthrough profiles (Figure 4.6). 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.

4.5 **Effect of H\textsubscript{2}O in both lean and rich phase on the NO\textsubscript{x} storage and reduction**

4.5.1 **Effect of reducing agent**

The data obtained at 100 min lean/80 min rich cycling conditions at 300 °C with H\textsubscript{2}O in both the lean and the rich phase and H\textsubscript{2}, CO or C\textsubscript{2}H\textsubscript{4} as reducing agent are shown in Figure 4.7 and 4.8. H\textsubscript{2}O and CO\textsubscript{2} signals are not shown, as H\textsubscript{2}O and CO\textsubscript{2} produced during NO\textsubscript{x} storage can hardly be distinguished from the noise in the MS signals because of the high inlet concentrations. For all the used reducing agents, the lean phase shows the same NO breakthrough profile and no NO\textsubscript{2} is observed. The lean phase shows complete NO\textsubscript{x} storage for 6.3 min. After 100 min no NO\textsubscript{x} is stored on the catalyst anymore and the NO-outlet is the same as the NO-inlet of 0.14 vol. \%. 0.59 mmol NO\textsubscript{x}/g catalyst has been stored as against 1.4 mmol NO\textsubscript{x}/g catalyst in experiments with only H\textsubscript{2}O in the rich phase. In the presence of H\textsubscript{2}O in the lean phase the NO\textsubscript{x} trapping capability of the catalyst has decreased compared to experiments without H\textsubscript{2}O in the lean phase.

In the presence of H\textsubscript{2}O in the lean phase, no NO\textsubscript{2} formation is detected. Olsson et al. [42] reported that H\textsubscript{2}O inhibits the NO oxidation activity of Pt/γ-Al\textsubscript{2}O\textsubscript{3} catalysts. Indeed, after the H\textsubscript{2}O supply is shut-off, NO\textsubscript{2} formation is seen in the lean phase (not shown). In the presence of H\textsubscript{2}O, NO\textsubscript{2} adsorption on γ-Al\textsubscript{2}O\textsubscript{3} sites is negligible [35, 43]. 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. [35] 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.

In the presence of H\textsubscript{2}O in the lean phase, no NO\textsubscript{2} formation is detected. Olsson et al. [42] reported that H\textsubscript{2}O inhibits the NO oxidation activity of Pt/γ-Al\textsubscript{2}O\textsubscript{3} catalysts. Indeed, after the H\textsubscript{2}O supply is shut-off, NO\textsubscript{2} formation is seen in the lean phase (not shown). In the presence of H\textsubscript{2}O, NO\textsubscript{2} adsorption on γ-Al\textsubscript{2}O\textsubscript{3} sites is negligible [35, 43]. 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. [35] 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.

The rich phase shows no NO\textsubscript{2} production, as opposed to experiments with only H\textsubscript{2}O in the rich phase where small amounts of NO\textsubscript{2} are observed (Figure 4.5). With H\textsubscript{2} immediate formation of N\textsubscript{2} can be seen, as well as NO release. The reduction of stored NO\textsubscript{x} in the rich phase is highly selective towards N\textsubscript{2} because only minor amounts of NO are observed (Figure 4.8). The reduction efficiency is 96 \% and the N-balance is closed for the lean/rich cycles. The RWGS reaction does not take place in the rich phase with H\textsubscript{2} as reducing agent since no CO formation is observed. For H\textsubscript{2} and CO as reducing agents, the rich phase shows exactly the same N\textsubscript{2} and NO production and no NO\textsubscript{2} is observed. The observed similarity is explained with the WGS reaction in which CO and H\textsubscript{2}O immediately react to H\textsubscript{2} and CO\textsubscript{2} and H\textsubscript{2} subsequently acts as reductant. The rich phase with C\textsubscript{2}H\textsubscript{4} shows similar results as the rich phase with H\textsubscript{2} and CO, although small differences are seen in the profile of N\textsubscript{2}. The formation of N\textsubscript{2} starts decreasing earlier and more gradually and also a longer tail of N\textsubscript{2} production is seen. The reduction efficiency is also 96 \% in case of C\textsubscript{2}H\textsubscript{4} as reducing agent and the N-balance is closed for the lean/rich cycles.
**Figure 4.9:** Rich outlet concentrations of NO and N₂ during lean/rich cycling experiments at 250 °C. (A) Rich phase: 1.2 vol. % H₂, 1 vol. % Ar, 10 vol. % CO₂, and 10 vol. % H₂O, 80 min. (B) Rich phase: 1.2 vol. % CO, 1 vol. % Ar, 10 vol. % CO₂, and 10 vol. % H₂O, 80 min. (C) Rich phase: 0.2 vol. % C₂H₄, 1 vol. % Ar, 10 vol. % CO₂, and 10 vol. % H₂O, 80 min.

**Figure 4.10:** Rich outlet concentrations of NO and N₂ during lean/rich cycling experiments at 200 °C. (A) Rich phase: 1.2 vol. % H₂, 1 vol. % Ar, 10 vol. % CO₂, and 10 vol. % H₂O, 80 min. (B) Rich phase: 1.2 vol. % CO, 1 vol. % Ar, 10 vol. % CO₂, and 10 vol. % H₂O, 80 min. (C) Rich phase: 0.2 vol. % C₂H₄, 1 vol. % Ar, 10 vol. % CO₂, and 10 vol. % H₂O, 80 min.

**Figure 4.11:** Rich outlet concentrations of NO, N₂ and N₂+0.5*NO during lean/rich cycling experiments at 250 °C with C₂H₄ as reductant.

**Figure 4.12:** NO desorption from γ-Al₂O₃ during rich phase without reducing agent at 200 °C.

**Figure 4.13:** NO evolution during rich phase with H₂ at 300 °C.
4.5.2 Effect of temperature

Experiments at 100 min lean/80 min rich cycling conditions with H₂O in both the lean and rich phase are also performed at 250 and 200 °C. Temperature only influences the lean phase with respect to the amount of NOₓ trapped. At 250 and 200 °C, 0.41 and 0.31 mmol NOₓ/g catalyst is stored, respectively as against 0.59 mmol NOₓ/g catalyst at 300 °C. Overall the breakthrough profiles of NO during lean operation show the same trends for all reductants at all temperatures. The reduction of stored NOₓ, however, is considerably affected by the temperature. Therefore, emphasis will be on the rich phase. Figure 4.8, 4.9 and 4.10 show the effect of the different reducing agents (H₂, CO and C₂H₄) on the reduction of NOₓ at 300, 250 and 200 °C, respectively.

At 250 °C, experiments with H₂ and CO show a similar production of N₂ and NO compared to experiments at 300 °C. The reduction efficiency is 97 %, slightly higher than at 300 °C. Also at this temperature, the resemblance between H₂ and CO experiments suggests that the WGS reaction takes place and that the formed H₂ acts as reducing agent. With C₂H₄ however the results show a considerably lower reduction efficiency (85 %), compared to experiments with H₂ and CO. Immediately after switching to the rich phase, N₂ and NO are observed at 0.15 vol. % at 250 °C while at the same time NO gradually decreases to 0 vol. %. Furthermore N₂ production shows a long tail, which implies that the time necessary for complete regeneration of the catalyst is also long. The lower reduction efficiency of C₂H₄, compared to H₂ and CO, is most likely related to the activation of the reductants. Hydrocarbons require higher temperatures to be activated, and the reduction rate is thus low [22, 58]. As already mentioned, C₂H₄ is unable to adsorb on oxygen covered Pt sites. At 200 °C the oxygen coverage of the Pt sites will be higher than at 300 °C and this also could explain the large amount of NO desorption and the low production of N₂. NOₓ can be released from nitrates with C₂H₄ as reducing agent, but NO released subsequently cannot be reduced effectively to N₂ on the Pt sites. The experiment with C₂H₄ suggests that the stored NOₓ is released as NO and subsequently reduction into N₂ takes place. As the hydrocarbons are not capable of reducing all NO into N₂, part of the NO is seen at the outlet of the reactor. In Figure 4.11 N₂ and NO profiles have been plotted together with a N₂+½*NO signal for the experiment with C₂H₄ at 250 °C. The volume concentration of N₂+½*NO is comparable with the volume concentration of N₂ in case of reduction with CO and H₂. This indicates that all C₂H₄ is consumed in the release and reduction of stored NOₓ.

At 200 °C, only H₂ is effectively able to regenerate the catalyst. The N₂ signal once again shows comparable results compared to experiments with H₂ at 300 °C. The reduction efficiency is 97 %. Both C₂H₄ and CO show insufficient capacity to reduce all of the stored NOₓ. This is probably a temperature effect, causing the rate of the release reactions to be low. Experiments with C₂H₄ show only small production of N₂ whereas CO shows almost no formation of N₂. Feeding CO as a reducing agent at 200 °C results in incomplete regeneration of the catalyst, contrary to experiments with H₂ at 200 °C. This indicates that at 200 °C CO does not participate in the WGS reaction forming H₂. Despite differences with respect to formation of N₂, NO observed is similar with all three reducing agents at this temperature. This suggests that the NO observed is involved in a reaction route which is independent on the kind of reducing agent. This is supported by the results of an experiment with a rich phase without reducing agent. Also in this experiment the same NO-profile is observed (not shown). A possible explanation for this NO-profile would be desorption of NO from the γ-Al₂O₃, on switching to conditions with no NO in the feed. An experiment performed with only γ-Al₂O₃ supports this theory, as the same NO desorption peak has been observed (Figure 4.12).

With the release of NO from γ-Al₂O₃ and the release of NO from nitrates, two different NO evolutions can be distinguished. Looking closer to the NO outlet concentration of the experiments at 300 and 250 °C, indeed two processes can be appointed. In Figure 4.13 this is shown for the experiment with H₂ as a reducing agent at 300 °C. First there is desorption of NO from γ-Al₂O₃ (evolution 2) and second there is formation of NO caused by release of NOₓ from nitrates (evolution 1).
Figure 5.1: Pictorial representation of surface, semi-bulk and bulk barium sites.

Table 5.1: The global reaction steps and rate equations used for modeling NO\textsubscript{x} storage and reduction. The reaction rate parameters $k_{s,\text{NO}_i}$, $k_{s,\text{dis},i}$, $k_{\text{reg},\text{nitrite},i}$, and $k_{\text{reg},\text{nitrate},i}$ have different units and values for the surface, semi-bulk and bulk barium sites with $i$ = surface, semi-bulk or bulk. See also Table 5.2.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Rate equation</th>
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<tr>
<td><strong>Lean phase</strong></td>
<td></td>
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<tr>
<td>$\text{BaCO}_3 + 2 \text{NO} + 0.5 \text{O}_2 \rightarrow \text{Ba(NO}_2)_2 + \text{CO}_2$</td>
<td>$R_{\text{st,NO}} = \theta \frac{k_{s,\text{NO}_2}(\text{BaCO}_3)(\text{NO}_2)(\text{CO}_2)}{\theta}$ (I)</td>
</tr>
<tr>
<td>$\text{Ba(NO}_2)_2 + \text{O}_2 \rightarrow \text{Ba(NO}_3)_2$</td>
<td>$R_{\text{st,oxi}} = \theta \frac{k_{s,\text{dis}}(\text{Ba(NO}_2)_2)(\text{CO}_2)}{\theta}$ (II)</td>
</tr>
<tr>
<td><strong>Rich phase with $\text{H}_2$</strong></td>
<td></td>
</tr>
<tr>
<td>$\text{Ba(NO}_2)_2 + \text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2\text{NO} + \text{H}_2\text{O}$</td>
<td>$R_{\text{reg,nitrite,H}<em>2} = \theta \frac{k</em>{\text{reg,nitrite,H}_2}(\text{Ba(NO}_2)_2)(\text{CO}_2)}{\theta}$ (III)</td>
</tr>
<tr>
<td>$\text{Ba(NO}_3)_2 + 3 \text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2\text{NO} + 3\text{H}_2\text{O}$</td>
<td>$R_{\text{reg,nitrate,H}<em>2} = \theta \frac{k</em>{\text{reg,nitrate,H}_2}(\text{Ba(NO}_3)_2)(\text{CO}_2)}{\theta}$ (IV)</td>
</tr>
<tr>
<td>$\text{NO} + \text{H}_2 \rightarrow \frac{1}{2} \text{N}_2 + \text{H}_2\text{O}$</td>
<td>$R_{\text{red,H}<em>2} = \theta \frac{k</em>{\text{red,H}_2}(\text{NO})(\text{H}_2)}{\theta}$ (V)</td>
</tr>
<tr>
<td><strong>Rich phase with $\text{CO}$</strong></td>
<td></td>
</tr>
<tr>
<td>$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$</td>
<td>$R_{\text{reg,nitrite,H}<em>2} = \theta \frac{k</em>{\text{reg,nitrite,H}_2}(\text{CO})(\text{H}_2)}{\theta}$ (VI)</td>
</tr>
<tr>
<td>$\text{Ba(NO}_2)_2 + 3 \text{H}_2 + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2\text{NO} + \text{H}_2\text{O}$</td>
<td>$R_{\text{reg,nitrate,H}<em>2} = \theta \frac{k</em>{\text{reg,nitrate,H}_2}(\text{Ba(NO}_3)_2)(\text{CO}_2)}{\theta}$ (VII)</td>
</tr>
<tr>
<td>$\text{NO} + \text{H}_2 \rightarrow \frac{1}{2} \text{N}_2 + \frac{1}{3} \text{CO}_2 + \frac{1}{3} \text{H}_2\text{O}$</td>
<td>$R_{\text{red,H}<em>2} = \theta \frac{k</em>{\text{red,H}_2}(\text{NO})(\text{H}_2)}{\theta}$ (VIII)</td>
</tr>
<tr>
<td><strong>Rich phase with $\text{C}_2\text{H}_4$</strong></td>
<td></td>
</tr>
<tr>
<td>$\text{Ba(NO}_2)_2 + \frac{1}{6} \text{C}_2\text{H}_4 + \text{CO}_2 \rightarrow$</td>
<td>$R_{\text{reg,nitrite,C}_2\text{H}_4} =$ (IX)</td>
</tr>
<tr>
<td>$\text{BaCO}_3 + 2\text{NO} + \frac{1}{3} \text{CO}_2 + \text{H}_2\text{O}$</td>
<td>$k_{\text{reg,nitrite,C}_2\text{H}_4}(\text{Ba(NO}_2)_2)(\text{C}_2\text{H}_4)$ (X)</td>
</tr>
<tr>
<td>$\text{Ba(NO}_3)_2 + \frac{1}{6} \text{C}_2\text{H}_4 + \text{CO}_2 \rightarrow$</td>
<td>$R_{\text{reg,nitrate,C}_2\text{H}_4} =$ (XI)</td>
</tr>
<tr>
<td>$\text{BaCO}_3 + 2\text{NO} + \text{CO}_2 + \text{H}_2\text{O}$</td>
<td>$k_{\text{reg,nitrate,C}_2\text{H}_4}(\text{Ba(NO}_3)_2)(\text{C}_2\text{H}_4)$ (XII)</td>
</tr>
<tr>
<td>$\text{NO} + \frac{1}{6} \text{C}_2\text{H}_4 \rightarrow \frac{1}{2} \text{N}_2 + \frac{1}{3} \text{CO}_2 + \frac{1}{3} \text{H}_2\text{O}$</td>
<td>$R_{\text{red,C}_2\text{H}<em>4} = \theta \frac{k</em>{\text{red,C}_2\text{H}_4}(\text{NO})(\text{C}_2\text{H}_4)}{\theta}$ (XII)</td>
</tr>
</tbody>
</table>
5  Modeling

The experimental data with as well CO₂ as H₂O in both the lean and rich phase will be used to adapt the model for NOₓ storage/reduction in the presence of CO₂ from Scholz et al. [3] to a model which describes lean/rich cycling experiments in the presence of as well CO₂ as H₂O.

5.1  Kinetic model construction

The experimental results show that initially in the lean phase fast NOₓ storage occurs, followed by slow storage. It is considered that this fast NOₓ storage occurs at the surface barium sites, which is determined by the reaction kinetics. The slow NOₓ storage takes place at the semi-bulk and bulk barium sites where diffusion plays a major role. It can be considered that in the presence of excess CO₂, barium is present mainly in the carbonate form. The surface, semi-bulk and bulk sites not only differ in physical appearance (as shown in Figure 5.1), but also in chemical reactivity; surface sites are being the most reactive, whereas bulk sites are the least reactive.

The global reaction steps and rate equations used for modeling NOₓ storage and reduction with surface, semi-bulk and bulk barium sites in the presence of CO₂ and H₂O are presented in Table 5.1. The reaction steps and rate equations are based on the original reaction steps and rate equations of the model from Scholz et al. [3] and adjusted for the experiments in this research.

Because no NO₂ formation is seen in the experiments during lean operation, the oxidation step of NO in the presence of Pt is not included. As no NO₂ is available, the direct storage of NO₂ into nitrates is also not included. Because of the absence of NO₂ for oxidation of nitrites to nitrates, the oxidation of nitrites into nitrates with O₂ is added. As already mentioned in the literature overview, bulk barium sites show negligible reactivity towards NOₓ storage. Therefore in the model these bulk barium sites are chosen to have no reactivity towards NOₓ storage.

In this modeling, it is considered that NOₓ storage occurs through nitrites and nitrates formation. First, NO will adsorb on the catalyst in the form of barium nitrites [10, 13], as presented in Reaction I. These nitrites can be further oxidized to nitrates by O₂ (Reaction II).

In the rich phase, it is considered that regeneration of barium sites takes place through nitrite/nitrate decomposition, as mentioned by Lietti et al. [12], and as presented in Reactions III, IV, VII, VIII, XI and XII. The released NOₓ is reduced on the Pt sites into N₂ with a reductant, as presented in Table 5.1. As mentioned in Section 4.5.2 NO release from γ-Al₂O₃ is observed during experiments. This reaction is not included in the model, because of the small amounts of NO involved. With CO as reducing agent, CO reacts with H₂O in the WGS reaction forming H₂ and CO₂ (Reaction VI). H₂ subsequently acts as the reducing agent releasing and reducing NOₓ.

From a 9 h/15 h lean/rich cycling experiment, the distribution of surface, semi-bulk and bulk sites of the catalyst has been acquired. This resulted in 73 % of the total barium corresponding with bulk barium sites, 7 % with surface sites, and 20 % with semi-bulk sites. These results were supported by a TGA experiment [3]. In order to obtain a proper fit of the model with experiments in the presence of H₂O in both the lean phase and rich phase, the distribution has slightly been altered: 83 % of the total barium sites correspond with bulk barium sites, 7 % with surface barium sites, and 10 % with semi-bulk barium sites. The diffusion coefficient of the gas phase components in the semi-bulk and bulk barium is taken as 3.64×10⁻¹⁵ m²/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 m²/s [59]. The pore size distribution measurement revealed an average pore diameter of 10 nm (not shown). In the model it is considered that the average size of the barium particles is also 10 nm. The model parameters and coefficients at 300 °C are also based on those of the model of Scholz et al. [3] and can be found in Table 5.2.
Table 5.2: Model parameters and coefficients at 300 °C [3].

<table>
<thead>
<tr>
<th>Catalyst parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{Pt}$</td>
<td>9.67 moles of active Pt surface sites per m$^3$ reactor, (mol m$^{-3}_{reactor}$)</td>
</tr>
<tr>
<td>$L_{Ba, surface}$</td>
<td>1.34×10$^2$ moles of active Ba surface sites per m$^3$ reactor, (mol m$^{-3}_{reactor}$)</td>
</tr>
<tr>
<td>$L_{Ba, semi-bulk}$</td>
<td>2.00×10$^2$ moles of active Ba semi-bulk sites per m$^3$ reactor, (mol m$^{-3}_{reactor}$)</td>
</tr>
<tr>
<td>$L_{Ba, bulk}$</td>
<td>1.75×10$^3$ moles of active Ba bulk sites per 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 barium cluster, (m$^3_{Ba}$)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reactor parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_b$</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$^{-15}$ diffusion coefficient, (m$^3_{gas}$ m$^{-1}_{Ba}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$\varepsilon_{cluster}$</td>
<td>0.5 cluster porosity, (m$^3_{gas}$ m$^{-3}_{Ba}$)</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>Storage parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface barium sites</td>
<td></td>
</tr>
<tr>
<td>$k_s, NO$</td>
<td>5.09×10$^2$ NO storage, (m$^{7.5}<em>{gas}$ mol$^{-2.5}</em>{i}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$k_s, dis$</td>
<td>3.74×10$^4$ nitrite oxidation, (m$^6_{gas}$ mol$^{-2}_{i}$ s$^{-1}$)</td>
</tr>
<tr>
<td>Semi-bulk barium sites</td>
<td></td>
</tr>
<tr>
<td>$k_s, NO$</td>
<td>1.95×10$^3$ NO storage, (m$^{7.5}<em>{gas}$ mol$^{-2.5}</em>{i}$ s$^{-1}$ mol$<em>{Ba}$ m$^{-3}</em>{Ba}$)</td>
</tr>
<tr>
<td>$k_s, dis$</td>
<td>9.10×10$^2$ nitrite oxidation, (m$^6_{gas}$ mol$^{-2}<em>{i}$ s$^{-1}$ mol$</em>{Ba}$ m$^{-3}_{Ba}$)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Regeneration parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface barium sites</td>
<td></td>
</tr>
<tr>
<td>$k_{reg, nitrite}$</td>
<td>5.96×10$^{-2}$ Ba(NO$<em>2$)$<em>2$ regeneration, (m$^3</em>{gas}$ mol$^{-1}</em>{i}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$k_{reg, nitrate}$</td>
<td>4.48       Ba(NO$<em>3$)$<em>2$ regeneration, (m$^3</em>{gas}$ mol$^{-1}</em>{i}$ s$^{-1}$)</td>
</tr>
<tr>
<td>Semi-bulk barium sites</td>
<td></td>
</tr>
<tr>
<td>$k_{reg, nitrite}$</td>
<td>1.45×10$^{-2}$ Ba(NO$<em>2$)$<em>2$ regeneration, (m$^3</em>{gas}$ mol$^{-1}</em>{i}$ s$^{-1}$ mol$<em>{Ba}$ m$^{-3}</em>{Ba}$)</td>
</tr>
<tr>
<td>$k_{reg, nitrate}$</td>
<td>1.09×10$^{4}$ Ba(NO$<em>3$)$<em>2$ regeneration, (m$^3</em>{gas}$ mol$^{-1}</em>{i}$ s$^{-1}$ mol$<em>{Ba}$ m$^{-3}</em>{Ba}$)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reduction parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{red}$</td>
<td>2.60×10$^4$ NO$_x$ reduction, (m$^6_{gas}$ mol$^{-2}_{i}$ s$^{-1}$)</td>
</tr>
</tbody>
</table>
5.2 Reactor model

The packed bed reactor is regarded as an ideal plug flow reactor, under isothermal conditions. The model is constructed to describe NOx storage and reduction at a temperature of 300 °C. 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:

$$
\frac{\partial C_i}{\partial t} = -\frac{F_v}{A_r} \frac{\partial C_i}{\partial z} - D_{\text{eff}} A_{\text{Ba}} \frac{\partial C_i}{\partial \xi} |_{\xi=R} + L_{\text{Pt},j} \sum_j v_{i,j} R_{\text{Pt},j} + L_{\text{Ba,surf}} \sum_k v_{i,k} R_{\text{Ba,surf},k} \quad (5-1)
$$

where $\varepsilon_b \left[ \text{m}^3_{\text{gas}} \text{m}^{-3}_{\text{reactor}} \right]$ is the bed porosity, $C_i \left[ \text{mol} \text{m}^{-3}_{\text{gas}} \right]$ is the gas phase concentration of component $i$ (NO, NO2, O2, H2 and N2), $t \left[ \text{s} \right]$ is time, $F_v \left[ \text{m}^3_{\text{gas}} \text{s}^{-1} \right]$ is the volumetric flow rate, $A_r \left[ \text{m}^2 \text{reactor} \right]$ is the surface area of the reactor, $z \left[ \text{m} \right]$ is the axial length, $D_{\text{eff}} \left[ \text{m}^2 \text{m}^{-1}_{\text{Ba s}^{-1}} \right]$ is the effective gas diffusion coefficient, $A_{\text{Ba}} \left[ \text{m}^2_{\text{Ba m}^{-3}_{\text{reactor}}} \right]$ is the specific barium surface, $\xi \left[ \text{m}_{\text{Ba}} \right]$ is the radial direction in the barium clusters, $L_{\text{Pt}} \left[ \text{mol}_{\text{Pt m}^{-3}_{\text{reactor}}} \right]$ is the specific number of moles of active Pt surface sites, $R_{\text{Pt},j} \left[ \text{mol} \text{mol}^{-1}_{\text{Pt s}^{-1}} \right]$ is the NO reduction rate described in Reactions V, IX and XII in Table 5.1, $L_{\text{Ba,surf}} \left[ \text{mol}_{\text{Ba m}^{-3}_{\text{reactor}}} \right]$ is the specific number of moles of active barium surface sites. $R_{\text{Ba,surf},k} \left[ \text{mol} \text{mol}^{-1}_{\text{Ba s}^{-1}} \right]$ is the NOx storage and regeneration rate at barium surface sites and can be determined from the reaction equations mentioned in Table 5.1. Equation 5-2 calculates the time-dependent change of the different species on the surface barium sites:

$$
\frac{\partial \theta_{m,surf}}{\partial t} = \sum_k v_{i,k} R_{\text{Ba,surf},k} \quad (5-2)
$$

where $\theta_{m,surf} \left[ - \right]$ 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 5-3:

$$
\theta_{\text{BaCO}_3,\text{surface}} = 1 - \theta_{\text{Ba(NO2)}_2,\text{surface}} - \theta_{\text{Ba(NO3)}_2,\text{surface}} \quad (5-3)
$$

Equation 5-4 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:

$$
\varepsilon_{\text{cluster}} \frac{\partial C_i}{\partial t} = \frac{1}{\varepsilon^2} \frac{\partial}{\partial \xi} \left( D_{\text{eff}} \varepsilon^2 \frac{\partial C_i}{\partial \xi} \right) + \sum_k v_{i,k} R_{\text{Ba,surf},k} \quad (5-4)
$$
Figure 5.2: Simulated and measured lean NO outlet concentrations. For experimental conditions, see Figure 4.7.
Chapter 5 - Modeling

where $\varepsilon_{\text{cluster}}$ [m$^3$ gas m$^{-3}$ Ba] is the porosity of the barium clusters, X is semi-bulk barium sites, and $R_{\text{Ba},X,k}$ [mol m$^{-3}$ Ba s$^{-1}$] is the NO$_x$ storage and regeneration rate for the semi-bulk sites and can be determined from the rate equations mentioned in Table 5.1. Equation 5.5 describes the time-dependent change of the different species on the semi-bulk barium sites:

$$\frac{L_{\text{Ba,semi-bulk}}}{f} \frac{\partial \theta_{m,\text{semi-bulk}}}{\partial t} = \sum_k v_{i,k} R_{\text{Ba,semi-bulk,k}}$$

where $L_{\text{Ba,semi-bulk}}$ [mol 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 sites is shown in Equation 5-6.

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

The initial and boundary conditions are given as:

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

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

$$\frac{\partial C_{i,z}^y}{\partial \xi} = 0$$ at $\xi = 0$ at any $t$.

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

5.3 Modeling results and discussion

Figure 5.2 shows the results from the model together with the measured outlet NO concentration for the 100 min lean phase with 0.14 vol. % inlet NO at 300 °C. Generally the model is well able to describe the lean phase, although minor deviations can be seen in the breakthrough profile of NO. In the experiments complete storage of NO$_x$ is observed for 6.3 minutes. The sudden increase of NO outlet concentration to 0.12 vol. % in the model shows some delay with respect to the breakthrough of NO in the experiments. It can also be seen that the experiments show a more gradual change in NO outlet concentration after breakthrough, compared to the change in NO outlet concentration in case of the model.

Upon rich conditions, N$_2$ formation and NO desorption are experimentally observed (Figure 5.3). The model adequately describes the N$_2$ formation and NO desorption. The model is also able to describe the small differences observed between experiments with H$_2$ and CO on the one hand, and experiments with C$_2$H$_4$ on the other hand. In the case of C$_2$H$_4$, the formation of N$_2$ starts decreasing earlier and more gradually and also a longer tail of N$_2$ production is seen. Also, the NO concentration is slightly higher in the case of C$_2$H$_4$. Both effects are described adequately.

Simulations show that at first all reducing agent (H$_2$, CO or C$_2$H$_4$) is completely consumed. As the rich phase proceeds, incomplete consumption of the reducing agent is seen. As CO participates in the WGS reaction forming H$_2$ and CO$_2$, CO therefore is not observed. Instead H$_2$ is observed at the outlet of the reactor.
Figure 5.3: Simulated and measured rich NO, H₂, and N₂ outlet concentrations. (A) Rich phase with H₂ (B) Rich phase with CO (C) Rich phase with C₂H₄. For experimental conditions, see Figure 4.8
6 Conclusions

Lean/rich cycling experiments at 300 °C without H₂O in the gas feed show a complete regeneration of the catalyst, except for the case with CO as a reducing agent. This is probably caused by the formation of isocyanates. These isocyanates are only formed in the rich phase in case of CO as a reducing agent and are removed in the subsequent lean phase in a reaction with O₂. Besides poisoning of the catalyst by the formation of isocyanates, also poisoning of the Pt sites by carbon deposition and by C₂H₄ derived species have been observed in case of, respectively, experiments with CO and experiments with C₂H₄. This causes a deactivation of the reduction function. With H₂ as reducing agent the RWGS reaction takes place once the production of N₂ declines, leading to the consumption of H₂ and CO₂ and simultaneous production of H₂O and CO. The production of CO in the RWGS reaction, however, does not result in carbon deposition or in the formation of isocyanates. A last conclusion for the rich phase of these experiments is that, as adsorption of ethylene on oxygen covered Pt sites is difficult, this results in a lower reduction towards N₂ and a breakthrough of C₂H₄ at the beginning of the rich phase.

The poisoning of the catalyst probably effects the lean phase, as different reaction routes during storage of NOₓ with H₂ as a reducing agent on the one hand and CO as a reducing agent on the other hand have been observed. In case of C₂H₄ as a reducing agent, storage of NOₓ during lean phase appears to occur through both reaction routes, as observed NO and NO₂ evolution exhibit resemblance with NO and NO₂ evolution of the experiments both with H₂ and CO.

The presence of H₂O in the rich phase at 300 °C does not influence the amount of NOₓ stored in the subsequent lean phase. Still, the lean phase is influenced by the presence of H₂O in the rich phase, as in that case lean phases of experiments with different reducing agents all show the same NO and NO₂ profile. The observed differences during lean operation in case of experiments without H₂O in the rich phase do not appear in these experiments due to H₂O preventing poisoning of the catalyst by isocyanates formation or carbon adsorbed species on the Pt sites. The observed similarity of the rich phase with H₂ and CO indicates that the WGS reaction is taking place and that H₂ subsequently acts as the reducing agent.

When feeding H₂O in both lean phase and rich phase, the lean phase of experiments with different reducing agents all show the same NO profile. Furthermore, no NO oxidation takes place, probably hindered by the presence of H₂O. In presence of water also no RWGS reaction takes place. With water in both the lean phase and the rich phase the NOₓ storage during lean phase decreases from approximately 1.4 to 0.6 mmol/g catalyst at 300 °C.

Experiments at 200, 250 and 300 °C show that H₂ is effective in releasing and reducing NOₓ towards N₂ at all temperatures investigated. CO and C₂H₄ on the other hand are able to regenerate the catalyst at 300 and 250 °C but not at 200 °C. Temperature also influences the stored NOₓ during lean phase. Most NOₓ is stored at 300 °C and least NOₓ is stored at 200 °C. Experiments at 200 °C furthermore show that NO desorbs from γ-Al₂O₃ and that this is independent on the kind of reducing agent.

A global reaction kinetic model has been developed for the NOₓ storage/reduction process in the presence of CO₂ and H₂O, based on the model of Scholz et al. The model is able to adequately describe the NO and N₂ release during rich operation. Also the differences in N₂ and NO formation for the several reducing agents are well described. The modeled NO evolution in time during the lean phase shows some deviations from the experimental data, but generally the model properly describes the lean phase behavior.
7 Reference list


4. Scholz, C.M.L., Gangwal, V.R., De Croon, M.H.J.M., Schouten, J.C., Submitted for publication, 2006. Influence of CO\textsubscript{2} and H\textsubscript{2}O on NO\textsubscript{x} storage and reduction on a Pt-Ba/γ-Al\textsubscript{2}O\textsubscript{3} catalyst


6. Olsson, L., Persson, H., Fridell, E., Skoglundh, M., Andersson, B., 2001. A kinetic study of NO oxidation and NO\textsubscript{x} storage on Pt/Al\textsubscript{2}O\textsubscript{3} and Pt/BaO/Al\textsubscript{2}O\textsubscript{3}. Journal of Physical Chemistry B 105 (29), 6895-6906.


