Influence of CO2 on the NOx storage and reduction behavior of a NOx storage-reduction catalyst

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Award date:
2006

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Influence of CO$_2$ on the NO$_x$ storage and reduction behavior of a NO$_x$ storage – reduction catalyst

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March 2006

Graduation project

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1. Summary

Stricter legislations on automotive emissions have led to the development of a NO\textsubscript{x} storage reduction (NSR) catalyst for lean-burn gasoline and diesel engines. These engines operate under oxygen rich conditions, which make three-way catalysts, used in conventional gasoline driven engines, unsuited for use. The NSR catalyst is one of the most promising technologies to overcome this problem. During lean conditions, the catalyst (Pt-Ba-\(\gamma\)-Al\(_2\)O\(_3\)) stores NO\textsubscript{x} as nitrates on barium. After a certain period the catalyst is filled with NO\textsubscript{x} and regeneration is necessary. The operation is switched to oxygen poor conditions, by injecting extra fuel. This causes release and reduction of the stored NO\textsubscript{x}. For lean operation, different Ba species have been reported, BaO, Ba(OH)\(_2\) and BaCO\(_3\). These species show differences in reactivity towards NO\textsubscript{x} storage: BaO>Ba(OH)\(_2\)>BaCO\(_3\). Moreover, different BaCO\(_3\) sites have been reported. First there are well dispersed Low Temperature (LT) BaCO\(_3\) sites, which cannot be detected by XRD. Secondly, bulky like High Temperature (HT) BaCO\(_3\) sites have been reported, which can be detected via XRD because of they are crystalline.

The aim of this project is to investigate the influence of CO\textsubscript{2} on the NO\textsubscript{x} storage and reduction behavior of the NO\textsubscript{x} storage-reduction (NSR) catalyst. Therefore, transient kinetic experiments were performed, making use of a catalytic fixed bed reactor. Two separate feed lines were used. One contained NO and O\(_2\) as oxidant (lean phase), the second contained H\(_2\) as reducing agent (rich phase). Both streams used He as carrier gas. The in and outlet gas mixtures were monitored with a mass spectrometer. Experiments with and without CO\textsubscript{2} in the feed were performed.

The experiments without CO\textsubscript{2} showed a change in activity of the catalyst at lean/rich cycling of 30 and 120 min respectively. An improvement was observed in the activity followed by decline, i.e. NO\textsubscript{x} storage first increased, then decreased, due to exchange of BaCO\(_3\) sites for Ba(OH)\(_2\). Furthermore, during rich conditions the selectivity towards N\(_2\) production decreased. BET surface area, pore volume and Pt dispersion were measured which showed a 40 % decrease compared to a pretreated catalyst. XRD measurements showed formation of Ba(NO\(_3\))\(_2\) indicating HT participation. Experiments with CO\textsubscript{2} in the reactor feed at lean/rich cycling of 9 and 15 hrs respectively showed no activity or selectivity change. Physical properties were measured and showed no deviations compared to a pretreated catalyst. XRD measurement showed no Ba(NO\(_3\))\(_2\), which implies that HT sites have not participated in the storage process.

Furthermore, lean/rich cycling of 9 and 15 hrs respectively were done at different temperatures. The results showed differences in NO breakthrough time, in the lean phase. The rich phase shows at lower temperature a decline in the selectivity towards N\(_2\) production. Moreover, NO production was higher at elevated temperatures, in the rich phase. At all temperatures, ultimately 30 % Ba utilization was reached.. With different lean/rich timing in the order of minutes, NO\textsubscript{x} breakthrough was observed earlier for longer rich timing, during lean operation. During rich operation, the same observation as during lean operation was observed for the N\(_2\) production timing.

Mechanistic studies showed that several routes towards NO\textsubscript{x} storage take place. Moreover, nitrites are formed which can be further oxidized by NO\(_2\) to nitrates. Also the rich phase showed that mostly nitrates have been formed during lean operation. The acquired data should lead to verification of a kinetic model describing the NO\textsubscript{x} storage and reduction behavior.
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Figure 1: Fuel consumption and TWC performance as a function of air to fuel ratio [1].

Figure 2: Schematic overview of a NO$_x$ storage reduction catalyst.
3. Introduction

3.1. General description

The environment is an important issue in today’s society. People have come to grip with the idea that the air pollution that is being produced by industry and the cars we drive, must be dealt with. In 1970 the Clean Air act in the USA set the standard for automotive emissions. This led to the development of the modern three-way catalyst (TWC). The TWC is able to reduce the emissions of hazardous components such as CO, C\textsubscript{x}H\textsubscript{y} and NO\textsubscript{x}. This catalyst was incorporated in petrol driven cars. From January 1\textsuperscript{st} 1993 all new petrol driven cars in the Netherlands are obligated to have such a TWC on board in order to comply with emission standards. The TWC consists of a γ-Al\textsubscript{2}O\textsubscript{3} support with Pt particles and small amounts of other metals, deposited on the surface. On these metal sites, the mentioned components are converted into less polluting ones. Important in the operation of the TWC is the air to fuel ratio (Figure 1). The typical operating window for the TWC is at an air to fuel ratio of 14.5 which corresponds to the combustion of petrol driven engines. But because of their high fuel consumption, diesel and lean-burn engines have become more and more interesting. For these engines a catalyst was not necessary in the early 1990’s because they still conformed to emission legislations. However, with more rigid legislations, these engines cannot escape the use of a catalyst anymore.

The diesel and lean-burn engines contain an excess amount of oxygen in their exhaust. As a result the engine is operated outside the operating window of the TWC, leading to a NO\textsubscript{x} conversion of almost 0 (Figure 1). One of the most suitable technologies to overcome this problem is the NO\textsubscript{x} trap, designed by Toyota Motor Company [1]. With this technology a component is added to the TWC, which functions as a trap. Suitable components are earth alkaline metal oxides such as BaO, of which a large amount is deposited on the TWC (Figure 2), i.e. on Pt-γ-Al\textsubscript{2}O\textsubscript{3}. These catalysts are called NO\textsubscript{x} storage reduction (NSR) catalysts.

The operation of a NSR catalyst consists of two parts. First the storage phase or lean phase takes place, followed by the reducing or rich phase. Lean operation takes place at high air to fuel ratio (Figure 1), i.e. oxygen rich conditions, whereas rich operation takes place in the operating window of the TWC, i.e. oxygen poor conditions. A schematic overview of the lean combustion process is depicted in Figure 3. During lean combustion, the catalyst starts to store NO\textsubscript{x} (the black particles). As the operating time increases, the catalyst bed gets saturated with NO\textsubscript{x}, approaching inlet concentration. Now the engine will be set to operate under rich conditions and the NO\textsubscript{x} is reduced, thus “cleaning” the catalyst.
**Figure 3:** Schematic overview of the operating mode of a NSR catalyst [21].

**Figure 4:** NO\textsubscript{x} storage characteristics: Complete uptake followed by rapid NO\textsubscript{x} uptake, leading to slow NO\textsubscript{x} uptake [10].
3.2. The NO\textsubscript{x} storage – reduction catalyst

3.2.1. Lean phase

During lean operation NO\textsubscript{x} storage takes place. This storage process can generally be divided into several pathways. One of the most important steps is the NO oxidation into NO\textsubscript{2} on Pt, represented in Equation 1 [3,17,18].

\[
\text{NO} + \frac{1}{2} \text{O}_2 \xrightarrow{\text{Pt}} \text{NO}_2 \quad \text{(Eq. 1)}
\]

NO\textsubscript{2} can subsequently be stored through the disproportionation mechanism (DPM) [3,4,12], resulting in NO release:

\[
3 \text{NO}_2 + \text{BaO} \rightarrow \text{Ba(NO}_3)_2 + \text{NO} \quad \text{(Eq. 2)}
\]

It is furthermore possible to have storage of NO\textsubscript{2} directly into nitrates, without NO formation, as shown in Equation 6 [3,17]. It is also reported in literature that NO can be stored into nitrites as described in Equation 4 [16].

\[
2 \text{NO}_2 + \text{BaO} + \frac{1}{2} \text{O}_2 \rightarrow \text{Ba(NO}_3)_2 \quad \text{(Eq. 3)}
\]

\[
2 \text{NO} + \text{BaO} + \frac{1}{2} \text{O}_2 \rightarrow \text{Ba(NO}_2)_2 \quad \text{(Eq. 4)}
\]

Ba(NO\textsubscript{2})\textsubscript{2} formed in Equation 4 can further be oxidized to form nitrates by reaction with NO\textsubscript{2} [3, 17]:

\[
\text{Ba(NO}_2)_2 + 2 \text{NO}_2 \rightarrow \text{Ba(NO}_3)_2 + 2 \text{NO} \quad \text{(Eq. 5)}
\]

Epling et al. described the NO\textsubscript{x} storage process divided into three stages [12], these are shown in Figure 4. First there is complete NO\textsubscript{x} storage. Secondly one can see rapid NO\textsubscript{x} uptake and an increase in the NO\textsubscript{x} output signal. Finally there is a slow but measurable NO\textsubscript{x} uptake. This rate does not quickly reach zero. Epling et al. mention that these stages can be associated with multiple storage sites involved in the storage. Depending on experimental conditions Ba will be present as BaO, Ba(OH)\textsubscript{2} and BaCO\textsubscript{3}. Equations 2, 3 and 4 can take place on Ba(OH)\textsubscript{2} and BaCO\textsubscript{3} as well, resulting in H\textsubscript{2}O and CO\textsubscript{2} formation respectively. In literature differences in reactivity are described for these components, specifically BaO > Ba(OH)\textsubscript{2} > BaCO\textsubscript{3} [5]. Mahzoul et al. [2] described a difference in Ba sites with respect to their geometry. They argue that Ba sites close to Pt, where NO is oxidized, are able to store oxidized NO\textsubscript{x}, whereas Ba sites further away from the oxidizing Pt sites are less reactive towards storage. Besides the different Ba sites, also a difference in BaCO\textsubscript{3} sites is described in literature. Recent work of Piacentini et al. [10,11] shows that two BaCO\textsubscript{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 connected to this TPD signal, are called Low Temperature BaCO\textsubscript{3} sites (LT), which are finely dispersed particles of BaCO\textsubscript{3} on the γ-Al\textsubscript{2}O\textsubscript{3} surface. These particles are amorphous and can therefore not be detected via X-ray diffraction (XRD). A second peak was observed at 1000 °C, which they denote as High Temperature BaCO\textsubscript{3} sites (HT). These sites are bulky like sites or clusters that are crystalline and can hence be detected via XRD measurements. This provides the possibility to discriminate between the different sites that participate in the storage process. Chen et al. [19] deposited Ba(NO\textsubscript{3})\textsubscript{2} on Pt-γ-Al\textsubscript{2}O\textsubscript{3} and performed thermal gravimetric analysis which
Figure 5: N₂, NH₃, H₂ outlet and H₂ inlet concentrations vs. time upon H₂ addition on Pt-Ba(x)/γ-Al₂O₃ at 350 °C. Ba loading is 23 % [7].

Figure 6: a) Lean outlet concentrations of NO, NO₂, CO₂ and H₂O signal during three subsequent cycles, starting with a pretreated catalyst. Lean phase: 0.2 vol. % NO, 4 vol. % O₂ and 1 vol. % Ar, 9 h. b) Rich outlet concentrations of NOₓ, N₂, O₂ and H₂O during three subsequent cycles. Rich phase: 0.8 vol. % H₂ and 1 vol. % Ar in He, 15 h. T= 643 K. Only the first 60 min of the rich phase are shown [13].
showed three peaks: the first is observed below 100°C, which is weight loss due to physically adsorbed H₂O. 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 Ba(NO₃)₂ or HT sites.

3.2.2. Rich phase

During rich operation, i.e. oxygen poor operation, the stored nitrates and nitrites are released and subsequently reduced on Pt to N₂ [12]. Several reducing agents are used in literature, such as CO, C₃H₆ and H₂; all of them are present in real life exhaust gases. In this research H₂ is chosen to be the reducing agent. The reactions towards N₂ production that can take place are depicted in Equations 6 and 7.

\[ \text{Ba(NO}_3\text{)}_2 + 5 \text{H}_2 \xrightarrow{\mu} \text{Ba(OH)}_2 + \text{N}_2 + 4 \text{H}_2\text{O} \quad \text{(Eq. 6)} \]
\[ \text{Ba(NO}_2\text{)}_2 + 3 \text{H}_2 \xrightarrow{\mu} \text{Ba(OH)}_2 + \text{N}_2 + 2 \text{H}_2\text{O} \quad \text{(Eq. 7)} \]

The N₂ production is observed immediately after switching to rich conditions (Figure 5). Besides N₂ formation, NOₓ release is observed during the rich phase [5,14]. The amount of NO released however, is quite small. Castoldi et al. observed during NOₓ release and reduction, at lower temperatures up to 300°C, NH₃ production [7]. NH₃ production takes place via Equation 8.

\[ \text{Ba(NO}_3\text{)}_2 + 8 \text{H}_2 \xrightarrow{\mu} 2 \text{NH}_3 + \text{Ba(OH)}_2 + 4 \text{H}_2\text{O} \quad \text{(Eq. 8)} \]

NH₃ production is only observed after N₂ production has decreased to zero (Figure 5). With H₂ as the reducing agent, the NOₓ reduction is highly selective towards N₂ production [5]. This selectivity can be calculated as presented in Equation 9, the reduction efficiency.

\[
\text{Reduction efficiency} = \frac{2 \times [\text{N}_2]}{2 \times [\text{N}_2] + [\text{NO}_x] + [\text{NH}_3]} 
\quad \text{(Eq. 9)}
\]

3.2.3. Catalyst activity

Recent work has been done on lean/rich cycling in the order of hours [13]. Figure 6 represents the experiments performed in this work. The first lean phase shows NO breakthrough after 14.1 min. NO₂ evolves after 16.5 min and shows a maximum after breakthrough. This indicates a change in the NO oxidation efficiency in time during NOₓ storage. During the corresponding rich cycle, not all of the Ba that has participated in the storage was regenerated (Table 1), even after a 15 hrs rich phase. The subsequent lean phase shows an increase in breakthrough time for NO and NO₂. During rich again not all of the Ba sites were regenerated. In addition an increase in NH₃ production was observed indicating that the selectivity towards N₂ production decreased. The lean phase of the third cycle shows a decrease in breakthrough timing for NO and NO₂. The Ba participation is 60%. The decrease in NO oxidation efficiency and incomplete regeneration of
Table 1: Barium utilization for lean and rich phases. Lean phase: 0.2 vol. % NO, 4 vol. % O<sub>2</sub> and 1 vol. % Ar in He, 9 hrs. Rich phase: 0.8 vol. % H<sub>2</sub> and 1 vol. % Ar in He, 15 hrs. T=643 K. Pretreated catalyst was used. See also Figure 6 [13].

<table>
<thead>
<tr>
<th>Cycle no</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean phase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Ba active</td>
<td>93</td>
<td>71</td>
<td>60</td>
</tr>
<tr>
<td>% Ba active as BaO</td>
<td>6</td>
<td>37</td>
<td>36</td>
</tr>
<tr>
<td>% Ba active as Ba(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>11</td>
<td>26</td>
<td>24</td>
</tr>
<tr>
<td>% Ba active as BaCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>76</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>Rich phase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Ba reduced</td>
<td>79</td>
<td>60</td>
<td>59</td>
</tr>
</tbody>
</table>

stored NO<sub>x</sub> during rich phase operations were also observed when performing the same experiment at different temperatures. These observations could be due to masking of Pt sites by barium. During the NO<sub>x</sub> storage, Ba(NO<sub>3</sub>)<sub>2</sub> is formed which has twice the molar volume of BaCO<sub>3</sub> resulting in coverage of Pt sites or blocking of catalyst pores. Therefore the BET surface area and Pt dispersion were measured (Table 2), which both showed a large decrease compared to a pretreated catalyst. According to these observations, Pt is essential for NO oxidation/reduction as well as for Ba(NO<sub>3</sub>)<sub>2</sub> decomposition [4,13]

Table 2: BET surface area, pore volume and Pt dispersion. 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 [13].

| Pretreated catalyst | 70 | 0.22 | 20 |
| After lean phase | 43 | 0.15 | 11 |
| After rich phase | 45 | 0.18 | 11 |

3.2.4. Influence of CO<sub>2</sub>

Although CO<sub>2</sub> is present in real exhaust gas, not much research has been done on the influence of CO<sub>2</sub> on the NO<sub>x</sub> storage reduction mechanism. CO<sub>2</sub> has a negative effect on the amount of NO<sub>x</sub> stored [5,6,12]. Lietti et al. found that this negative effect is most significant at low temperatures [6]. Epling et al. however, found that CO<sub>2</sub> has a large inhibiting effect at especially high temperatures [15]. Further Epling et al. found, although CO<sub>2</sub> significantly influences the initial interval of NO<sub>x</sub> trapping, CO<sub>2</sub> has a smaller influence on the capture efficiency after NO<sub>x</sub> starts breaking through. The significant decrease of NO<sub>x</sub> storage in the presence of CO<sub>2</sub> suggests there is a competitive storage between NO<sub>x</sub> and CO<sub>2</sub> [3,22]. Rodrigues et al. concluded furthermore, that the well dispersed BaCO<sub>3</sub> sites form probably the NO<sub>x</sub> trapping sites [22].

By introducing CO<sub>2</sub> to the helium flow a significant increase in the NO<sub>x</sub> release rate is observed [14]. This observation has also been made by Amberntsson et al. who explained this on thermodynamic grounds [20]. For the reduction, with H<sub>2</sub>, CO<sub>2</sub> has only an inhibiting effect on the reduction towards N<sub>2</sub> at higher temperatures [5,15]. Furthermore, Lietti et al. [5] found that during reduction with H<sub>2</sub> the Ba sites are transformed into BaO and Ba(OH)<sub>2</sub>, while in the
presence of CO\textsubscript{2} all the Ba sites are transformed into BaCO\textsubscript{3}. With the introduction of CO\textsubscript{2} in the rich phase the reversed water gas shift reaction will take place as described in Equation 10 [12].

$$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \text{(Eq. 10)}$$

3.3. Project outline

This study is part of a major STW Ph.D. project entitled: “A model-based controller for diesel and lean burn engines, to optimize both emissions and fuel consumption.”

In order to come up with a proper model, a detailed understanding of the kinetics taking place is important. The kinetic model should be able to describe the lean/rich cycling operation. This should be able to predict the lean/rich switching times needed to have optimal storage and reduction conversions. Experimental data with different conditions are of course required to verify the described kinetic model.

As described in section 3.2.3. Catalyst activity, the catalyst performance changes at lean/rich cycling of 9 and 15 hrs respectively. With shorter cycling times it could well be that these changes are not achieved. Therefore, lean/rich cycling experiments in the order of minutes will be discussed to trace if this change can also be observed when there is a much shorter lean/rich exposure.

1. Investigation of catalyst activity at lean/rich cycling times in the order of minutes.

In the automotive exhaust CO\textsubscript{2} is present in a large quantity. Therefore, it is useful to investigate the influence it has on the storage and reduction process of the NSR catalyst. Attention will be given to the activity change of the catalyst, since it changes when no CO\textsubscript{2} is present.

2. Investigation of catalyst activity at lean/rich cycling times in the order of hours, with CO\textsubscript{2} in lean and rich feed.

These experiments will be performed at different temperatures and lean/rich timing.
Figure 7: Schematic overview of the reactor set-up.
4. Experimental set-up

The experimental data are obtained by performing feed cycling experiments with a lean (oxygen rich) and rich feed (fuel rich) over a catalytic fixed bed. The experimental set-up consists of a reactor system with two different feed lines and an analysis section. A schematic overview is shown in Figure 7.

4.1. Feed section

The inlet consists of two separate feed lines, depicted in Figure 7 as feed 1 and 2. The composition of feed 1 and 2 represent the composition of the rich and lean phase, respectively. Each feed line has its own set of mass flow controllers. In this way, two different gas compositions can be created independently. The stream which is not fed to the reactor is directed to the ventilation in order to avoid pressure changes after the feed switches, e.g. if feed 1 is led over the reactor, feed 2 is directed to the ventilation.

When switching between two reactor feeds, with different composition, the overlap between the feeds during the switch should be minimal in order to avoid mixing of feeds as much as possible. For this reason, fast magnetic valves, which open and close in a couple of milliseconds, are used for switching the feed between the reactor and the ventilation. Upon switching between feed A and B it is necessary to have as little overshoot as possible, i.e. on or of switching should result in a block shaped signal. This can be controlled by two back pressure controllers placed in the feed lines.

The feed section is provided with a pre-heater making sure the desired reactor temperature is reached. This temperature is measured with a thermocouple placed in the pre-heated section just above the reactor. Furthermore, the gas lines are heated throughout the system.

4.2. Reactor section

The reactor is a fixed bed reactor made of titanium. It has a length of 15 mm and a diameter of 14 mm. The catalyst bed consists of 1.9 g. Pt-Ba-Al$_2$O$_3$ in powder form, with a particle size of 212-250 µm, as provided by Engelhard, and is retained by two sintered plates. The reactor tube is heated by a coil wrapped around the reactor jacket. The temperature is controlled at three sections on the outside of the reactor wall. The temperature inside the catalyst bed can be monitored with three thermocouples placed in different axial positions: in the center of the reactor and 3 mm above and below the center, to check isothermal conditions. The radial temperature profiles are monitored via a thermocouple placed on the outside of the reactor wall. This thermocouple is used as input for a PID controller, which sets the reactor temperature.
4.3. Analysis section

The online measuring takes place via an ESS quadrupole mass spectrometer (MS). Capillary inlets are placed right above and below the reactor bed. In order to have an internal standard during experiments and calibration, a fixed amount of argon is fed. Furthermore, argon can be used to compensate for any intensity loss of the mass spectrometer. Appendix 2 shows how this compensation is achieved.

The gas analysis were performed on m/e 2 (H₂), 14 (N₂, NO, NO₂), 17 (NH₃), 18 (H₂O), 28 (N₂ + CO₂ + CO), 30 (NO + NO₂), 32 (O₂), 40 (Ar), 44 (CO₂) and 46 (NO₂, CO₂). For the overlap of CO₂, overlap on m/e 14, 28 and 30, corrections are performed.

4.4. Characterization methods

Besides monitoring reaction conditions and composition changes, the physical changes in the catalyst have been investigated. The following methods have been used:

- Brunauer Emmett Teller adsorption measurements. The surface area per gram catalyst can be measured, including the pore volume of the catalyst. These measurements were conducted with the use of a Micromeritics Tristar instrument, at -196 °C, with N₂ as adsorbent.
- Pt-dispersion measurements. This chemisorption is conducted at 25 °C using a Micromeritics ASAP 2000 and 2020 instrument. This measurement is conducted on pretreated catalyst samples and catalyst samples used in lean/rich cycling experiments.
- X-ray diffraction. This method is used to investigate the composition of the catalyst. The powder XRD measurements were performed on a Rigaku Geigerflex diffractometer. The spectra were recorded in the range 15° < 2θ < 75° using CU-Kα radiation.
- Thermal gravimetric analysis (TGA). Via this method desorption of the gaseous products from the surface of solids has been studied in vacuum under the desired temperature profile. The gases released are monitored by a MS. The temperature interval was set at 25-1100 °C, with a temperature ramp of 10 °C/min. The vacuum reaches a pressure up to 10⁻⁶ bar. The amount of sample required for interpretable results is 50 to 100 mg. Via this method, the temperature of desorption of certain compounds, the relative strength of the active sites and their relative amount can be measured. In this study this was done for CO₂.

4.5. Experimental conditions

4.5.1. Catalyst pretreatment

In order to be able to perform reproducible kinetic experiments, the catalyst must be conditioned properly before starting experiments. The experimental sequence performed in pre-treating the catalyst is depicted in Table 3.
Table 3: Experimental sequence for the pretreatment of the catalyst.

<table>
<thead>
<tr>
<th>Pretreatment phase</th>
<th>Conditions</th>
<th>Temp. (°C)</th>
<th>He (v%)</th>
<th>O₂ (v%)</th>
<th>H₂ (v%)</th>
<th>Duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating</td>
<td></td>
<td>25 → 500</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>Oxidation</td>
<td></td>
<td>500</td>
<td>99</td>
<td>1</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>Purge</td>
<td></td>
<td>500</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>Reduction</td>
<td></td>
<td>500</td>
<td>98</td>
<td>0</td>
<td>2</td>
<td>120</td>
</tr>
<tr>
<td>Cooling</td>
<td></td>
<td>500 → 25</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>--</td>
</tr>
</tbody>
</table>

4.5.2. Experimental procedure

As mentioned in section 3.3. Project aim, 2 different types of experiments have been conducted: Experiments with and without CO₂ in the feed. The experiments without CO₂ have been performed with lean/rich cycling in the order of minutes. Furthermore, experiments with lean/rich cycling in the order of hours and CO₂ in the feed have been conducted. The experiments with CO₂ in the feed, have been differentiated in temperature and lean/rich cycle times. Finally experiments with fast lean/rich cycling have been conducted which come close to real time operating conditions. The conditions used for these experiments are depicted in Table 4.

Table 4: Experimental sequence, with lean/rich timing and temperature.

<table>
<thead>
<tr>
<th>Lean (min)</th>
<th>Rich (min)</th>
<th>Temp. (°C)</th>
<th>CO₂</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>60</td>
<td>300</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>120</td>
<td>300</td>
<td>No</td>
</tr>
<tr>
<td>3</td>
<td>540</td>
<td>900</td>
<td>300</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>540</td>
<td>900</td>
<td>300</td>
<td>Yes</td>
</tr>
<tr>
<td>5</td>
<td>540</td>
<td>900</td>
<td>240</td>
<td>Yes</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>120</td>
<td>300</td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>50</td>
<td>300</td>
<td>Yes</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>120</td>
<td>300</td>
<td>Yes</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>900</td>
<td>300</td>
<td>Yes</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>1</td>
<td>300</td>
<td>Yes</td>
</tr>
<tr>
<td>11</td>
<td>4</td>
<td>1</td>
<td>370</td>
<td>Yes</td>
</tr>
<tr>
<td>12</td>
<td>4</td>
<td>1</td>
<td>240</td>
<td>Yes</td>
</tr>
</tbody>
</table>

The lean and rich feed concentrations expressed in v% are depicted in Table 5; He was used as carrier gas.

Table 5: Lean and rich feed concentrations in v%, used in the experiments described in Table 4.

<table>
<thead>
<tr>
<th>Lean</th>
<th>NO</th>
<th>O₂</th>
<th>H₂</th>
<th>Ar</th>
<th>(CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rich</td>
<td>0.2</td>
<td>4</td>
<td>0</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0.8</td>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure 8: Results for lean/rich cycling of 15 and 60 min respectively, without CO₂ in the feed. T=300 °C. Cycle nrs. 1, 2, 6 are shown. Lean phase: 0.2 v% NO, 4 v% O₂, 1 v% Ar. Rich phase: 0.8 v% H₂, 1 v% Ar. He as carrier gas was used.

Figure 9: Results for lean/rich cycling of 30 and 120 min respectively, without CO₂ in the feed. T=300 °C. Cycle nrs. 1, 5, 10 and 25 are shown. Lean phase: 0.2 v% NO, 4 v% O₂, 1 v% Ar. Rich phase: 0.8 v% H₂, 1 v% Ar. He as carrier gas was used.
5. Results

5.1. Activity change

Figure 8 represents the results for the experiment with lean/rich cycling of 15 and 60 min respectively, in terms of concentration in v% as a function of time in minutes. Cycles 1, 2 and 6 are shown.

From the start of the first lean phase, H₂O evolution is seen. This indicates Ba(OH)₂ participation in the storage process. After approximately 6 min CO₂ evolves. This evolution indicates participation of BaCO₃ in the storage process. A reason for this delay can be the lower reactivity towards NOₓ storage than BaO and Ba(OH)₂ [5]. Breakthrough of NO is observed after 8.5 minutes of lean operation and NO₂ evolution is observed about 1 min later. The involvement in storage of the different Ba containing species with respect to the total amount of Ba present is presented in Table 6. The Ba(OH)₂ participation is 3.1 %, BaCO₃ participation in the storage is 5.6 % and BaO participates for 6.3 %. The total amount of NOₓ that is stored corresponds to 15 % Ba utilization, on the basis of 2 moles of NOₓ being stored on 1 mole of Ba. Furthermore, in the calculations NOₓ is only stored on Ba sites.

The subsequent rich phase shows immediate N₂ production and NO release. The N₂ production almost immediately reaches a level of 0.14 v% and remains constant for about 8.5 min after which it rapidly decreases to zero. NH₃ formation is observed right after this rapid decrease of N₂. The mentioned NO desorption decreases gradually to zero. The total amount of reduced Ba(NO₃)₂ is 14.3 %. Reduction of Ba(NO₃)₂ to N₂ is 13 %, with 1 mole of N₂ corresponding to 1 mole Ba(NO₃)₂. NO release is responsible for 0.7 %, with 2 moles of NO corresponding to 1 mole Ba(NO₃)₂. The NH₃ formation corresponds to 0.6 % Ba(NO₃)₂ released. The reduction efficiency is equal to 86.7 %.

Table 6: Quantitative results, lean/rich cycling of 15 and 60 min respectively, T=300 °C and no CO₂ in the feed.

<table>
<thead>
<tr>
<th>Cycle nr.</th>
<th></th>
<th>1</th>
<th>2</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba(OH)₂ %</td>
<td>3.1</td>
<td>8.4</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>BaCO₃ %</td>
<td>5.6</td>
<td>1.4</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>BaO %</td>
<td>6.3</td>
<td>5.8</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>Ba% total</td>
<td>15</td>
<td>15.6</td>
<td>15.8</td>
<td></td>
</tr>
<tr>
<td>Breakthrough time NO (s)</td>
<td>510</td>
<td>710</td>
<td>840</td>
<td></td>
</tr>
<tr>
<td>Rich</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba% total</td>
<td>14.3</td>
<td>15.1</td>
<td>16.3</td>
<td></td>
</tr>
<tr>
<td>Ba% N₂</td>
<td>13</td>
<td>13.5</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td>Ba% NOₓ</td>
<td>0.7</td>
<td>0.7</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Ba% NH₃</td>
<td>0.6</td>
<td>0.9</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Reduction efficiency (%)</td>
<td>86.7</td>
<td>89.4</td>
<td>81.6</td>
<td></td>
</tr>
</tbody>
</table>

Switching to cycle number 2, an improvement of the catalyst’s performance in the lean phase is observed. This is represented by an increased NO breakthrough time, resulting in a higher NOₓ storage. Furthermore CO₂ breaks through later in this cycle, which is an indication that there are
less BaCO$_3$ sites available for storage. During the previous rich phase, Ba(NO$_3$)$_2$ was exchanged for Ba(OH)$_2$ and not for BaCO$_3$ because CO$_2$ was absent in the feed. With more BaCO$_3$ being exchanged for Ba(OH)$_2$ the storage increases. This is an indication for a difference in reactivity in favor of Ba(OH)$_2$. The corresponding rich phase shows that the amount of stored NO$_x$ is released and/or reduced. However, the amount of NH$_3$ that is formed is higher than for the first cycle. This indicates an unwanted loss in selectivity towards N$_2$ formation of the catalyst during rich operation. Cycle nr. 6 shows again an improvement of the catalyst’s performance in the way described for cycle 2. Moreover, the rich phase shows complete regeneration and a decrease in selectivity.

Because there is almost no CO$_2$ in the outlet signal, a switch is made towards lean/rich cycling experiments of 30 and 120 min respectively. The results are depicted in Figure 9 with concentrations in v% as a function of time in minutes. Cycles 1, 5, 10 and 25 are shown.

Starting from cycle nr. 1 we can observe immediate H$_2$O formation. After 14.3 min we can see BaCO$_3$ participating in the storage process. NO breaks through slowly at the same moment as CO$_2$, followed by NO$_2$ at approximately 14.5 min. The total amount of NO$_x$ that is stored is 25.5% (Table 7). The amount of NO$_x$ stored on Ba(OH)$_2$ sites is 13.5%, BaCO$_3$ involvement is 7.3%. The remaining 4.7% accounts for the BaO involvement. The catalyst’s performance is still improving as can be seen from the breakthrough timing of NO$_x$.

**Table 7: Quantitative results, lean/rich cycling of 30 and 120 min respectively, T=300 °C, no CO$_2$ was present in the feed.**

<table>
<thead>
<tr>
<th>Cycle nr.</th>
<th>1</th>
<th>5</th>
<th>10</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba(OH)$_2$ %</td>
<td>13.5</td>
<td>15.9</td>
<td>16.4</td>
<td>15.6</td>
</tr>
<tr>
<td>BaCO$_3$ %</td>
<td>7.3</td>
<td>1.0</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>BaO %</td>
<td>4.7</td>
<td>11.9</td>
<td>11.9</td>
<td>10.6</td>
</tr>
<tr>
<td>Ba % total</td>
<td>25.5</td>
<td>28.8</td>
<td>28.7</td>
<td>26.7</td>
</tr>
<tr>
<td>Breakthrough time (s)</td>
<td>860</td>
<td>1260</td>
<td>1260</td>
<td>1070</td>
</tr>
<tr>
<td>Rich</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba % total</td>
<td>23.9</td>
<td>27.4</td>
<td>28.2</td>
<td>27</td>
</tr>
<tr>
<td>Ba % N$_2$</td>
<td>20.5</td>
<td>20.5</td>
<td>19.8</td>
<td>17.2</td>
</tr>
<tr>
<td>Ba % NO$_x$</td>
<td>1.2</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Ba % NH$_3$</td>
<td>2.2</td>
<td>6.0</td>
<td>7.5</td>
<td>8.9</td>
</tr>
<tr>
<td>Reduction efficiency (%)</td>
<td>85.8</td>
<td>74.8</td>
<td>70.2</td>
<td>63.7</td>
</tr>
</tbody>
</table>

The subsequent rich phase shows immediate N$_2$ formation and NO release. The N$_2$ formation reaches a level of 0.14 v% and stays constant for 12.5 min, after which it rapidly decreases. The NO release decreases towards zero immediately after the start. NH$_3$ formation is again observed after the decrease in N$_2$ concentration and decline of NO. The peak is about 0.1 v% and decreases slowly towards zero. The amount of N$_2$ that is formed is 20.5%, NO$_x$ release is 1.2% and NH$_3$ accounts for 2.22% of the reduced Ba. The reduction efficiency is 85.8%.

For cycles 2-10 during lean operations, an improvement of the catalyst’s storage performance is observed, indicated by an increase in the NO breakthrough time. Moreover a decrease in BaCO$_3$ participation is observed which can be ascribed to the exchange of BaCO$_3$ for Ba(OH)$_2$. The rich phase shows similar results for N$_2$ and NH$_3$ production compared to the previous experiment,
Figure 10: XRD patterns of a fresh catalyst (A), after lean/rich cycling without CO2, ending with lean exposure (B), after lean/rich cycling with CO2, ending with lean exposure (C).

Figure 11: TG-DTG curve with TGA heating rate of 10 °C/min for thermal decomposition of Pt-Ba-γ-Al₂O₃. The TGA heating rate was set at 10 °C/min, starting from room temperature.
immediate N\textsubscript{2} formation and an increase in NH\textsubscript{3} production. The released/reduced amount is however not same as the amount stored. When observing cycle nr. 25 deterioration of storage is observed. The amount stored however, is now again completely released and reduced. The decline in storage could be due to coverage of Pt sites by Ba. The stored Ba(NO\textsubscript{3})\textsubscript{2} has twice the molar volume of BaCO\textsubscript{3}, coverage can thus be extended and blocking of catalyst pores can occur. The blocking of pores results in a decrease in pore volume and BET surface. Therefore a BET measurement was performed. The results are depicted in Table 8, where a comparison is made with a fresh pretreated catalyst. Indeed, the adsorption measurement shows a decrease in surface area and pore volume. Also, the Pt dispersion has decreased. Furthermore, an XRD measurement was performed to see which type of BaCO\textsubscript{3} sites participate in the storage process. The result is shown in Figure 10(B). Here Ba(NO\textsubscript{3})\textsubscript{2} is observed, implying that bulky sites have participated in the process which correspond to HT sites. This however, does not exclude the possibility that LT sites have participated in the storage process.

Table 8: BET, Pore volume and Pt dispersion for Pt-Ba-\textgamma-Al\textsubscript{2}O\textsubscript{3}, for a fresh catalyst, after lean exposure and after rich exposure.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>BET (m\textsuperscript{2}/g)</th>
<th>Pore volume (cm\textsuperscript{3}/g)</th>
<th>Pt – dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreated catalyst</td>
<td>74</td>
<td>0.22</td>
<td>20</td>
</tr>
<tr>
<td>Without CO\textsubscript{2}, after lean</td>
<td>42</td>
<td>0.16</td>
<td>11</td>
</tr>
<tr>
<td>Without CO\textsubscript{2}, after rich</td>
<td>47</td>
<td>0.18</td>
<td>11</td>
</tr>
</tbody>
</table>

5.2. Characterization of BaCO\textsubscript{3}

In order to quantify the BaCO\textsubscript{3} sites present in the catalyst sample, a TG/DTG experiment has been performed on a fresh sample. The TGA heating rate was set at 10 °C/min. The results are shown in Figure 11, with weight loss % as a function of temperature in degrees Celsius. The TGA analysis shows 4 peaks. The first peak is observed at 100 °C and can be ascribed to H\textsubscript{2}O desorbing from the catalyst. The catalyst has been exposed to air for a long time resulting in the presence of H\textsubscript{2}O. The second peak starts at approximately 600 °C and ends at 800 °C. It corresponds to findings of Piacentini et al. [10] who also found a CO\textsubscript{2} peak at this temperature and denounced it LT sites. Next a sharp peak is observed at 800 °C. The BaCO\textsubscript{3} sites that correspond with this peak are most probably also LT sites. Piacentini et al. describe BaO sites that can be converted into BaCO\textsubscript{3} when exposed to air for a considerable amount of time. They mention that the second peak can be ascribed to these sites. In this case, the catalyst has been exposed to air for several years. Thus these sites can probably be ascribed to what has been reported by Piacentini. Finally a peak is observed at 1000 °C and corresponds to the results obtained by Piacentini for the HT sites. The data of the MS show peaks at the same temperatures as for the weight loss as can be observed in Figure 12, indicating that indeed the CO\textsubscript{2} evolves from the catalytic surface at the discussed temperatures. Next calculations have been performed to obtain quantitative data of the different BaCO\textsubscript{3} species. Represents the simulated data from which the relative amounts of LT and HT sites have been calculated. These calculations show that the 30 % of the BaCO\textsubscript{3} sites are LT and 70 % are HT.
Figure 12: Results for CO$_2$ desorption and weight loss. TGA heating rate of 10 °C/min

Figure 13: Experimental results for lean/rich cycling of 9 and 15 hrs respectively for cycles 1, 2 and 3. Performed at T=370°C, lean phase: 0.2 v% NO, 4 v% O$_2$, 10 v% CO$_2$, 1 v% Ar. Rich phase: 0.8 v% H$_2$, 10 v% CO$_2$, 1 v% Ar. He used as carrier gas.
5.3. Experiments with CO$_2$

5.3.1. Activity change

Figure 13 represents the results for the 9/15 hrs. lean/rich cycling experiment performed at 370°C, with the concentration in v% as a function of time in minutes the quantitative results are depicted in Table 9.

**Table 9: Quantitative results for lean/rich cycling of 9 and 15 hrs respectively at T=370°C with CO$_2$ in lean and rich.**

<table>
<thead>
<tr>
<th>Cycle nr:</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba% stored</td>
<td>24.9</td>
<td>27.7</td>
<td>27.8</td>
</tr>
<tr>
<td>Ba(OH)$_2$ %</td>
<td>9.1</td>
<td>15.8</td>
<td>16.3</td>
</tr>
<tr>
<td>Breakthrough time (s)</td>
<td>395</td>
<td>395</td>
<td>385</td>
</tr>
<tr>
<td>Rich</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba% reduced</td>
<td>23.4</td>
<td>25.1</td>
<td>25.8</td>
</tr>
<tr>
<td>Ba% N$_2$ based</td>
<td>19.4</td>
<td>15.7</td>
<td>16.1</td>
</tr>
<tr>
<td>Ba% NO$_x$ based</td>
<td>4</td>
<td>9.3</td>
<td>9.6</td>
</tr>
<tr>
<td>Ba% NH$_3$ based</td>
<td>0.003</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Reduction efficiency</td>
<td>82.9</td>
<td>62.5</td>
<td>62.5</td>
</tr>
</tbody>
</table>

Cycle nr. 1 shows immediate H$_2$O formation during lean operation, indicating Ba(OH)$_2$ participation. This participation is 8.8 %. NO breaks through after 390 s. The NO signal shows a maximum after approximately 15 min. NO$_2$ breaks through after approximately 540 s. BaCO$_3$ also participates in the storage process, because CO$_2$ formation is observed. However, this is not shown in the figure due to the excess CO$_2$ present. The total amount of NO$_x$ stored is approximately 25 %. Ba(OH)$_2$ participates for 9.1 % in the NO$_x$ storage.

Switching to the rich phase immediate N$_2$ formation and NO release are observed. The N$_2$ production reaches a constant level of 0.14 v% and remains constant for 6.3 min.. The NO release shows an increase towards a plateau. The NH$_3$ formation is very small, almost zero. CO formation is also observed due to the discussed reversed water gas shift reaction, (Equation 10). CO concentration reaches a level of 0.4 v%. Both CO and NH$_3$ are observed after N$_2$ and NO decline. The total amount of reduced Ba(NO$_x$)$_2$ is 23.4 %, with N$_2$ formation responsible for 19.4 %, NO release for 4 % and NH$_3$ almost 0. The reduction efficiency is 82 %.

The second lean phase shows similar results as for the first cycle. However, the amount of NO$_x$ stored is slightly higher and reaches about 28 %. The corresponding rich phase shows no differences compared to the first cycle. Approximately all of the stored NO$_x$ is again released and/or reduced. The N- mass balance is closed within 5 %. The third cycle is a repetition of the second cycle. The NO$_x$ storage is equal in amount and breakthrough timing, again 28 % storage is observed. The NO and NO$_2$ signal obey NO oxidation behavior at the end of the lean phase. Moreover, the corresponding rich phase shows the same results as well.
Figure 14: Lean/rich cycling of 9 and 15 hrs respectively. At: 370, 300 and 240 °C. Lean phase: 0.2 v% NO, 4 v% O₂, 10 v% CO₂ and 1 v% Ar. Rich phase: 0.8 v% H₂, 10 v% CO₂ and 1 v% Ar. He as carrier gas.

Figure 15: Lean/rich cycling of 9 and 15 hrs respectively. At: 370, 300 and 240 °C. Lean phase: 0.2 v% NO, 4 v% O₂, 10 v% CO₂ and 1 v% Ar. Rich phase: 0.8 v% H₂, 10 v% CO₂ and 1 v% Ar. He as carrier gas.
Thus with CO\(_2\) in the feed and at high temperature, about 30% storage is observed and no activity or selectivity change takes place. To support these observations, the physical properties of the catalyst have been measured. The results are depicted in Table 10, where the BET surface area, pore volume and Pt dispersions are depicted. It is shown that the BET surface has barely changed compared to the fresh catalyst. In addition the Pt dispersion has remained the same. The XRD spectrum in Figure 10(B) shows the results for the catalyst after a lean phase. There is no Ba(NO\(_3\))\(_2\) observed, while storage has taken place. This implies that almost no bulk sites have participated in the storage process. Furthermore, the TGA showed a value of 40 % for the LT BaCO\(_3\) sites. With a storage of 30 % it is possible that only LT sites have participated.

**Table 10: BET surface area, pore volume and Pt dispersion**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>BET (m(^2)/g)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Pt – dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreated catalyst</td>
<td>74</td>
<td>0.22</td>
<td>20</td>
</tr>
<tr>
<td>With CO(_2) after lean</td>
<td>70</td>
<td>0.23</td>
<td>20</td>
</tr>
<tr>
<td>With CO(_2) after rich</td>
<td>70</td>
<td>0.22</td>
<td>20</td>
</tr>
</tbody>
</table>

5.2.2. Influence of temperature

For the study on the temperature influence, the cyclic steady states of three different temperatures are observed. The results are depicted in Figure 14 with the concentration in v% as a function of time in min. The quantitative data obtained from these experiments are depicted in Table 11.

**Table 11: Quantitative results at 240, 300 and 370 °C. Lean/rich cycling of 9 and 15 hrs respectively.**

<table>
<thead>
<tr>
<th>Temperature (°C):</th>
<th>Lean</th>
<th>370</th>
<th>300</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba% stored</td>
<td>27.8</td>
<td>27.5</td>
<td>29.1</td>
<td></td>
</tr>
<tr>
<td>Ba(OH)(_2) %</td>
<td>16.3</td>
<td>11.3</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>Breakthrough time (s)</td>
<td>385</td>
<td>380</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Rich</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba% reduced</td>
<td>25.8</td>
<td>26.9</td>
<td>34.3</td>
<td></td>
</tr>
<tr>
<td>Ba% N(_2) based</td>
<td>16.1</td>
<td>21.0</td>
<td>20.4</td>
<td></td>
</tr>
<tr>
<td>Ba% NO(_x) based</td>
<td>9.6</td>
<td>2.4</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Ba% NH(_3) based</td>
<td>0.1</td>
<td>3.5</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td>Reduction efficiency</td>
<td>62.5</td>
<td>78%</td>
<td>59.5%</td>
<td></td>
</tr>
</tbody>
</table>

When comparing the lean phases, the differences lie in the NO end level and the breakthrough timing. With higher temperature the overshoot in the NO signal becomes higher. The change in steepness of the NO\(_2\) signal can have something to do with Ba(NO\(_2\))\(_2\) to Ba(NO\(_3\))\(_2\) oxidation (Equation 5). This phenomenon will be elaborated on in section 6. The total NO\(_x\) storage for all three temperatures has been depicted in Figure 13. Here, NO\(_x\) storage amounts are approximately the same for all three experiments.
Figure 16A: Lean operation at 300°C at different rich timing. 30/120 (r), 30/50 (black), 30/120+1.2v%H₂ (g), 30min/15hrs (blue). Lean phase: 0.2 v% NO, 4 v% O₂, 10 v% CO₂ and 1 v% Ar.

Figure 16B: Rich operation at 300°C: 0.8 v% H₂ (and 1.2v%), 10 v% CO₂ and 1 v% Ar.
However, the rich phase shows more dissimilarity. The NO desorption at 370°C is much higher than for the lower temperatures. In addition at lower temperatures NH₃ formation is observed with an increase in the amount as the temperature decreases. This is an indication that at lower temperatures the selectivity of the catalyst towards N₂ production goes down, as represented by the reduction efficiency. However, the activity of the catalyst stays the same. Overall one can state that the temperature influences can be found in the way storage and reduction are achieved and not in the amount of NOₓ that can be stored. The evidence is provided in Table 11. Furthermore, figure 15 shows NOₓ profiles for all three experiments. The surface area above the NOₓ signal and below 0.2 v%, which is the inlet concentration, represents the storage. This area is approximately the same for all three experiments. Only the 370 °C shows a small deviation.

5.2.3. Influence of Rich timing

Figure 16 shows the results for the experiments conducted to study the influence of rich timing on the NOₓ storage behavior. For this experiment a reference experiment is used with lean/rich cycling of 30 and 120 min respectively. For all experiments the cyclic steady state was reached.

First lean/rich cycling was set at 30/50 minutes. Comparison of the lean phase shows differences in the NO breakthrough time. The total amount of NOₓ that is stored corresponds to about 14 %Ba participation. The NO and NO₂ end levels are approximately the same compared to the reference experiment. H₂O is observed from the start indicating Ba(OH)₂ participation. The amount is the same for all experiments. The rich phase itself shows a change in N₂ formation time.

Next the lean/rich cycling experiment of 30 and 120 min respectively was started with the rich conditions changed to 1.2v% H₂. Here H₂O formation is observed from the start at a slightly higher level during lean operation. This can be ascribed to the fact that because of the higher H₂ concentration more Ba(OH)₂ has been formed during rich operation. NOₓ storage has again changed by a decrease in breakthrough time. The total amount stored however, is about 14 %. The rich phase shows a shorter N₂ production time, caused by the higher H₂ concentration; more H₂ means more sites that can react simultaneously. An equal amount of NOₓ has been stored but is reduced in a shorter period of time causing the N₂ level to rise. NO desorption and NH₃ formation show the same deviations as were observed with the N₂ signal.

Finally the lean/rich cycling was set at 30 min and 15 hours respectively. Similar results can be expected as for the previous experiment. A long rich phase with a certain amount of H₂ should have the same effect as a short time in which a much larger amount of H₂ is fed. However, this is not the case. H₂O evolves again from the start but the amount that is produced corresponds to the reference experiment. Furthermore, there are no changes in lean behavior except for earlier breakthrough of NO. When we switch to the rich phase, all of the stored NOₓ is reduced as was the case with the previous experiments. NO desorption, NH₃ formation and N₂ formation show similar changes compared to the reference experiment as the previous discussed experiments.
Figure 17: Transient lean/rich cycling of 4 and 1 min respectively, at T=300 °C. Lean phase: 0.2 v% NO, 4 v% O₂, 10 v% CO₂ and 1 v% Ar. Rich phase: 0.8 v% H₂, 10 v% CO₂ and 1 v% Ar. He was used as carrier gas.
5.2.4. Transient experiments

With lean/rich cycling of 4 and 1 min respectively, we can approach real life application. The results for this experiment are shown in Figure 15, with the concentration in v% as a function of time in minutes.

Observing cycles 1-4, one can see that during the first cycle, complete NO\textsubscript{x} storage is obtained. During the following rich phase, immediate N\textsubscript{2} production is observed, at a level of 0.13 v%. One minute rich time is too short to release/reduce all of the stored NO\textsubscript{x}. This leads to an accumulation of Ba(NO\textsubscript{3})\textsubscript{2}. Furthermore there is no NH\textsubscript{3} formation. Cycle nr. 2 shows NO breakthrough at the end of the 4 min lean phase, NO\textsubscript{2} still shows no breakthrough which is in correspondence with the results for longer switching times. Because there NO\textsubscript{2} was breaking through later than NO, as is happening with this experiment. The rich phase shows again immediate N\textsubscript{2} formation with a small increase in concentration. The following cycles show similar behavior, apart from the NO which breaks through earlier.

Next cycles 15-18 are plotted. The NO breakthrough time has reached a steady point. The concentration at the end of the lean phase has reached a higher level. Furthermore NO\textsubscript{2} has started to break through during the lean phase. The N\textsubscript{2} levels in the rich phases are approximately of the same level. Observing cycle nr. 27-30, a decrease in NO end level is observed. For the experiments performed at lean/rich cycling of 9 and 15 hrs respectively, a maximum for NO was observed. The red dotted line shows that the NO level also reaches a maximum in this short switching experiment. Overall it is shown that the characteristics of the long switching experiments are observed in the short switching experiments as well, i.e. a maximum for NO, NO\textsubscript{2} breakthrough later than NO and immediate N\textsubscript{2} production.
Figure 18: Lean profile for NO and NO$_2$, performed at 370 $^\circ$C, 9 hrs. With 0.2 v% NO, 4 v% O$_2$, 10 v% CO$_2$, 1 v% Ar. The blue line represents NO concentration in case of DPM.

Figure 19: Ratio H$_2$O : N$_2$ in the rich phase with 0.8 v% H$_2$, 10 v% CO$_2$ and 1 v% Ar. He was used as carrier gas.
6. Discussion

6.1. Lean characteristics.

As mentioned in section 3.2, several routes can be distinguished towards NO\textsubscript{x} storage. The generally most used is the disproportionation mechanism (DPM) [4,5,12], resulting in storage through NO\textsubscript{2} only. If it is considered that during the discussed experiments, only the DPM is taking place, a calculation can be made what the amount of NO should be. Consider the experiment at 370 °C with lean/rich cycling of 9 and 15 hrs respectively. The lean phase is depicted in Figure 18. The NO oxidation (Equation 1) precedes the DPM and is assumed to set in rapidly. Furthermore, at the end of the 9 hrs lean phase, the storage has “stopped” and only the NO oxidation takes place. The concentrations for NO and NO\textsubscript{2} observed there would be observed throughout the 9 hrs lean phase, if NO oxidation was the only reaction taking place. The DPM is described in Equation 2 and shows for 3 moles of NO\textsubscript{2} stored, 1 mole of NO is formed. The blue line in Figure 17 shows the result for 9 hrs lean operation with only DPM occurring. The NO concentration is calculated with the mentioned assumptions as follows:

\[
\text{NO}_{\text{DPM}} = C_{\text{NO,ox}} + \left(\frac{(C_{\text{NO,ox}} - C_{\text{NO}}(t))}{3}\right)
\]  
(Eq. 11)

As can be observed in Figure 17, the NO concentrations of the DPM case and the experimental results differ. After all, no dead time for NO is observed when DPM takes place. This shows that DPM is not the only mechanism that is involved in the NO\textsubscript{x} storage. However, the DPM can be responsible for early sorption times. This is described by Epling et al. [12]. They state that it is possible for released NO to be captured downstream in the reactor bed to be oxidized to NO\textsubscript{2} and subsequently be stored. Moreover, NO\textsubscript{2} can also be stored directly without the formation of NO into Ba(NO\textsubscript{3})\textsubscript{2} as described in Equation 3. This can then explain why no NO is observed during storage of NO\textsubscript{2}. Another eligible explanation for the dead time of NO, is the nitrite route (Equation 4) by which NO is stored directly on Ba sites to form Ba(NO\textsubscript{2})\textsubscript{2}. This leads to another observation made in previous sections, that a maximum in the NO signal can be detected. With the nitrite route, per mole Ba(NO\textsubscript{2})\textsubscript{2} oxidized to Ba(NO\textsubscript{3})\textsubscript{2}, 2 mole NO is formed. The maximum in the NO signal (Figure 18) corresponds to a gradient change in the NO\textsubscript{2} signal. During the maximum, the NO\textsubscript{2} breaks through quite rapidly, implying less NO\textsubscript{2} is used for storage. This is an indication that Ba(NO\textsubscript{2})\textsubscript{2} have been oxidized to Ba(NO\textsubscript{3})\textsubscript{2}.

6.2. Rich characteristics

In the results different components have been discussed during rich operation. In addition H\textsubscript{2}O and O\textsubscript{2} can be examined. H\textsubscript{2}O, O\textsubscript{2} have in common that they show a dead time or very low value during the first 30-50 seconds of the rich operation. If we look at the release mechanism more closely, we can describe it as depicted in Equations 13 to 16.

\[
\text{Bar(Y)}_2 + \text{H}_2 + \text{CO}_2 \rightarrow \text{BarCO}_3 + 2 \text{N} + \text{O}_2 + \text{H}_2 \text{O} \quad (\text{R-eq. 12})
\]
\[
\text{Bar(Y)}_2 + \text{H}_2 + \text{CO}_2 \rightarrow \text{BarCO}_3 + 2 \text{NO} + \text{H}_2 \text{O} \quad (\text{R-eq. 13})
\]
\[
\text{Bar(Y)}_2 + \text{H}_2 + \text{CO}_2 \rightarrow \text{BarCO}_3 + 2 \text{NO} + \text{H}_2 \text{O} \quad (\text{R-eq. 14})
\]
\[
2 \text{NO} + 2 \text{H}_2 \rightarrow \text{N}_2 + 2 \text{H}_2 \text{O} \quad (\text{R-eq. 15})
\]
During the first 30 to 50 s, O$_2$ and H$_2$O show a dead time. After this period, O$_2$ and H$_2$O increase to a constant value of 0.02 v% and 0.8 v% respectively. The delay in H$_2$O evolution can be due to adsorption on Ba sites resulting in Ba(OH)$_2$. Lietti et al. [5] described this phenomenon. They describe that the 50 s dead time corresponded to desorption of CO$_2$, in which case BaCO$_3$ is exchanged for Ba(OH)$_2$. Furthermore, it is possible for H$_2$O to adsorb on $\gamma$-Al$_2$O$_3$. The delay in O$_2$ evolution can be explained with adsorption of O$_2$ on Pt sites. If O$_2$ is assumed to evolve from the start with a constant value of 0.02 v%, calculations can be made on the amount of Pt sites involved. Furthermore the assumption is made that O$_2$ is bridged on two Pt sites. The Pt dispersion must also be taken into account to perform calculations on the available Pt sites. The calculation is depicted in Appendix 3. The Pt participation is about 40%. Apparently this leaves enough sites to perform reduction of NO$_2$ ad NO to N$_2$. However, for a short period of time.

In the rich phase evidence on what species are formed ultimately in the lean phase, Ba(NO$_2$)$_2$ or Ba(NO$_3$)$_2$, can be found. If we consider the overall reaction towards N$_2$ production from nitrates then for each mole of N$_2$ produced, 5 moles of H$_2$O are produced (R-eq. 15).

$$
\text{Ba(NO})_3 + 5 \text{H}_2 + \text{CO}_2 \xrightarrow{\text{Pt}} \text{BaCO}_3 + \text{N}_2 + 5 \text{H}_2\text{O} \quad (\text{R-eq. 15})
$$

$$
\text{Ba(NO})_2 + 3 \text{H}_2 + \text{CO}_2 \xrightarrow{\text{Pt}} \text{BaCO}_3 + \text{N}_2 + 3 \text{H}_2\text{O} \quad (\text{R-eq. 16})
$$

If we consider nitrite release/reduction, the mole ratio of N$_2$:H$_2$O is 1:3. In figure 18 the N$_2$ and H$_2$O concentrations in v% are plotted as a function of time (s). The figure shows a N$_2$/H$_2$O ratio 1:5. This is in correspondence with nitrate release/reduction. Therefore, we can state that at the end of the lean phase the catalyst overall consists of Ba(NO$_3$)$_2$.

Finally there have been observations during rich operation of NH$_3$ (Equation 8) and CO formation (Equation 10). The production of these components takes place after N$_2$ production and NO desorption have declined. For the formation of NH$_3$ Ba(NO$_3$)$_2$ or Ba(NO$_2$)$_2$ is necessary as N donor. The N$_2$ production and NO release are faster reactions than NH$_3$ formation [7]. This can explain why NH$_3$ formation starts when N$_2$ and NO concentrations have declined. For CO, the reason for delay in evolution is that the amount of H$_2$ fed is completely used for reduction of Ba(NO$_3$)$_2$ into N$_2$ and release of NO.
7. Conclusions and recommendations

The activity change experiments without CO₂ lead to the following conclusions:

- Activity change can be observed even at short lean/rich cycling times in the order of minutes.
- Selectivity change can be observed.
- BET and Pt-dispersion showed changes of about 40% decrease.
- HT sites participate in the storage process.

Experimentation with CO₂ in the feed showed the following:

- No activity change is observed even after lean/rich cycling of 9 and 15 hrs respectively.
- The BET and Pt dispersion did not change compared to a fresh catalyst.
- XRD showed BaCO₃ sites, indicating no HT sites participation in the storage process. With TGA measurements indicating 40% of Ba present as LT sites, the Ba utilization of 30% is possible without the participation of HT sites.
- Temperature has influence on the NOₓ storage behavior. Breakthrough profiles are different. However, the total amount NOₓ stored seems temperature independent.
- Higher temperature leads to higher NO desorption values. NO desorption is observe from the start of the rich phase.
- Longer rich timing leads to a decrease in NO breakthrough time. This also holds for the N₂ production time.
- Transient experiments show similar results compared to long cycling experiments: For NO breakthrough a maximum is observed, NO₂ shows a delay compared to NO.

The discussion has shown that:

- The DPM is not the only mechanism taking place during storage.
- Stored nitrites have been oxidized to nitrates.
- After lean operation mostly Ba(NO₃)₂ has been formed.
- Storage of O₂ on Pt sites during rich phase operation, does not influence the release and reduction of Ba(NO₃)₂.

Overall, extensive modeling is necessary to make sure that the stated pathways towards NOₓ storage are correct. When a proper model is constructed it should then converge with the measured data. Furthermore, when the experiments must come a step closer to real life application, the incorporation of H₂O is a possibility. Some research has already been done on this subject and often in combination with CO₂.
Appendix 1: References


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Appendix 2: Argon correction

In order to compensate for intensity loss of the MS, the Argon signal was fixed to an intensity of 1.42e-9 for 1 v% of Ar in the feed. The other m/e’s were corrected for this value according to the following equation:

\[
\text{Int}(X)_{\text{cor}} = \frac{\text{IntAr(fix)}}{\text{IntAr(MS)}} \times \text{IntX(MS)}
\]

IntAr(fix) = fixed Ar intensity of 1.42e-9
IntAr(MS) = Ar intensity at \( t = t \)
IntX(MS) = intensity component X at \( t = t \)
Appendix 3

Calculation for Pt participation in possible O\(_2\) storage.

\[
C_{Pt} = \frac{w_{Pt} \cdot m_{cat} \cdot Disp_{Pt}}{M_{Pt}} \\
C_{O_2} = \frac{c_{O_2} \cdot t \cdot f}{100\%} \\
Pt\ participaction = \frac{C_{O_2} \cdot 2}{C_{Pt} \cdot m_{cat}} \cdot 100
\]

\(C_{Pt}\) = mole Pt  
\(C_{O_2}\) = concentration O\(_2\) stored in moles  
\(w_{Pt}\) = weight fraction Pt  
\(m_{cat}\) = catalyst weight in gram  
\(M_{Pt}\) = molar weight of Pt in mole/gram  
\(Disp_{Pt}\) = Pt dispersion  
\(t\) = dead time of O\(_2\)  
\(f\) = molar feed  
\(m_{cat}\) = weight fraction Pt  
\(m_{cat}\) = catalyst weight in gram  
\(M_{Pt}\) = molar weight of Pt in mole/gram  
\(Disp_{Pt}\) = Pt dispersion  
\(t\) = dead time of O\(_2\)  
\(f\) = molar feed

- \(C_{Pt}\) = mole Pt  
- \(C_{O_2}\) = concentration O\(_2\) stored in moles  
- \(w_{Pt}\) = weight fraction Pt = 0.01  
- \(m_{cat}\) = catalyst weight in gram = 1.9386 g  
- \(M_{Pt}\) = molar weight of Pt in mole/gram = 195.08 g/mole  
- \(Disp_{Pt}\) = Pt dispersion = 0.2  
- \(t\) = dead time of O\(_2\) = 30 s  
- \(f\) = molar feed = 7.43e\(^{-4}\) mole/s