Next Generation Automotive DeNOX Catalysts: Ceria What Else?

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Next Generation Automotive DeNO$_x$
Catalysts: Ceria What Else?
Next Generation Automotive DeNO$_x$ Catalysts: Ceria What Else?

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. ir. K.C.A.M. Luyben,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen op
3 november 2017 om 12:30 uur

door

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Science is a wonderful thing if one does not have to earn one’s living at it.

Albert Einstein
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Saving our planet, lifting people out of poverty, advancing economic growth... these are one and the same fight. We must connect the dots between climate change, water scarcity, energy shortages, global health, food security and women’s empowerment.

Solutions to one problem must be solutions for all.

Ban Ki-moon
This chapter gives an overview of automotive pollutant emissions reduction regulations, NO\textsubscript{x} emission strategies and challenges, the objectives, and outline of this thesis.
### 1.1. CO₂ legislation

Atmospheric carbon dioxide (CO₂) grows rapidly and is accompanying to the economic growth [1]. Cars are responsible for around 12% of total EU emissions of CO₂ [2]. Therefore, EU legislation sets mandatory CO₂ emission reduction targets for new vehicles from 2013 onwards. The average emissions level of a new car sold in 2016 was 118.1 g/km CO₂, significantly below the 2015 target of 130 g/km. By 2021, phased in from 2020 onwards, the CO₂ emission has to be lower to 95 g/km for all average new cars of the company [2], which corresponds to a fuel consumption of around 3.8 L/100 km. All these CO₂ emission standards are given under the current approved NEDC driving cycle. With the introduction of the (more realistic real driving emissions) “WLTP” driving cycle (Worldwide harmonized Light vehicles Test Cycle), CO₂ emission levels of vehicles and the related pollutant emissions (mainly NOₓ) will be significantly higher.

The legislation on CO₂ emission drives the development of increasingly more fuel efficient cars with lower fuel consumptions than those in conventional gasoline engines, *e.g.*, lean burn engines including lean-burn gasoline and diesel engine. The lean burn engine operates with excess oxygen and the presence of nitrogen at the high flame temperature will result in more NOₓ formation in the combustion chamber than with stoichiometric combustion [3]. Due to legislation all cars could have DeNOₓ technologies on board, the conversion of NOₓ under lean conditions is however much more cumbersome. Therefore, it will be anticipated that by the effective introduction of the new certification test such as WLTO or Real Driving Emissions the NOₓ emission will increase. As a consequence, the automotive industry faces enormous challenges to compromise the balance between drivability (passengers’ satisfaction), fuel efficiency (CO₂ emission), and pollutant emission legislation. Increasing fuel efficiency is a way to reduce fuel consumption of vehicles, which brings economic profits for car owners, decreases the CO₂ emission and increases energy sustainability. It should be noted that in the life time of car already 50% of the CO₂ emission is related to the production of the car. The most important way to reduce carbon dioxide emissions on the road is via the vehicle weight reduction by engine downsizing. Among others, engine downsizing can be enabled by advances in turbocharging and fuel injection. In order to deliver the same or even more required power as
engines with a large displacement for driving, engine downsizing (a smaller displacement) requires higher peak brake mean effective cylinder pressures (BMEPs) [4]. For diesel engines, aggressive downsizing tends to increase the specific load, which, in turn, increases the pollutants emission, e.g., oxides of nitrogen (NO\textsubscript{x}) [5]. In the automotive industry, the volume of after-treatment systems as rule of thumb are the same as the volume of the displacement in the engine. In other words, the smaller engines will decrease the relative contact time (or increase the gas hourly space velocity). Therefore, the introduction of CO\textsubscript{2} legislation requires an even more efficient after treatment system for the pollutants, e.g., nitrogen oxides (NO\textsubscript{x}), carbon monoxide (CO), Ozone (O\textsubscript{3}), Particulate Matter (PM).

1.2. Automotive exhaust gas pollutants emission

1.2.1. Legislated pollutants and EU emission standards

Air pollution is a problem for both environment and society since it causes a multitude of adverse effects on human health, environment, and climate [6, 7]. The air pollutant emissions from the automotive contributed significantly to the overall air quality in Europe. Emissions of PM, NO\textsubscript{x}, HCs, and CO are pollutants regulated by Euro emissions standards.

EU Emission standards specify the maximum amount pollutant that is allowed to emit from the exhaust gasses of a vehicle when it is tested under laboratory conditions or using a specific driving cycle. Table 1.1 shows the EU emission standard of the PM, NO\textsubscript{x}, HCs, and CO for a passenger car. From Euro 3 to 6, diesel engines have a lower CO emission standards while a higher NO\textsubscript{x} emission is allowed. Gasoline vehicle starts regulation on PM from Euro 5, indicating that the PM emission from the gasoline is an issue as well. From Euro 5 for a diesel engine, the PM emission standard remains the same value at 0.005 g/km. However, the emission standards on NO\textsubscript{x} dropped from 0.5 (Euro 3) to 0.08 (Euro 6) g/km. In the future, the NO\textsubscript{x} emission standard will become even more stringent.
1.2. Automotive exhaust gas pollutants emission

Table 1.1: Euro emission standards for passenger cars in g/km [8].

<table>
<thead>
<tr>
<th>Stage</th>
<th>Date</th>
<th>CO</th>
<th>HCs</th>
<th>HC$\text{S}$$+\text{NO}_x$</th>
<th>NO$_x$</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diesel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Euro 1</td>
<td>1992.07</td>
<td>2.72</td>
<td>-</td>
<td>0.97</td>
<td>-</td>
<td>0.14</td>
</tr>
<tr>
<td>Euro 2</td>
<td>1996.01</td>
<td>1.0</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>Euro 3</td>
<td>2000.01</td>
<td>0.64</td>
<td>-</td>
<td>0.56</td>
<td>0.5</td>
<td>0.05</td>
</tr>
<tr>
<td>Euro 4</td>
<td>2005.01</td>
<td>0.50</td>
<td>-</td>
<td>0.30</td>
<td>0.25</td>
<td>0.025</td>
</tr>
<tr>
<td>Euro 5</td>
<td>2009.09b</td>
<td>0.50</td>
<td>-</td>
<td>0.23</td>
<td>0.18</td>
<td>0.005</td>
</tr>
<tr>
<td>Euro 6</td>
<td>2014.09</td>
<td>0.50</td>
<td>-</td>
<td>0.17</td>
<td>0.08</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasoline</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Euro 1</td>
<td>1992.07</td>
<td>2.7</td>
<td>-</td>
<td>0.97</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Euro 2</td>
<td>1996.01</td>
<td>2.2</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Euro 3</td>
<td>2000.01</td>
<td>2.3</td>
<td>0.20</td>
<td>-</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>Euro 4</td>
<td>2005.01</td>
<td>1.0</td>
<td>0.10</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
</tr>
<tr>
<td>Euro 5</td>
<td>2009.09b</td>
<td>1.0</td>
<td>0.10</td>
<td>-</td>
<td>0.06</td>
<td>0.005</td>
</tr>
<tr>
<td>Euro 6</td>
<td>2014.09</td>
<td>1.0</td>
<td>0.10</td>
<td>-</td>
<td>0.06</td>
<td>0.005</td>
</tr>
</tbody>
</table>
1.2.2. Emission test cycles

Emission testing (verification) cycles are used to evaluate whether a type of vehicle meets the emission requirement set by the European Commission before it is allowed to be available in the market. For the light-duty vehicles, a combined chassis dynamometer test is used for emission testing and certification in Europe, including four ECE Urban Driving Cycles, simulating city driving in combination with one Extra Urban Driving Cycle (EUDC), simulating highway driving conditions [9]. This New European Driving Cycle (NEDC) was introduced in 2000 together with a cold-start test procedure [9]. This (currently approved) NEDC cycle is working under an extremely mild condition for engines, which is too unrealistic from the real driving. Therefore, a more realistic driving cycle, Common Artemis Driving Cycles (CADC), is to replace the NEDC [10]. In order to lower the NO\textsubscript{x} emission from the diesel car on the road, the RDE testing (analogous to the CADC) requirements will be introduced from September in 2017 [11].

- **ECE cycle**
  The ECE is an urban driving cycle characterising with a low vehicle speed, low engine load, and low exhaust gas temperature (Figure 1.1A).

- **EUDC cycle**
  The Extra Urban Driving Cycle has been added after the fourth ECE cycle to simulate a high-speed driving mode (Figure 1.1B). The maximum speed of the EUDC cycle is 120 km/h.

- **NEDC cycle**
  Before the emission test in EUDC cycle, the vehicle is allowed to soak for at least 6 hours at temperature of 20-30°C, and 40 s idle period is allowed. In NEDC cycle, the cold start test is added into the EUDC cycle to eliminate this idling period. This modified cold-start procedure is referred to as the New European Driving Cycle (NEDC).

- **CADC cycle**
  The Common Artemis Driving Cycles (CADC) was developed based on the European real world driving behaviour. Artemis means Assessment and Reliability of Transport Emission Models and Inventory Systems. CADC cycle contains Urban, Rural road, and Motorway driving cycles, as shown in Figure 1.2 [9].
1.2. Automotive exhaust gas pollutants emission

Figure 1.1: (A) ECE test cycle and (B) EUDC test cycle [9].

Figure 1.2: Artemis Driving Cycles: (A) urban cycle; (B) rural road cycle; and (C) motorway cycle [10].
Table 1.2: Air quality Guideline for Europe in 1987 first edition (WHO Regional Office for Europe).

<table>
<thead>
<tr>
<th></th>
<th>Time-weighted average</th>
<th>Average time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen dioxide</td>
<td>400 µg/m³</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>150 µg/m³</td>
<td>24 hours</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>100 µg/m³</td>
<td>15 minutes</td>
</tr>
<tr>
<td></td>
<td>30 µg/m³</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>10 µg/m³</td>
<td>8 hours</td>
</tr>
<tr>
<td>Ozone</td>
<td>150-200 µg/m³</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>100-1210 µg/m³</td>
<td>8 hours</td>
</tr>
<tr>
<td>Sulphur dioxide and PM</td>
<td>125 µg/m³</td>
<td>24 hours</td>
</tr>
<tr>
<td></td>
<td>50 µg/m³</td>
<td>1 year</td>
</tr>
</tbody>
</table>

Table 1.3: Air quality Guideline for Europe in 2015 (WHO Regional Office for Europe).

<table>
<thead>
<tr>
<th></th>
<th>Time-weighted average</th>
<th>Average time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen dioxide</td>
<td>200 µg/m³</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>40 µg/m³</td>
<td>24 hours</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>30 µg/m³</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>10 µg/m³</td>
<td>8 hours</td>
</tr>
<tr>
<td>Ozone</td>
<td>180 µg/m³</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>120 µg/m³</td>
<td>8 hours</td>
</tr>
<tr>
<td>PM₁₀</td>
<td>50 µg/m³</td>
<td>24 hours</td>
</tr>
<tr>
<td></td>
<td>40 µg/m³</td>
<td>1 year</td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>25 µg/m³</td>
<td>1 year</td>
</tr>
</tbody>
</table>
1.3. Air quality and NO\textsubscript{x} in particular

Since the mid-1980s the WHO Regional Office for Europe has developed standards and goals for air quality management. As shown in Table 1.2 and 1.3, the Air quality standard for CO and O\textsubscript{3} hardly changed from 1987 till now. In the 2nd edition in the year 2000, a particulate matter (PM) limit was recommended to be provided separately from SO\textsubscript{2}. Particularly, in the report of WHO Regional Office for Europe (1987), Table 1.2, the guideline for NO\textsubscript{2} 1 h and 24 h mean concentration is 400 µg/m\textsuperscript{3} and 150 µg/m\textsuperscript{3}, respectively. Moreover, this number dropped to 200 µg/m\textsuperscript{3}, and 40 µg/m\textsuperscript{3}, respectively, in the 2nd edition (2000) of WHO Regional Office for Europe and onwards. Nitrogen oxides (NO\textsubscript{x}, including NO and NO\textsubscript{2}) are a group of hazardous, toxic, and harmful gasses, which have an adverse effect on both environment and human health, \textit{e.g.}, the cause of acid rain, photochemical smog, and affecting the human respiratory system.

As shown in Figure 1.3, NO\textsubscript{x} is globally distributed over the world, especially in China, Europe, and USA [12]. A high concentration of NO\textsubscript{x} is observed in the northeast of China, as indicated by dark red colour. However, even in Europe where the NO\textsubscript{x} concentration is much lower than that in China, the level of NO\textsubscript{x} concentration in most of the EU cities is still higher than those of the safety limit [13] as shown in Figure 1.4 presenting the NO\textsubscript{x} concentration in the EU cities in 2014. Red and dark red dots indicate where the EU daily limit value (40 µg/m\textsuperscript{3}) is exceeded. Regarding the source of NO\textsubscript{x}, around 40% is reported from the on road transport, as shown in Figure 1.5 [6, 14, 15]. Therefore, the regulation on NO\textsubscript{x} emission is an efficient way to lower down the NO\textsubscript{x} concentration in the air and improve the air quality.

European legislative authorities have addressed the NO\textsubscript{x} emissions of passenger diesel vehicles by introducing NO\textsubscript{x} emissions standards from Euro 3 in 2000 with the allowed level at 0.5 g/km (Table 1.1). NO\textsubscript{x} emission regulation becomes more and more stringent from Euro 3 to Euro 6 (Table 1.1) [8]. The introduction of Euro 6 led to NO\textsubscript{x} emission at the level of 80 mg/km. In the past 14 years, NO\textsubscript{x} emission was aimed to be 80% lower. However, the real on-road emission levels were much higher than the actual allowed by the regulation [16–18]. As shown in Figure 1.6, on-road car emissions during Euro 3 (2000) were closer to 1000 mg/km. Although the
Figure 1.3: NO$_2$ pollution around the world in 2010 [12].

Figure 1.4: The annual mean NO$_2$ concentration observed in EU in 2014 [13].
1.3. Air quality and NO\textsubscript{x} in particular

Figure 1.5: NO\textsubscript{x} emission by sector in EU [14, 15].

![Bar chart showing NO\textsubscript{x} emissions by sector.]

- **Others**: 6%
- **Industry**: 16%
- **Agriculture**: 2%
- **Household**: 14%
- **Energy**: 21%
- **Traffic**: 40%

Figure 1.6: NO\textsubscript{x} emission under real driving condition (black line) and NO\textsubscript{x} emission standards for light-duty diesel vehicle (grey line), according to the Euro standards [8, 16].

![Line graph showing NO\textsubscript{x} emissions under real driving condition and standards.]

<table>
<thead>
<tr>
<th>Euro</th>
<th>NO\textsubscript{x} (mg/km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>(1000)</td>
</tr>
<tr>
<td>4</td>
<td>(500)</td>
</tr>
<tr>
<td>5</td>
<td>(800)</td>
</tr>
<tr>
<td>6</td>
<td>(800)</td>
</tr>
</tbody>
</table>

The line graph shows the decrease in NO\textsubscript{x} emissions with each Euro standard upgrade.
1. Introduction

Euro 4 emission standard (2005) set a limit of 250 mg/km for NO\textsubscript{x} diesel emissions, followed by 180 mg/km in Euro 5 (2009). However, the on-road concentrations did not change at all from 2005 to 2009, which were in the range of 800 mg/km. The real NO\textsubscript{x} emission in Euro 5 was more than four times higher than allowed. The real NO\textsubscript{x} emission in Euro 5 was only 20% lower than the actual NO\textsubscript{x} emission in Euro 3. Even in Euro 6, NO\textsubscript{x} emissions were on average 400% higher than the Euro 6 limit (sometimes even more) if measured under real driving conditions. However, the vehicles that emitted more NO\textsubscript{x} than allowed still received their type-approval and could be sold on the market because they needed only to meet the requirement under laboratory conditions only (NEDC testing protocol). Currently, the NO\textsubscript{x} emission from a diesel car is only able to pass an current approved laboratory test. Therefore, on 28\textsuperscript{th} October 2015, Member States of the European Union agreed on the application of new real driving emissions (RDE) tests to determine whether a new car model is allowed to be introduced on the market from 1\textsuperscript{st} September 2017 \cite{11}. In a first step, car manufacturers are allowed to emit 2.1 times higher NO\textsubscript{x} emission (relatively to Euro 6) for the new models from September 2017 onwards. In a second phase, only 1.5 times higher NO\textsubscript{x} emission (relatively to Euro 6) is allowed for all new models from January 2020 onwards.

1.4. Automotive NO\textsubscript{x} emission strategies

1.4.1. Engine modification

1.4.1.1. Fuel injection strategy

Fuel injection delivers the fuel into the combustion chamber of the engine. However, fuel injection strategy has significant influences on the performance of engine and pollutant emissions. High fuel injection pressures and flexible injection rate shaping can effectively reduce the pollutant formation in the engine.

In a diesel engine, the use of high fuel injection pressures (2000 bar), combined with smaller injection holes with a diameter between 120 and 150 µm, can reduce PM emissions by the formation of smaller fuel droplets and a better air-fuel mixing. Conventional fuel injection system employed a sin-
single injection for every engine stroke cycle, but in newer systems multiple injection events are applied (Figure 1.7).

For the pilot injection (pre-injection), a small amount of the fuel is injected before the main fuel injection, allowing for a smaller and more delayed main injection event and reduced NO\textsubscript{x} emissions. Moreover, for post injections, a small amount of fuel is injected after the main injection, which provides hydrocarbon supply to the exhaust stream, allowing for more efficient exhaust pollutant control technologies (discussed below in section 1.4.2.2).

1.4.1.2. EGR: Exhaust Gas Recirculation

NO\textsubscript{x} is formed during the engine combustion in a temperature above 1300 °C [20]. The main precursors for NO\textsubscript{x} formation are N\textsubscript{2} and O\textsubscript{2} from the intake air. A small fraction of N\textsubscript{2} and O\textsubscript{2} can dissociate atoms to form NO\textsubscript{x}. The amount of NO\textsubscript{x} formation is a function of combustion temperature. High compression ratios of diesel engines and excess of O\textsubscript{2} in the combustion chamber directly causes the higher NO\textsubscript{x} emissions than those from a gasoline combustion chamber. Exhaust Gas Recirculation (EGR) is an effective in-cylinder method to reduce NO\textsubscript{x} emissions from diesel engines by lowering the flame temperature and the oxygen concentration in the combustion chamber. Incorporated (even cooled) EGR into the diesel engine, some exhaust gas can be recycled to the combustion chamber. The recycled gas can act as a diluent to reduce the combustion temperatures and hence lower the NO\textsubscript{x} emissions. However, application of EGR to reduce NO\textsubscript{x} emissions (reduction of the maximum combustion temperature) will result in a less efficient combustion process and to a higher fuel consumption.
Overall, the engine modifications adapt the combustion process in the engine and will diminish the formation of hazardous emission, especially of NO\textsubscript{x} and PM. However, the engine modification, which decreases NO\textsubscript{x}, often increases the PM formation from the engine, and \textit{vice versa}. This so-called NO\textsubscript{x}-PM trade-off presents a critical challenge to diesel emission reduction strategies [21]. Euro 6 requires a significant advancement over Euro 5 on the NO\textsubscript{x} emission limit, reducing it from 0.18 g/km to 0.08 g/km. The engine modification itself will be not sufficient to meet the Euro 6 and more stringent future requirements. The introduction of Euro 6 for the lower limit of NO\textsubscript{x} requires after-treatment control technologies, such as Selective Catalytic Reduction (SCR), NO\textsubscript{x} Storage Reduction (NSR), or other after-treatment.

1.4.2. Development of after-treatment technology

A three-way catalyst (TWC) mounted in a gasoline vehicle is capable to a simultaneous removal of NO\textsubscript{x}, CO, and unburnt HCs for stoichiometric air-fuel supply. The main reactions are described as followed.

\[
\begin{align*}
CO + NO & \rightarrow CO_2 + N_2 \\
CO + O_2 & \rightarrow CO_2 \\
HC + O_2 & \rightarrow CO_2 + H_2O
\end{align*}
\]

However, it does not remove NO\textsubscript{x} in the case of diesel and lean burn gasoline engines due to the excess of O\textsubscript{2} present in the exhaust gas. Therefore, other deNO\textsubscript{x} systems need to be developed for diesel and lean-burn gasoline engines.

1.4.2.1. Selective catalytic reduction (SCR)

1.4.2.1.1 NO\textsubscript{x} reduction with NH\textsubscript{3}

Ammonia-SCR is a mature and widely commercialised technology for NO\textsubscript{x} removal from stationary sources. From 2004, SCR technology is selected for the part of the heavy-duty vehicles in the EU, Japan, and the USA to meet the NO\textsubscript{x} emission standards [22]. Instead of ammonia, an aqueous urea solution is used as reductant, which can be refilled at fuel stations. From 2015, all new model diesel passenger cars in Europe have to meet the Euro
6 legislation, which leads partially to the application of Urea-SCR in diesel passenger cars, in particular for an engine displacement capacity of 1.6L or more [23]. Passenger vehicles require their refilling of the AdBlue tank [23].

• Catalyst development

Typically, V$_2$O$_5$ catalysts supported on TiO$_2$, with different promoters (WO$_3$ and MoO$_3$), are commercially employed in monolith type catalysts. However, the strong disadvantages of the vanadium-based catalysts include the toxicity of V$_2$O$_5$ and the narrow operation temperature window (300-400°C) [24]. Therefore, much work focused on developing vanadium-free NH$_3$-SCR catalysts, with emphasis on a high deNO$_x$ efficiency and N$_2$ selectivity, excellent hydrothermal stability, and insensitivity to co-existing poisoning components in the SCR (automotive exhaust) atmosphere such as H$_2$O, SO$_2$, or HCs.

Alternative Mn-based catalyst has been developed on laboratory scale as an alternative to the vanadium catalyst [25, 26]. The Mn-based catalyst showed a broader operating temperature window (150-350°C), but is sensitive to sulfur poisoning, although the addition of CeO$_2$ or Co to the Mn-based catalyst was found to improve the SO$_2$ resistance [27]. Additionally, many efforts have also focused on the development of zeolite based catalyst. Cu-ZSM-5 and Fe-ZSM-5 have been extensively studied. They showed excellent low-temperature NH$_3$-SCR activity and a broad operation temperature window, but a limited hydrothermal stability [28].

Recently, a series of Cu-chabazite (Cu-CHA) catalysts containing eight-membered ring pores with a small pore size (0.38 × 0.38 nm) are reported and commercially approved, which showed a high NH$_3$-SCR activity, a very good N$_2$ selectivity and an excellent hydrothermal stability with great application potential in the deNO$_x$ process of diesel engines [29, 30].

• Chemical reaction

Firstly urea forms ammonia via a hydrolysis reaction, before the actual SCR reactions start. Then the ammonia will react with NO or NO$_2$ via several reactions steps. The overall reactions are described as follows [31]:

\[
\text{Standard SCR : } 4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (NO/NH_3/O_2)
\]

\[
\text{Fast SCR : } NO_2 + NO + 2NH_3 \rightarrow 2N_2 + 6H_2O \quad (NO/NH_3/NO_2)
\]
The high deNO\textsubscript{x} efficiency is related to the ‘Fast SCR” (NO/NH\textsubscript{3}/NO\textsubscript{2}, due to the presence of NO\textsubscript{2}) and the lower reduction rate to the “standard SCR” (NO/NH\textsubscript{3}/O\textsubscript{2}).

- **Issues in Urea-SCR system**

  Although NH\textsubscript{3} (or urea) was very efficient as a reducing agent, some problems still existed. The NH\textsubscript{3} adsorption on the catalyst, via the urea dosing system, is the first step achieving conversion of NO\textsubscript{x} to N\textsubscript{2}. However, NH\textsubscript{3} can desorb from the catalyst and result in the release of unreacted NH\textsubscript{3} (‘ammonia slip’) [32, 33]. The challenge of Urea-SCR control strategy is to solve the trade-off NO\textsubscript{x} conversion against ammonia slip. Major factors affecting system performance are urea input (injection and hydrolysis) and NO\textsubscript{x} concentration in the feed gas. Therefore, Urea-SCR system will perform well if under controlled and very well defined conditions, e.g., temperature and NO\textsubscript{x} concentration in the feed. Furthermore, an additional tank for storing urea makes the car bulky and heavier, resulting in additional fuel consumption and smaller car “free” space. For a truck, for 1000 L diesel fuel consumption at least 50 L of urea is required. For a passenger car, an urea tank of 10-15 L is required for an average 20.000 km interval service of the car. The actual urea consumption is closely related to the driven ambition. Additionally, the downsizing of the engine will increase the gas hourly space velocity through the catalyst bed and temperature of exhaust gas from the combustion engine (described in section 1.1). These have clearly affected the overall NO\textsubscript{x} conversion efficiency of Urea-SCR.

### 1.4.2.1.2 NO\textsubscript{x} reduction with hydrocarbons (HCs)

The unique advantage of HC-SCR is that the diesel fuel can be used as a reductant for NO\textsubscript{x} reduction, thus reducing the cost involved in infrastructure development for delivering of the urea reductants to the heavy-duty engine exhaust system. Therefore, HC-SCR of NO\textsubscript{x} will be a potential alternative to the NH\textsubscript{3}/urea-SCR.

Many catalysts, such as zeolite, base oxide/metal, and noble metal catalysts have been found to be effective for the SCR of NO\textsubscript{x} with hydrocarbons (HC-SCR) in the presence of excess oxygen. Zeolite catalysts (Cu, Fe-ZSM-5) are effective for the NO\textsubscript{x} reduction, but the water tolerances are a large hurdles
to be taken (hydrothermal stability). The small pore chabazite shows an extremely high hydrothermal stability. However, the largest pore window in the chabazite framework is an 8-ring (3.8 Å × 3.8 Å), which strongly limits the diffusion of diesel fuel molecules (even isobutane as a model component) into the structure. Cu or Fe-chabazite hardly works in HC-SCR. Noble metal based catalysts, such as Pt/Al₂O₃ and Pd/Al₂O₃, exhibit a high deNOₓ activity in a very narrow temperature range (200-300 °C), as shown in Figure 1.8 [34]. Metal oxide catalysts for the reduction of NOₓ with hydrocarbons have received an extensive attention due to their high-temperature activity and hydrothermal stability. Up to now, Ag/Al₂O₃ is one of the most promising catalysts for the HC-SCR. However, the thermal stability strongly depends on the preparation method and reaction conditions [35]. Furthermore, the poor low-temperature activity (below 300 °C) and narrow temperature window are additional challenges for these Ag/Al₂O₃ catalysts. For aromatic hydrocarbons, typically present up to 15% in diesel fuel, exhibit very low activity for the NOₓ reduction, which indicates that the issues of catalyst activity and deactivation by hydrocarbons poisoning still need to be solved for the commercial application of HC-SCR. It should be noted that HC-SCR will increase the overall fuel consumption and, as a consequence, increase the CO₂ emissions.

1.4.2.2. NOₓ storage reduction (NSR)

NOₓ Storage and Reduction (NSR) system, developed by Toyota researchers, is regarded as the leading technology to control NOₓ emission under lean-burn conditions. The engine is continuously operating under the excess of oxygen (lean) conditions. Short hydrocarbon pulses are periodically injected into the engine to create short periods with reducing (rich) conditions. NSR catalysts comprise of precious metals, NOₓ storage components, and support metal oxides. Pt/BaO/Al₂O₃ and Rh/BaO/Al₂O₃ are the most commonly applied NSR catalysts. Figure 1.9 schematically illustrates the generally accepted mechanisms of NOₓ storage/reduction in the Pt/BaO/Al₂O₃ catalyst. Under lean conditions, NOₓ is trapped in the storage components of the NSR catalyst and subsequently reduced by reductants (CO, H₂, hydrocarbons) under fuel rich conditions [36]. The following five steps can describe the NSR system operation during the lean-rich cycle:
Figure 1.8: Reduction of NO by C₃H₆ under lean conditions vs. temperature on monometallic Pt, Rh, and Pd based catalysts (500 ppm NO, 1000 ppm C₃H₆, and 5% O₂, gas hourly space velocity 60 000 L/L/h) [34].

Figure 1.9: Illustration of the possible mechanism of the NOx storage/reduction [36].
1.4. Automotive NO$_x$ emission strategies

Figure 1.10: Effect of reaction temperature on NO$_x$ conversion over Pt/BaO/Al$_2$O$_3$ with a 90 s lean phase (SN= 12.3) and a 30 s rich phase (SN= 0.86). Stoichiometry number (SN) = 2[O$_2$]+[NO]/[CO] +9[C$_3$H$_8$]), GHSV=35.000 L/L/h [37].

- Oxidation of NO to NO$_2$ (lean period)
- Storage of NO or NO$_2$ in the form of nitrites or nitrates (lean period)
- Formation of reductants (HCs, CO, and H$_2$) during rich condition (rich period)
- Release some of NO$_x$ from the stored nitrite or nitrate (rich period)
- Reduction of NO$_x$ into N$_2$ (rich period)

One major challenge for the NSR system is that NO$_x$ conversion decreases at high gas hourly space velocity (GHSV, short contact times) and high temperatures. Only a high activity can be maintained around 300-350 °C [37, 38], shown in Figure 1.10 at a moderate GHSV of 35.000 L/L/h. The lower NO$_x$ conversion at high temperature is caused by the low NO$_x$ trapping performance with increasing temperature. As shown in Figure 1.11 [39], the catalyst conversion performance severely decreased when the GHSV increased above 30.000 L/L/h. At higher space velocities due to kinetic limitation, the exhaust gasses passing through the catalyst will not have sufficient resi-
1. Introduction

Figure 1.11: Influence of gas hourly space velocity on NSR activity (Catalyst: Pt/BaO/Al₂O₃ particles, alternative pulses of lean and rich were injected under 120 s/20 s lean/rich cycles, lean: 500 ppm NO + 7.5% O₂ + 10% CO₂ + 10% H₂O, rich: 500 ppm NO + 7.5% CO + 10% CO₂ + 10% H₂O) [39].

...cence (contact) time to store the NOₓ and convert the stored NOₓ with the help of reductants. Both will result in a declined conversion performance. Another partially unsolved problem of this NSR catalyst is its deactivation caused by SO₂/SO₃. The formation of stable barium or potassium sulfates and PtS (RhS) species are the main reason for these catalyst deactivations [40, 41].

1.4.2.3. Coupled NSR and SCR system

Recently, coupled NSR and SCR systems are introduced. Ammonia is produced during the regeneration step of the NSR catalyst and then stored on the downstream SCR catalyst. The stored ammonia will further react with NOₓ passing through the NOₓ-trap during the next lean period, shown in Figure 1.12 [42]. This system requires extensive and detailed chemical engineering knowledge. This coupled system aims to increase the overall NOₓ reduction and maximise the N₂ selectivity while preventing ammonia slip. An upstream Diesel particulate filter (DPF) for diesel soot trapping is, however,
required. The NSR-SCR system must be compatible with the DPF working mode. Filter regeneration (the exothermic oxidation of diesel to CO₂) induces severe isotherms (600-700 °C), which exposes NSR-SCR catalysts to a harsh (high temperature) environment. To maintain the durability of this coupled system, the catalysts must exhibit a high thermal stability.

It should be noted once more that the NSR and the NSR-SCR systems will increase the overall fuel efficiency of the cars, up to 2% are claimed, but in practise upto 10% are required.

1.4.2.4. Combined PM and NOₓ system

1.4.2.4.1 NOₓ reduction with soot
Soot (active carbon) has been used as a reducing agent and a catalyst support for the NO removal from exhaust gasses. However, the application of active carbon as a support is not practical due to its degradation during the oxidation reaction by the exhaust gas stream. Using carbon as a reductant offers obvious advantages, these include: (1) soot is present in the exhaust gas or produced from injected fuel and (2) its oxygen scavenging capability
The NO reduction by activated carbons originating from different raw materials shows that the NO reduction begins in the temperature range from 250 to 400 °C and exhibits a sharp increase up to 100% conversion above 650 °C [45]. Alkali metals are effective catalysts for the gasification of carbon by $\text{H}_2\text{O}$, $\text{CO}_2$, and $\text{NO}_x$ [46, 47]. Potassium is the most efficient catalyst: the presence in carbons is responsible for high NO removal at a temperature around 200 °C, and 100% NO reduction at 500 °C [48]. However, this system will be not applicable for the automotive $\text{NO}_x$ abatement technologies due to the consumption of soot and/or active carbon during the $\text{NO}_x$ reduction process. The refilling of active carbon in the catalyst bed of vehicle after-treatment system is inconvenient. This system will not work for $\text{NO}_x$ abatement when no carbon is present.

### 1.4.2.4.2 Continuously Regenerating Trap (CRT)

Continuously Regenerating Trap (CRT) systems have been used to remove diesel soot, in which a diesel soot oxidation catalyst installed upstream of a wall-flow monolith diesel soot filter will oxidise NO into $\text{NO}_2$. Subsequently, $\text{NO}_2$ reacts with the deposited soot on the filter to form $\text{CO}_2$ and NO. The soot oxidation accelerated by the presence of $\text{NO}_2$ [49]. Simultaneously, only up to 10-15% of NO is converted into $\text{N}_2$ [43]. This method is regarded as a successful method to remove the soot, however, for $\text{NO}_x$ reduction, this technology will be not able to meet any of the $\text{NO}_x$ emission standards.

### 1.4.2.4.3 Diesel particulate-$\text{NO}_x$ Reduction (DPNR)

Based on the CRT and the $\text{NO}_x$ storage reduction technology, Toyota Company has developed the diesel particulate-$\text{NO}_x$ Reduction (DPNR) system to remove simultaneously soot and $\text{NO}_x$. The DPNR system contains a cell wall of the diesel particulate filter (DPF) base, coating with $\text{NO}_x$ storage and reduction catalyst in the internal pore surfaces. The structure of DPNR is illustrated in Figure 1.13 [50]. NO is oxidised to $\text{NO}_2$ and oxygen is converted to adsorbed oxygen atoms on the Pt-active sites under fuel lean conditions. Most of the $\text{NO}_2$ is converted further to nitrate species and nitrite species on the surface of the storage catalyst. The remaining $\text{NO}_2$ and the absorbed oxygen atoms can directly react with diesel soot. When the exhaust atmosphere becomes rich by fuel injection, nitrate species and nitrite species will
decompose into NO₂, which is then further reduced to N₂ by soot, HCs, H₂, and CO over noble metal sites.

This DPNR system is working under fuel lean and fuel rich conditions. However, during the NOₓ storage phase, the PM cannot be oxidised, which affect the efficiency of PM abatement. Moreover, during the fuel rich condition where both NOₓ reduction and PM oxidation take place, some of the stored NOₓ will be released.

1.4.2.5. Diesel NOₓ after treatment by Adsorbed Intermediate Reductants (Di-Air)

Both HC-SCR and NSR systems have a narrow temperature window in which NOₓ reduction occurs with an adequate activity. Additionally, the low NOₓ storage rate and the relatively low operation temperatures, which are required to store NOₓ in NSR systems, limits its application at high gas hourly space velocity (GHSV) condition and temperatures, characteristic for real driving emission performance test (included in future standardised emission tests). The Di-Air (Diesel NOₓ after treatment by Adsorbed Intermediate Reductants) system was recently developed by Toyota [51, 52], as illustrated in Figure 1.14. Rather than using post-injection to create fuel rich conditions (NSR system) in the combustion chambers in the engine, the Di-Air system uses high-intensity and high frequency short time fuel injection in the ex-
haust pipe upstream of an NSR catalyst to increase the number of richness periods with a small fuel penalty of only 2%. Compared to the NSR system this Di-Air system was found to display a high NO\textsubscript{x} reduction activity under overall lean conditions in the exhaust system (shown in Figure 1.15):

- At high gas hourly space velocity (GHSV)
- Over a very broad temperature range, up to 800 °C

As evident from Figure 1.16, small amplitude HC post-injections in the engine are not capable of achieving sufficiently high NO\textsubscript{x} conversions, while short duration and high-intensity of HC injections in the exhaust pipe can achieve high NO\textsubscript{x} conversions with the same amount of fuel injection. HCs are much more effective reductants than H\textsubscript{2} and CO, although the reason remained largely unclear. As claimed by the Toyota, the formation of intermediates containing C and N, such as iso-cyanates (R-NCO) and nitriles (R-CN) led to the high deNO\textsubscript{x} activity under lean conditions. These iso-cyanates (R-NCO) and nitriles (R-CN) were generated from the reaction of HCs with surface adsorbed NO\textsubscript{x}. These formed intermediates are thought to be responsible for prolonging the metallic state of noble metal NSR catalyst components under lean conditions and were more thermally stable than intermediates (-NCO and -CN) formed when CO was used as a reductant. Some of these hydrocarbons derived intermediates were presumed to convert to N\textsubscript{2} e-
1.4. Automotive NO\textsubscript{x} emission strategies

Figure 1.15: Comparison of NO\textsubscript{x} conversion between conventional storage and reduction method (NSR) and the Di-Air method as a function of (A) temperature and (B) space velocity (SV) [51].

Figure 1.16: Changes in outlet NO\textsubscript{x} concentration as a function of HC oscillation amplitude, while the amount of HCs is the same. AFR: air/fuel ratio. Reaction condition: GHSV = 75,000 L/L/h, “NSR” catalyst temperature = 550 °C, (a) = post injection, (b) = fuel injector, injection frequency f = 0.5 Hz [51].
ther independently or by reacting with close-by NO\textsubscript{x}, while some were converted to -CN and -NCO by hydrolysis and could be selectively reduced to NO\textsubscript{x}. Upon hydrolysis of these intermediates, many by-products can be expected, and some have been observed in another type of NO\textsubscript{x} abatement technology at relatively high NO\textsubscript{x} conversion [52, 53], like aldehydes (R-CHO), carboxylic acids (R-COOH), amines (R-NH\textsubscript{2}), oximes (R-CNOH), and hydroxylamine (NH\textsubscript{2}OH). The proposed Di-Air reaction mechanism is shown in Figure 1.17.

The specific function of HC as a reductant for the NO\textsubscript{x} reduction reaction in the Di-Air system remained largely unclear, certainly when considering that an NSR catalyst contains many catalytic components, e.g., Al, Ce, K, Ba, Rh and Pt, further research will be required to explain the reaction mechanism and role of these components.

1.5. Objectives of PhD thesis

Focusing on the Toyota Di-Air deNO\textsubscript{x} system, this thesis is aimed to understand and improve this system further to reduce NO\textsubscript{x} emissions from lean-burn gasoline and diesel vehicles and to be in compliance with the future stringent NO\textsubscript{x} emission standards.

The thesis will emphasise on solving the following research questions:
Q1: What are the mechanistic aspects of the Di-Air process, and the role of each catalytic component (Pt, Rh, K, Ba, Ce, and Al₂O₃) and combinations thereof? Do their combinations have possible synergistic effects on NOₓ reduction (conversion rate and temperature)? (Chapter 4 and 5)

Q2: What is the most powerful reductant produced by the fuel injection? Is the formation of “coke” beneficial for NOₓ reduction? What is/are the intermediate product(s)? Is it “active coke,” “active hydrocarbons,” organo-nitrogen species, or hydrocarbon oxygenates? Or reduced (mixed) metal (oxides)? (Chapter 3)

Q3: What role does oxygen in the lean burn engine exhaust gas play in the deNOₓ process? Is it beneficial for NOₓ reduction or inhibiting this reaction? What is the performance of the different catalyst components in the presence or absence of oxygen? As the real exhaust contains 5-10% of CO₂ and H₂O, what are the effects of H₂O and CO₂? (Chapter 6 and 7)

1.6. Outline of the thesis

A brief introduction of NOₓ abatement and the motivation for developing the new efficient DeNOₓ system is presented in Chapter 1. The Temporal Analysis of Products (TAP) [54] technique is the main tool to study the reaction mechanism of the Di-Air system. Therefore, Chapter 2 describes the dedicated home-made instrument for this technique. In addition, the method of experiments data analysis is also included. In Chapter 3, the difference in reductant pre-treatment of ceria is discussed. Fuel pre-treatment will lead to a deeper reduction of ceria support. In additionally, the fuel pre-treatment will result in carbon deposition. These findings are significant to understand why fuel injection is needed for the Di-Air system, and why fuel injection is the most efficient reductant than other reductants, e.g., CO and H₂. Chapter 4 covers the study of the NO reduction mechanism over the reduced ceria catalyst. This understanding is essential to explain the working principle of the Di-Air system. Chapter 5 discusses the role of the noble metals Pt, and Rh on ceria reduction and NO reduction. The competition between NO and an excess of O₂ (simulated exhaust conditions) is shown in Chapter 6, both for ceria, Rh/ceria and Pt/ceria. Chapter 7 further discusses the influence of
the mild oxidant CO₂ on the NO reduction. The competition of NO and (an excess of) CO₂, was further studied in a continuous flow reactor, showing that the presence of excess CO₂ hardly affected the NO reduction process into N₂.

The thesis concludes with a summary of the major results and presents an outlook for further study.

As several chapters have been published in international scientific journals some overlap in information is unavoidable, but they can be read independently.
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Temporal Analysis of Products

*If you can’t explain it simply, you don’t understand it well enough.*

Albert Einstein
This chapter will give an overview of the Temporal Analysis of Products technology, the developed and home-built instrument, and its application to the project described in this thesis.
2.1. Introduction

2.1.1. What is TAP

_Temporal Analysis of Products (TAP)_ is a vacuum pulse-response technique, developed by John T. Gleaves in 1988 \[1\]. By using a pulse valve small and narrow reactant gas pulses are introduced to a small finite volume (pre-volume) upstream of a packed catalyst bed. The introduced molecules, and eventually formed products upon interaction with the catalyst, diffuse through the packed catalyst bed in the Knudsen diffusion transport regime until they leave the packed bed, where they are recorded _versus_ time (temporal response) by a mass spectrometer (MS). The TAP is working at an ultra- to high vacuum condition ($<$10$^{-8}$-10$^{-9}$ mbar).

A typical TAP pulse-response concept is presented in Figure 2.1. The key components of a TAP setup include a fast gas pulse feed system, a reactor, a mass spectrometer, and a high-throughput (ultra-)high vacuum system. Upstream of the reactor the gas pulse from the gas feedline will be introduced, and downstream of the reactor is close to the MS that detects the eluting gas. The eluting gas leaving the reactor through is detected as a flux by the MS. The contribution of the local concentration in the vacuum chamber at the point of the MS can be neglected as: (1) the MS is located directly under the reactor exit; (2) the MS has a cross-beam ionisation chamber, which prevents molecules that have collided from the vacuum vessels wall to enter the ionisation chamber; and (3) the concentration at the MS is very low (maximum pressure in the order of 3.10$^{-7}$ mbar after pulse introduction). For a typical experiment it has been calculated that at the worst 2.5% of the response is comprised of a contribution from the increased vacuum chamber concentration due to the reactor exit flux. During the experiments, the whole reactor is continuously evacuated.

In a typical TAP pulse experiment, the pulsed mixture contains reactant and an inert gas, which acts as an internal standard. Consequently, the flux of reactants, products, and inert gas are monitored by the MS.
2.1.2. Why TAP

The TAP technique has applications in many areas, *e.g.*, chemical kinetics and chemical engineering [2, 3] due to the following characteristics [1]: (1) Submillisecond time resolution. TAP provides sufficient time resolution for reactions thus offering two or more orders of magnitude better time resolution, as compared to other techniques [4, 5], *e.g.*, flow reactor studies with gas chromatography, Infrared and UV-Vis spectroscopic analyses. (2) Negligible change in the catalyst (oxidation state) upon a single pulse, *i.e.*, a single reactant pulse does not significantly influence the state of the catalyst. (3) Gas transport is well-defined and external mass-transfer limitations are implicitly handled by the Knudsen diffusion model. Knudsen diffusion governs gas transport through the catalyst bed and void volumes (unpacked channels). In the Knudsen diffusion regime molecules collide mainly with the catalyst or channel walls and the diffusivity in a packed bed is given by Equation 2.1 and 2.2 [6, 7]:

\[
D_{kn} = \frac{\varepsilon_b}{\tau} \frac{2\tilde{r}}{3} \sqrt{\frac{8RT}{\pi M}} 
\]

\[
\tilde{r} = \frac{2\varepsilon_b}{3(1 - \varepsilon_b)} \gamma_p \]

With:
- \(D_{kn}\): Knudsen diffusion coefficient
- \(\varepsilon_b\): bed porosity
- \(\tau\): bed tortuosity
- \(\gamma_p\): average particle radius
- \(\tilde{r}\): the average particle distance

The exit flux of an inert, non-interacting gas (Ar, Kr, or Ne, etc.) is purely
governed by a diffusional transport. The inert gas response can be regarded as a standard diffusion response curve for the packed bed, while a viscous flow contribution can be neglected [2]. In the case of a reaction or surface interaction, the exit flux will contain information about reactions, interactions (adsorption and desorption), and diffusion. Deviation from the standard diffusion response curve is an evidence of an additional gas-solid interaction or reaction, including the elementary steps of reactant adsorption, desorption, surface diffusion, surface reaction, and product desorption. TAP response data provide the identity, amount, and residence time of different species exiting from the TAP reactor, which makes it an ideal tool to investigate catalytic reaction mechanisms.

Inspired by the TAP system developed by John T. Gleaves, Delft University built a small new TAP instrument. Figure 2.2 shows the photograph of the new TAP machine in our lab.
2.1.3. Knudsen diffusion

Gas diffusion is a process where gas molecules randomly move from a region of high concentration (pressure) to a low concentration (pressure).

When the gas molecules collide with the walls of the reactor more frequently than with each other, this diffusion process is known as Knudsen diffusion. The diffusion is controlled by Knudsen diffusion, when the scale length of a system (diameter in the case of a circular channel, L) is comparable to, or smaller than the mean free path of the molecules (λ).

The Knudsen number (Kn), expressed as the mean free path divided by the scale length (Equation 2.3), provides a good measure of the relative importance of Knudsen diffusion.

\[
Kn = \frac{\lambda}{L} \gg 1
\]  

(2.3)

When Kn \( \gg 1 \), it indicates that Knudsen diffusion starts to become dominant.

When Kn > 1-10, collisions with reactor channel walls start to prevail over collisions with other molecules. As a consequence homogeneous reactions between molecules in the gas-phase can be considered non-existent in the Knudsen diffusion regime.

When Kn < 0.1, the transport of gas molecules is governed by a mix of molecular diffusion and viscous flow. In this (flow) regime, gas molecules frequently collide with each other, but less frequently with the channel walls. Molecules push each other forward. Therefore, the mean free path of the gas molecules is significantly shorter than the dimensions of the channel of reactor. This unwanted regime is poorly amenable for a good modeling description.

2.1.4. Typical TAP pulse experiments

2.1.4.1. Single-pulse TAP experiments

A single pulse TAP experiment can be considered as a state-defining experiment, since the catalyst surface state will hardly change. The number of catalyst surface atoms is typically 100,000 times that of the number of
2.1. Introduction

Figure 2.3: $N_2$ response upon a single NO pulse over H$_2$ pre-reduced Zr-La doped ceria at 500 °C. The given response is the average of 8 pulse responses with pulse size at $1.6 \cdot 10^{15}$ molecules in a pulse [1]. In that sense the single pulse experiment probes or characterises the catalyst state. This single-pulse TAP experiment is mostly used qualitatively. In practice the data cannot be quantified unless it is part of a multi-pulse sequence. Figure 2.3A and B shows a $N_2$ product response during a single NO reactant pulse over a H$_2$ reduced ceria at 500 °C for a 1 s and 60 s time sample period, respectively. In addition to, a relatively fast $N_2$ formation visible in Figure 2.3A, a much slower $N_2$ formation process can be identified from Figure 2.3B, as is evident from the slower decay of the $N_2$ signal over the period 5-30 s.

2.1.4.2. Multi-pulse TAP experiments

A multi-pulse TAP experiment involves injecting a series of reactant gas pulses over a catalyst sample, i.e., a sequence of single pulse experiments. A multi-pulse experiment gradually alters the catalyst surface and/or bulk. For example, the reduction of ceria can be characterised by the total amount of H$_2$O formation in an H$_2$ multi-pulse experiment. Moreover, multi-pulse experiments are useful to probe the reactivity and selectivity of reactants for catalytic reactions as a function of catalyst oxidation state (Chapter 3).


2.1.4.3. Pump-probe TAP experiments

In a pump-probe experiment, two different reactants are sequentially pulsed from two pulse valves with a certain delay time ($\Delta t$) between the two pulses. The delay time between the two pulses can be varied from 0 to several seconds. In such a pump-probe experiment, information about the lifetime, reactivity and selectivity of ‘invisible’ adsorbed surface species can be obtained (Chapter 5).

2.2. Description of TAP system

The basic operation of our new TAP system is similar to that of the TAP system developed by John T. Gleaves. Our new TAP system consists of a
gas-supply system, heated reactor, detector, and a vacuum system. Figure 2.4 shows a schematic flow diagram of the new TAP setup in Delft. The main difference between our new TAP and that of Gleaves are:

- The use of turbo-molecular vacuum pumps (1800 L/s) instead of an oil diffusion pump (10000 L/s), and therefore, there is no need for a liquid nitrogen oil trap system (no oil contamination). The base pressure achieved by the vacuum system is in the range of $10^{-9}$-$10^{-10}$ mbar, which is even lower than that obtained by using an oil diffusion pump of a much higher capacity

- Higher measurement frequency. Sampling rates up to 500 kHz are possible to obtain clear response shapes. In a typical experiment, 10 kHz was applied, which already provides a clear response

- A smaller vacuum chamber in order to obtain lower based pressure

- Reactor is placed inside the vacuum chamber in order to minimise/avoid leakage

2.2.1. Gas supply

The four reactant feed gas lines are evacuated using a Pfeiffer Uno 2.5 rotary vane pump. A Pfeiffer DVI 005 M low leak rate (< $1 \times 10^9$ mbar L/s) electromagnetically actuated dosing valve (A in Figure 2.4) is used to fill a pulse-valve line with reactant gas and seal-off its calibrated volume (13.6 mL). The pressure of a pulse-valve line is measured by a Pfeiffer CMR 271 high precision temperature controlled capacitive gauge (0-1100 mbar, B in Figure 2.4) and logged using the serial interface of its Pfeiffer TPG 256 A controller. The temperature of a pulse-valve line pressure gauge is measured by a type K thermocouple (B in Figure 2.4). The temperature data was logged using a National Instruments USB-9211A thermocouple ADC.

Four ultra-high speed pulse-valves, Parker Hannifin Series 9, are used to supply a pulse to the reactor. Theses pulse valves and the reactor are installed on a water-cooled custom conflat manifold (B in Figure 2.5). The pulse valve connection is sealed with a Viton O-ring. The pulse valves are activated by externally triggered Parker Hannifin Iota One pulse-valve drivers. The pulse valves have an opening delay of approximately 370 μs upon a 380 Vdc over-
driven voltage pulse, which is provided by the pulse valve driver when the voltage pulse duration is < 160 μs. The maximum pulse size is currently limited to $5 \cdot 10^{15}$ molecules under MS operation, as larger pulse sizes trigger the mass spectrometers ionisation filament protection circuit. The practical minimum pulse size is about $1 \cdot 10^{13}$, as smaller pulse sizes cannot be quantified accurately. The pulse-valve timing and triggering is processed by a National Instruments PCIe-6341 data acquisition card.

2.2.2. Reactor and oven

The stainless steel 304L reactor consists of two sections. The top section, which can be filled or left void (optional second grid) has a length of 3 mm and an internal diameter of 1 mm. The bottom section, which is meant to be packed, has a length of 27 mm and an internal diameter of 3 mm (C in Figure 2.5, Figure 2.6). The catalyst is sandwiched between two quartz particles (150-212 μm) yielding a total bed length of 27 or 30 mm and held in place by two or a stainless steel grid(s), for a void or filled first section, respectively (Figure 2.7). In the experiments performed for this thesis a filled top section
2.2. Description of TAP system

Figure 2.6: Drawing of the reactor heating system.

is always used. A stainless steel 304L extension tube mounted on top of the reactor fixes the (lower) grid and guides the reactor exit to within 7 mm of the mass spectrometer cross-beam ionisation entrance (Figure 2.7).

The reactor is coupled to the pulse-valve manifold and sealed by a Kalrez O-ring. The volume between the pulse-valve exit and the packed catalyst bed, called pre-volume, is around 12.09 µL for a packed top section or 14.45 µL for a void top section (F in Figure 2.5).

A three-segment stainless steel 304L oven surrounds the reactor (Figure 2.6), two snap rings press the oven segments against the reactor. Each oven segment is heated by a heating element (Watlow Firerod, 35 mm x 6.5 mm, 80 VAc, 50 W). The heating rod elements are connected in series and receive power from a Eurotherm TE10A (16 A, advanced single cycle) thyristor. The reactor temperature is currently limited to a maximum temperature of 600 °C (85-87% output power) due to an unfavourable magnetic pole configuration formed by the 3 oven segments, which causes segment repulsion and causes unstable temperatures at higher output power. The reactor temperature is measured by a type K thermocouple placed in the reactor wall at the height of the catalyst bed (Figure 2.6) and controlled by a Eurotherm 2216e single loop controller. The temperature of the reactor is logged using the oven temperature controller’s serial interface.
Figure 2.7: Photograph and drawing of the reactor.
2.2. Description of TAP system

2.2.3. Detector

A quadrupole mass spectrometer is used to measure the response of a specified mass. The used Pfeiffer QMG 422 Quadrupole mass spectrometer system consists of a QMA 125 mass analyser, QME 125 mass filter electronics (0-100 amu), QC 422 quadrupole controller, and an EP 422 electrometer. The QMA 125 mass analyser is composed of a crossbeam ionizer, two tungsten filaments and a discrete dynode secondary electron multiplier (E in Figure 2.4 and Figure 2.8). The EP 422 electrometer is employed at the lowest amplification setting, yielding an output signal rise time of 50 μs.

A Faraday shield (gauze) mounted beneath the oven and surrounding the reactor extension tube prevents electromagnetic interference from the oven heaters with the mass spectrometer. This yields response signals void of 50 Hz noise. The collected response signals contain only random noise, no noise related to a specific frequency could be identified. The response obtained upon a single pulse already has a good signal-to-noise ratio, 260 at the response signal maximum of 7.0 V at an average noise level of 0.027 V (Figure 2.9A). A clean noise free response is typically obtained after averaging 10 responses (Figure 2.9B). The mass spectrometers current amplifier (electrometer) has four physical gain levels, set by selecting feedback resistors (a higher feedback resistor value means a higher gain). The feedback
resistor, together with the operational amplifiers input capacitance and stray capacitance on the circuit board, form an input RC filter. This means that although the signal-to-noise ratio can considerably be improved by selecting a higher gain value, the amplifiers voltage output might not longer be able to follow the input SEM current signal (too large output signal rise time). For typical TAP experiments only the two lowest gain settings of the electrometer guarantee that undistorted response signals are obtained. All presented TAP results are obtained using the lowest gain setting of the electrometer. The mass spectrometer electrometer output signal data acquisition is processed by a National Instruments PCIe-6341 (500 kHz 16-bit ADC) data acquisition card.

2.2.4. Vacuum system

Ultra-high-vacuum (base pressure < 5·10⁻¹⁰ mbar) is generated by a Pfeiffer TPU 2301 P turbomolecular pump (1800 L/s N₂, F in Figure 2.4) and a Varian vacuum backing pump (H in Figure 2.4). In order to enhance the pumping effectiveness of light gases, e.g., H₂, a Pfeiffer TMH 071 P turbomolecular drag pump (60 L/s N₂, G in Figure 2.4) is switched in series with the main turbomolecular pump. The vacuum level is measured by a Pfeiffer PBR 260 automatically switching Bayard Alpert hot cathode ionisation or Pirani gauge and logged using the serial interface of its Pfeiffer TPG 256 A controller.
2.3. TAP experimental

Typically 10 to 20 mg of catalyst is sandwiched between two quartz particles (150-212 μm) beds, approximately 128 mg above and 90 mg below (Figure 2.6), yielding a total bed height of 30 mm. The packed bed is held in place by a stainless steel grid. The pre-volume between the four pulse-valve exits and the packed catalyst bed amounts to 12.09 μL.

All used gases contained either 20 vol.% Ar (33 vol.% Ar for H₂) or Ne (C₃H₆ and C₃H₈) as internal standard. For a reliable quantification, the use of an internal standard is required in order to compensate for drift in the mass spectrometer’s secondary electron multiplier. All the¹⁸O₂ experiments were performed without internal standard and are, therefore, not quantified.

In multi-pulse and co-pulse experiments a starting pulse size of approximately 1.6·10¹⁵ molecules/pulse, excluding internal standard, was applied. The starting pressure in a closed off and calibrated volume (13.6 mL) of the pulse valve feed line was between 900 and 1000 mbar. For a multi-pulse experiment the collection time used to collect a single mass was 5.1 s, the pulse valve was triggered at 0.1 s. For a co-pulse experiment this collection time was 10.1 s, while the first pulse valve was triggered at 0.1 s and the second at 5.1 s. The sample frequency of the amplified MS signal was 10 KHz, using the lowest gain setting of the electrometer.

Typically in a TAP experiment, a sequence of several masses (m/e) is sampled alternatingly, e.g., 5.1 s for the first mass in the sequence, followed by 5.1 s for the next mass in sequence until after the last mass in sequence this sequence is repeated. The number of masses, and hence the number of pulses, required are determined by the used reactants, internal standard, the expected products and the interference of their ionisation fragments.

Before the start of an experiment, after loading the reactor at least 24 h is delayed, the background MS signal is recorded for 5.1 s per mass, while no pulses are introduced, for at least an hour for all masses to be sampled in the actual experiment (system baseline level). After an experiment (which might be an oxidation pulse train followed by an immediate reduction pulse train), all masses used in the actual experiment are sampled for 5.1 s per mass, while no pulses are introduced, until all background levels have decayed to stable levels, after this the background MS signal is recorded for 5.1 s per
mass, while no pulses are introduced, for at least an hour for all masses to be sampled in the actual experiment (system baseline level).

Besides the collection of the MS response data for all masses sampled, the following process variables are collected at 1 minute intervals:

- pressures and temperatures of the pulse valve feed lines
- pressure in the vacuum chamber
- reactor temperature
- oven heating output power

### 2.4. Quantification of TAP data

This section describes the quantification of a TAP multi-pulse experiment. In order to perform a meaningful quantification it is vital to have a stable catalyst, e.g., no irreversible catalyst weight loss, no substantial irreversible loss of (specific) surface area and repeatable catalytic performance. Further prerequisites are a stable mass spectrometer with regards to ionisation yields and the amplification by means of the secondary electron multiplier.

The collected MS signal for all relevant masses is used to quantify the observed reaction products and unreacted reactants, while the recorded feed line pressure and temperature (used to correct the feed line pressure for temperature fluctuations) are used to obtain an equation that gives the pulse size of a known composition for any pulse in the multi-pulse experiment. During a multi-pulse experiment the pulse size decreases over the experiment, as the molecules are pulsed from a calibrated volume. As both the input and output molecules are quantified, a molar balance can be obtained. These molar balances for C, N and O species close within 15% for the quantified TAP experiments within this thesis.

#### 2.4.1. MS signal integration

The quantification of weakly interacting species is fairly straight-forward, as a distinct response is observed, which after baseline correction can be numerically integrated over time. Reaction products and unreacted reactants
can, however, have a strong interaction with the catalyst, quartz bed, and reactor walls. No interaction have been found between neither quartz nor reactor in the performed experiments leading up to this thesis. Several components did, however, exhibit a strong interaction with the catalyst, e.g., CO with oxidised and reduced La- and Zr- doped ceria. This interaction can be so strong, that the resulting response would have a width spanning several minutes. In these situations it is not practical to record the whole response, as experiments would simply take too long. Within the 5.1 s data collection time typically used for obtaining the response of one single mass, for a strongly interacting species no distinct response will be observed. Besides CO, also CO$_2$ and H$_2$O had no distinct response over the ceria-based catalysts. However, quantification is still possible when the increase in the baseline signal of these strongly interacting species (CO, CO$_2$, and H$_2$O) are considered.

A general procedure regarding the quantification of TAP response data is desired, as for example a TAP multi-pulse experiment can consist of 20,000 response data files or more. The quantification is, therefore, split in two parts, the integration of the ‘visible’ response (response signal area) and the integration of the slow desorbing molecules ‘hidden’ in the baseline level (baseline signal area). Hereafter the used terminology and procedures are explained. For that purpose an illustration multi-pulse experiment is shown in Figure 2.10. This illustration multi-pulse experiment, of which one response is shown in Figure 2.10A for a single arbitrary mass and the evolution of the baseline signal for that same arbitrary mass in Figure 2.10B, consists of the following stages:

- pulse number 0 – 2000, period in which the system baseline level is determined prior to the actual multi-pulse experiment, no pulses are given
- pulse number 2000 – 7000, period in which the actual multi-pulse experiment is performed
- pulse number 7000 – 10000, period in which molecules are allowed to desorb from the catalyst surface, no pulses are given
- pulse number 10000 – 12000, period in which the system baseline level is determined after the actual multi-pulse experiment, no pulses are given

It should be noted that up to 12000 pulses, the MS should be extremely
2. Temporal Analysis of Products

stable in order to obtain quantification.

2.4.1.1. System baseline level

The system baseline level represents the (fictitious) MS signal for a certain mass that would have been obtained when no pulse experiment is performed, i.e., the long-term background MS signal for that mass. These signals arise from molecules desorbing of vacuum vessel walls, e.g., H₂O, which have not been pumped, back-diffusion through the vacuum pumps, and MS electrometer/current amplifier offset voltage. These signals, with the exception of the offset voltage, have the tendency to decay especially following a change of reactor contents or an increase in reactor temperature.

The system baseline level is collected for all masses used in the actual multi-pulse experiment over a period prior to (pulse number 0 – 2000, Figure 2.10B) and well after the experiment to allow for sufficient desorption time (pulse number 10000 – 12000, Figure 2.10B). The system baseline level, indicated by the red line in Figure 2.10B, during a multi-pulse experiment and the subsequent desorption period is interpolated using the following exponential function (Equation 2.4):

\[ V_{SB,i}(t) = A e^{-Bt} \]  (2.4)

where \( V_{SB,i}(t) \) is the system baseline level at time \( t \), and \( A \) and \( B \) are fitting parameters. The time, \( t \), is considered to start at the beginning of the system baseline level collection preceding the multi-experiment (pulse number 0, Figure 2.10B).

2.4.1.2. Experiment/desorption baseline level

The experiment baseline level (\( V_{EBL,i} \)) represents the increase in background level, mainly due to strong adsorption to the catalyst surface (CO, CO₂, and H₂O over ceria based catalysts), during a multi-pulse experiment (pulse number 2000 – 7000, Figure 2.10B). The desorption baseline level (\( V_{DBL,i} \)) represents the decline in background level immediately after the multi-pulse experiment (pulse number 7000 – 10000, Figure 2.10B), as strong adsorbed species desorb from the catalyst surface.
Figure 2.10: (a) a collected response shape, the green areas indicate the areas over which the experiment baseline is determined; (b) the experiment baseline evolution prior, during (green area) and after an experiment, the red line indicates the predicted system baseline level.
In general, a collection time of 5.1 s is used to collect a response for a certain mass, as the pulse is triggered at 0.1 s the experiment baseline level \(V_{EBL,i}\) can be determined from the average level over the period spanning from 0 - 0.1 and 5.0 - 5.1 s, indicated by the green areas in Figure 2.10A. The desorption baseline level \(V_{DBL,i}\) is determined in a similar way, although no pulse is given.

### 2.4.1.3. Response signal area

The response signal area \(A_{RSA,i}\) is determined by subtracting the experiment baseline level \(V_{EBL,i}\) or the desorption baseline level \(V_{DBL,i}\) for each data point in the range 0.1-5.0 s (Figure 2.10A), after which the resulting experiment/desorption baseline level corrected response signal is numerically integrated over that time range using the trapezium rule (Equation 2.5).

\[
A_{RSA,i} = \int_{t=0.1}^{5.0} (V_{QMS,i}(t) - V_{EBL,i}(t)) \, dt
\]

\[
= \frac{1}{2f} \sum_{N=0}^{N-1} (V_{QMS,i}(t_{n+1}) - V_{EBL,i}(t_{n+1}) + V_{QMS,i}(t_n) - V_{EBL,i}(t_n))
\]

\(A_{RSA,i}\): response signal area of component i (V s)

\(V_{QMS,i}\): MS signal obtained for component i (V)

\(V_{EBL,i}\): experiment baseline level of component i (V)

\(t\): time (s)

\(f\): sampling frequency (Hz)

\(N\): number of samples in the 0.1 to 5.0 s interval

### 2.4.1.4. Baseline signal area

The baseline signal area \(A_{BSA,i}\) is determined by subtracting the system baseline level \(V_{SB,i}\) from the experiment baseline level \(V_{EBL,i}\) or the desorption baseline level \(V_{DBL,i}\) and multiplying the result by the total data collection time \(\Delta t\), defined as the collection start time of the current response minus the collection start time of the following response (Equation 2.6).

\[
A_{BSA,i} = (V_{EBL,i}(t) - V_{SB,i}(t)) \times \Delta t
\]
2.4. Quantification of TAP data

\[ A_{BSA,i} \]: baseline signal area of component i (V s)
\[ V_{EBL,i} \]: experiment baseline level of component i (V)
\[ V_{SB,i} \]: system baseline level of component i (V)
\[ t \]: time (s)
\[ \Delta t \]: the total data collection time (s)

2.4.1.5. Total signal area

The total signal area \( (A_{TSA,i}) \) is obtained by the summation of the response signal area \( (A_{RSA,i}) \) and baseline signal area \( (A_{BSA,i}) \) (Equation 2.7).

\[
A_{TSA,i} = A_{RSA,i} + A_{BSA,i} \tag{2.7}
\]

\[ A_{TSA,i} \]: total signal area of component i (V s)
\[ A_{RSA,i} \]: response signal area of component i (V s)
\[ A_{BSA,i} \]: baseline signal area of component i (V s)

2.4.2. MS signal quantification and calibration

The obtained total signal areas \( (A_{TSA,i}) \) in the MS signal integration procedure, which are linearly proportional to the total number of molecules, of those masses that have passed through the ionisation volume of the MS, are firstly fragmentation corrected using the fragmentation factors found in the calibration procedure. These fragmentation factors are collected in a fragmentation matrix \( (F) \), horizontally this matrix (Table 2.1) indicates, for example, that CO\(_2\) \((m/e = 44)\) has a fragmentation with a magnitude of 0.209 times that of CO \((m/e = 44)\) at the mass of CO \((m/e = 28)\). The ‘unfragmented’ total signal areas \( (A) \) are obtained via matrix inversion of the transposed fragmentation matrix \( (F) \) (Equation 2.8):

\[
F^T \cdot A = A_{TSA} \iff A = (F^T)^{-1} \cdot A_{TSA} \tag{2.8}
\]

\[ F \]: the fragmentation matrix
\[ A \]: a vector containing the ‘unfragmented’ total signal areas
\[ A_{TSA,i} \]: a vector containing the (fragmented) total signal areas

In the cross beam ioniser of the MS positive ions are created upon interaction with electrons thermally ejected electrons from the filament. These positive ions are accelerated by an electric field towards the quadrupole rods, in
Table 2.1: Fragmentation matrix (F) for the components CO₂, CO and Ar

<table>
<thead>
<tr>
<th></th>
<th>CO₂ (m/e=44)</th>
<th>CO (m/e=28)</th>
<th>Ar (m/e=40)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>1.000</td>
<td>0.209</td>
<td>0.000</td>
</tr>
<tr>
<td>CO</td>
<td>0.000</td>
<td>1.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Ar</td>
<td>0.000</td>
<td>0.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

which all masses except the selected one are rejected. The ions of the selected mass are bent by an electric field towards the secondary electron multiplier. The MS signal is the result of electrons freed from the surface of a discrete dynode of the secondary electron multiplier upon an ion collision. These freed electrons upon ion impact, free more electrons upon a collision with another discrete dynode (cascade). This cascade of electrons forms the current amplified and transformed to a voltage signal by the electrometer. This voltage signal is sampled by the analog to digital converter at discrete times only. Therefore, the integral of this signal over time (V s), an area, is linearly proportional to the total amount of ionised molecules (approximately 10% of the molecules passing through the ionisation volume) of the selected mass over the same time. For this reason an area, integrated voltage signal over time (V s), can be fragmentation corrected as it is linearly proportional to the amount molecules of the selected mass passing through the ionisation volume.

The ‘unfragmented’ total signal areas (A) are divided by the total signal area of the internal standard, yielding the relative signal areas (Areli). Areli represents the relative signal area of component i.

The response factor \( f_i \) for a component i, is calculated using the following equation, assuming a linear relation between the signal and the introduced amount of that component. Signal offsets are implicitly handled by the above described signal integration procedures, provided that a high enough secondary electron multiplier voltage (resolved system baseline signals) is used (Equation 2.9):
### 2.4. Quantification of TAP data

Table 2.2: Equimolecular response factor, $f^0_i$, for different components.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration (vol%)</th>
<th>Relative Area, $A_{rel,i}$</th>
<th>$f^0_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ in Ar</td>
<td>0.662</td>
<td>0.278</td>
<td>0.142</td>
</tr>
<tr>
<td>CO in Ar</td>
<td>0.801</td>
<td>3.881</td>
<td>0.964</td>
</tr>
<tr>
<td>CO$_2$ in Ar</td>
<td>0.797</td>
<td>3.853</td>
<td>0.981</td>
</tr>
<tr>
<td>NO in Ar</td>
<td>0.800</td>
<td>4.439</td>
<td>1.112</td>
</tr>
<tr>
<td>O$_2$ in Ar</td>
<td>0.797</td>
<td>3.048</td>
<td>0.776</td>
</tr>
<tr>
<td>C$_3$H$_6$ in Ne</td>
<td>0.788</td>
<td>16.959</td>
<td>4.563</td>
</tr>
<tr>
<td>C$_3$H$_8$ in Ne</td>
<td>0.787</td>
<td>36.171</td>
<td>9.790</td>
</tr>
<tr>
<td>N$_2$ in O$_2$</td>
<td>0.788</td>
<td>4.767</td>
<td>1.279</td>
</tr>
</tbody>
</table>

The equimolecular response factor is determined by pulsing a mixture of a known composition, according to the following Equation 2.10:

$$ f^0_i = \frac{A_i}{A_{std}} = \frac{s_i n_i}{s_{std} n_{std}} = \frac{s_i}{s_{std}} \frac{x_i}{(1 - x_i)} = f^0_i \frac{x_i}{(1 - x_i)} $$  \hspace{1cm} (2.9)

where:

- $s_i$: the sensitivity factor for component i in V s molecule$^{-1}$
- $x_i$: the molar fraction of component i
- $n_i$: the number of molecules of component i pulsed
- $n_{std}$: the number of molecules of internal standard pulsed
- $f^0_i$: dimensionless equimolecular response factor.

This equimolecular response factor is determined by pulsing a mixture of a known composition, according to the following Equation 2.10:

$$ f^0_i = \frac{A_i}{A_{std}} * \frac{x_i}{1 - x_i} $$  \hspace{1cm} (2.10)

The equimolecular response factors, $f^0_i$, for several components are shown in Table 2.2. In order to interconvert between equimolecular response factors obtained for different internal standards, the equimolecular response factors for one internal standard over the other are determined.
The detected amount of component $i$, $S_i(n)$ in molecules, can then be calculated using the Equation 2.11:

$$S_i(n) = S(n) \frac{A_{rel,i}(1 - x_f)}{f_i^0}$$  \hspace{1cm} (2.11)

where:

$S_i(n)$: number of molecules of component $i$ contained in the pulse at pulse number $n$

$S(n)$: pulse size in molecules at pulse number $n$

$A_{rel,i}$: relative signal area (measured signal in V s of component $i$ divided by the internal standard signal in V s)

$x_f$: molar fraction of the reactant in the reactant pulse

$f_i^0$: unitless equimolecular response factor for component $i$

The number of molecules desorbed from the catalyst after the experiment is determined by subtracting the interpolated system baseline level from the measured post-experiment baseline level followed by fragmentation correction of their experiment baseline areas and quantified using their last known sensitivity factor (obtained from last experiment pulse sequences).

Calibration, in order to obtain the equimolecular response factors and ionisation fragmentation, is performed by pulsing a gas component over a quartz bed at ambient temperature, while recording the sequence of mass responses of the internal standard, the gas component and its known ionisation fragments. This sequence is repeated several times (normally 20,000 pulses) to improve the signal to noise level. The Ar to Ne internal standard conversion factor is determined by pulsing a known amount of Ar and Ne gas from 2 pulse-valve lines at ambient temperature. The H$_2$O signal was calibrated by pulsing H$_2$ over a quartz packed Pt sponge bed at 250 °C which was maintained in an oxidised state by an O$_2$ pulse prior to the H$_2$ pulse yielding 87% H$_2$ conversion.

The number of molecules desorbed from the catalyst after the experiment is determined by subtracting the predicted system baseline level from the measured post-experiment baseline level followed by fragmentation correction of their experiment baseline areas and quantified using their last known sensitivity factor (obtained from last experiment pulse sequences).
2.4.3. Pulse size quantification

To quantify the number of molecules in a pulse via the ideal gas law, corrections are made for the decreasing pressure in the pulse valve line during pulsing, and variations in ambient temperature. All data was normalised to 293 K. The logged pressure, P (Pa), in a pulse-valve line (B in Figure 2.4) is temperature corrected using the equation 2.12:

\[ P^0 = T^0 \frac{P}{T} \]  

(2.12)

where:

- \( P^0 \): temperature corrected pulse line pressure (Pa) at reference temperature \( T^0 \)
- \( T^0 \): 293 K
- \( T \): the logged pulse line gauge temperature (K)

The pulse size is proportional to the pressure in the pulse-valve line. Therefore, the temperature-corrected pressure as a function of the pulse number can be fitted using an exponential equation (Equation 2.13):

\[ P^0(n) = Ae^{Bn} \]  

(2.13)

where: \( n \) is the pulse number, and A and B fitting constants.

The pulse size, \( S \) (molecules) at pulse number \( n \) is determined using the Equation 2.14:

\[ S(n) = \frac{N_A(P^0(n) - P^0(n+1))V_{line}}{RT^0} \]  

(2.14)

where:

- \( N_A \): Avogadro number
- \( V_{line} \): calibrated pulse-line volume (m³)
- \( R \): gas constant
References


Fundamental understanding of the Di-Air system I: The difference in reductant pre-treatment of ceria

*Science is about knowing; engineering is about doing.*

Henry Petroski
3. The difference in reductant pre-treatment of ceria
Toyota’s Di-Air DeNO$_x$ system is a promising DeNO$_x$ system to meet NO$_x$ emission requirements during the real driving. A fundamental understanding of why and how it works, however, largely lacks.

Ceria is one of the main ingredients in the Di-Air catalyst composition and will undergo oxidation-reduction cycles during operation due to pulsed fuel injection. In this Chapter, the reduction of ceria by reductants, e.g., CO, H$_2$, and hydrocarbons (C$_3$H$_6$ and C$_3$H$_8$), is investigated with the Temporal Analysis of Products (TAP) technique. The results show that the reduction by CO yields a faster catalyst reduction than by H$_2$, but in both cases the same final degree of ceria reduction is reached. Hydrocarbons generated an almost three times deeper degree of ceria reduction, and moreover resulted in carbonaceous deposits on the ceria surface. The total amount of converted NO over the C$_3$H$_6$ reduced sample is around ten times higher than over CO reduced ceria. The deeper degree of reduction and the deposition of carbon by hydrocarbon explain why hydrocarbons are the most powerful reductants in Toyota’s Di-Air NO$_x$ abatement system.

This chapter is based on the following publication:

Y.Wang, M.Makkee, Applied Catalysis B; Environmental, doi: 10.1016/j.apcatb.2017.04.054
3. The difference in reductant pre-treatment of ceria

3.1. Introduction

In the European Union (EU) the regulated NO\(_x\) emissions have decreased over the past two decades. Nevertheless, 9% of EU-28 urban live in areas in which NO\(_x\) concentrations still exceed regulated NO\(_x\) standards in 2013, according to the Air quality for EU in 2014 [1]. In the European Union, around 40% of the NO\(_x\) emissions are from the traffic sector [2]. Due to the limited effectiveness of currently available NO\(_x\) emission abatement technologies, as of September 2017, 2.1 times the current Euro 6 NO\(_x\) emission standard (as measured with the conservative, less demanding ECE & EDCE test cycle) is allowed for in the newly established real driving emission (RDE) test [3]. In the future NO\(_x\) emission will become even more stringent, which clearly indicates that currently available technologies: Urea-SCR (Selective Catalytic Reduction) and Lean NO\(_x\) Traps (NSR - NO\(_x\) Storage & Reduction), still need significant improvements. Therefore, efficient exhaust emissions after-treatment technologies are highly demanded. Recently, Bisaiji et al., (Toyota company) developed the Di-Air system (Diesel DeNO\(_x\) System by Adsorbed Intermediate Reductants). Short rich and longer lean time intervals are created by high frequency direct injection of hydrocarbons (diesel fuel injection) into the exhaust upstream of a typical NSR catalyst (Pt/Rh/Ba/K/Ce/Al\(_2\)O\(_3\)) [4, 5]. The Di-Air system has shown promise to meet future NO\(_x\) emission standards under realistic driving test conditions.

In the Di-Air system, hydrocarbons are the most powerful reductants in the reduction of NO\(_x\), as compared to other reductants, e.g., CO and H\(_2\) [5]. However, the working mechanism is still not clear. Before system optimisation with regard to catalyst formulation and fuel injection strategies, the principle and fundamental understanding of the Di-Air system are a prerequisite. Ceria is an essential catalyst ingredient in the Di-Air system, as it acts as an oxygen buffer. The ceria lattice oxygen can react with hydrocarbons, CO, and H\(_2\) under rich conditions [6]. In our research, a commercially available Zr and La-doped ceria is used. The Zr-Ce solid solution, in which zirconium partially replaces cerium, provides a higher hydrothermal stability and a larger oxygen storage capacity [7], whereas lanthanum is present to increase the rate of oxygen bulk diffusion [8]. A reduced ceria can selectively convert NO into (di)nitrogen (N\(_2\)), even in the presence of an excess of oxygen [9, 10] (Chapter 4 and 6).
In this study, we mainly focus on the investigation of the reduction behaviour of the Zr and La-doped ceria catalyst, using $\text{H}_2$, $\text{CO}$, $\text{C}_3\text{H}_6$, and $\text{C}_3\text{H}_8$ as reductants. Temporal Analysis of Products (TAP) is used to ascertain the reaction between the reductants and the catalyst. Since a high frequency of hydrocarbon reductant injections is applied in the Di-Air system, these pulses will create a locally and temporally reducig environment. Therefore, all the experiments in this study are performed in the absence of gas-phase $\text{O}_2$. To demonstrate the effect of different reductants on NO reduction, NO pulsing is performed over the Zr-La doped ceria after pre-reduction treatment. The re-oxidation of the reduced ceria by NO is identical to the conversion of NO into $\text{N}_2$ over reduced ceria. These performed experiments will provide an insight in the product evolution as a function of the catalyst-reduction degree in an attempt to obtain a fundamental understanding of the Di-Air system.

### 3.2. Experimental

#### 3.2.1. Catalyst and catalyst characterisation

The catalyst used is a commercial Zr-La doped ceria (BASF company, denoted further in this Chapter as ‘ceria’), which serves as a core component in the Di-Air catalyst formulation. In brief, the typical fluorite structure of ceria was detected by Raman and XRD. The BET area was $65 \pm 2 \text{ m}^2/\text{g}$. The crystal size of ceria determined by the Scherrer’s equation and TEM analysis was on average 5 nm. The characterisation of this ceria is described in more detail in Chapter 4.

#### 3.2.2. TAP multi-pulse experiments

The multi-pulse experiments were carried out in an in-house developed TAP (Temporal Analysis of Products) reactor. In all experiments a starting pulse size of approximately $1.6 \cdot 10^{15}$ molecules was used, the pulse size gradually decreases during an experiment as the reactant is pulsed from the closed and calibrated volume of the pulse-valve line. More details about TAP can be found in Chapter 2 [10, 11]. 21.2 mg was used in the TAP reactor. Prior to a ceria reduction, the catalyst was firstly re-oxidised at the same temperature at which the reduction was to be performed, using pulsing of 80 vol. % $\text{O}_2$. 
The difference in reductant pre-treatment of ceria in Ar until a stable \( \frac{O_2}{Ar} \) signal ratio was obtained.

The reduction was carried out by pulsing reductant of either 80 vol.% \( C_3H_6 \) in Ne, or 80 vol.% \( C_3H_8 \) in Ne, or 80 vol. % CO in Ar, or 67 vol. % \( H_2 \) in Ar until a stable reactant and product to the internal standard (Ne or Ar) signal ratio was achieved, indicating that the ceria was equilibrated (reduced). NO multi-pulse experiments were performed using 80 vol.% NO in Ar.

The consumption of the oxygen species from the ceria during \( H_2, CO, C_3H_8, \) and \( C_3H_6 \) multi-pulse experiments was calculated using Equation 3.1:

\[
n_{O,\text{consumed}} = n_{CO,\text{in}} - n_{H_2O,\text{obs}} + n_{CO,\text{obs}} + 2n_{CO_2,\text{obs}} \tag{3.1}
\]

where \( n \) is the number of molecules or atoms of the specified species observed (obs), consumed, or introduced (in), based on the calibration of the MS signals \( (m/e) \) used and of the pulse size. For details on the quantification see Chapter 2.

The number of carbon species deposited on the doped ceria surface in the \( C_3H_6 \) multi-pulse experiments was calculated using Equation 3.2:

\[
n_{C,\text{deposited}} = 3n_{C_3H_6,\text{in}} - 3n_{C_3H_6,\text{obs}} - n_{CO,\text{obs}} - n_{CO_2,\text{obs}} \tag{3.2}
\]

Similarly, the number of carbon species deposited on the ceria surface in the \( C_3H_8 \) multi-pulse experiments was calculated using Equation 3.3:

\[
n_{C,\text{deposited}} = 3n_{C_3H_8,\text{in}} - 3n_{C_3H_8,\text{obs}} - 3n_{C_3H_6,\text{obs}} - n_{CO,\text{obs}} - n_{CO_2,\text{obs}} \tag{3.3}
\]

The number of carbon species during CO multi-pulse experiments on the ceria surface was calculated using Equation 3.4:

\[
n_{C,\text{deposited}} = n_{CO,\text{in}} - n_{CO,\text{obs}} - n_{CO_2,\text{obs}} \tag{3.4}
\]

The hypothetical ceria layers concept was used in order to obtain insight in the reductant reactivity as a function of the degree of ceria reduction (surface oxidation state). As the ceria (111) crystal plane is a stoichiometric O-Ce-O tri-layer stacked along the [111] direction, we regarded each O-Ce-O tri-layer as one hypothetical ceria layer. Assuming that Zr is identical to Ce, a maximum of 25% of the number of O ions in each crystal layer can be removed by reduction, the number of reducible oxygens in one hypothetical ceria layer. With a BET area of 65 m\(^2\)/g the number of reducible oxygens in one exposed surface layer is calculated to be \( 5.4\cdot10^{18} \) in 21.2 mg\( \text{Cat} \). Details can be found in Chapter 4 [10].
3.2.3. Operando Raman spectroscopy study

Operando Raman spectra (Renishaw, 2000) were recorded using a temperature controlled Raman cell (Linkam, THMS 600). Ten scans were collected for each spectrum in the 100-4000 cm\(^{-1}\) range using continuous grating mode with a resolution of 4 cm\(^{-1}\) and scan time of 10 s. The spectrometer was calibrated daily using a silicon standard with a strong absorption band at 520 cm\(^{-1}\).

The samples were excited with 514 nm Ar line in the Raman cell, at 560 °C under atmosphere pressure. The spectra were recorded during the flow of C\(_3\)H\(_6\) (1000 ppm in N\(_2\), flow rate 200 mL/min).

3.3. Result

3.3.1. Reduction of ceria by CO

Figure 3.1 shows the result of the CO pulses experiment at 580 °C. During the initial period (pulse number 0-2000, Figure 3.1A), the CO was completely converted into CO\(_2\). Pulse number 2000 corresponded to 0.4 hypothetical reduced ceria layers (Figure 3.1B). After this initial period, the CO conversion and CO\(_2\) production progressively decreased, but never reached a zero conversion level during the duration of the experiment. In the CO oxidation process, only oxygen from the catalyst is consumed, as can be concluded from the oxygen balance (Table 3.2). No carbon deposits were observed on the catalyst within experimental error.

Similar results were obtained at 400-500 °C (Appendix A), but CO conversion did never reach full conversion in this temperature window. At 200 °C and lower, no significant CO oxidation activity was observed (not shown). The number of hypothetical reduced ceria layers (1.2 to 1.0) were relatively constant in the 400 to 580 °C temperature window (Table 3.2).

3.3.2. Reduction by H\(_2\)

Figure 3.2 shows the result of H\(_2\) pulses experiment at 560 °C. For a very short period (pulse number 0-210, Figure 3.2A), hydrogen conversion was relatively high without a clear desorption of water. In contrast to the CO
The difference in reductant pre-treatment of ceria

Figure 3.1: CO multi-pulse experiment over a pre-oxidised ceria at 580°C, (A) with pulse number and (B) with hypothetical reduced ceria layers.

Figure 3.2: H₂ multi-pulse experiment over the pre-oxidised ceria at 560°C, (A) with pulse number (B) with hypothetical reduced ceria layers.
3.3. Result

Table 3.1: Definition of different stages during the C₃H₆ and C₅H₈ pulses in TAP.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Hydrocarbon Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Initial full conversion of hydrocarbon</td>
</tr>
<tr>
<td>II</td>
<td>Hydrocarbon conversion decline</td>
</tr>
<tr>
<td>III</td>
<td>Hydrocarbon conversion increase</td>
</tr>
<tr>
<td>IV</td>
<td>Period of constant hydrocarbon conversion</td>
</tr>
<tr>
<td>V</td>
<td>Hydrocarbon conversion decrease</td>
</tr>
</tbody>
</table>

experiment, the H₂ conversion was never complete. The H₂ conversion and H₂O production decreased progressively during the remainder of the experiment (pulse number 210 - end, Figure 3.2B). At the end of experiment, the number of extracted oxygen atoms, characterised as the number of hypothetical reduced ceria layers, corresponded with 1 reduced layer (Table 3.2).

3.3.3. Reduction by C₃H₆

Figure 3.3 shows the result of C₃H₆ pulses experiment at 580 °C. Different stages are used to define C₃H₆ reactivity profiles with pulse number, as shown in Table 3.1. The definition of different stages was also applied to C₅H₈ reactivity in Figure 3.5.

Figure 3.3A shows the product and reactants evolution versus pulse number during C₃H₆ pulses. In stage I (pulse number 0-80), a high activity was observed, where predominantly total oxidation products, i.e., CO₂ and H₂O were formed. The H₂ formation was observed from the start of the experiment, while CO production was initially zero. Both H₂ and CO production increased during this stage I. After this short highly active stage I, C₃H₆ conversion rapidly declined in stage II (pulse number 80-500). In stage III and IV (pulse number 400-8000) predominantly partial oxidation took place and mainly CO and H₂ were observed. From pulse number 2800 to 8000 (stage III), C₃H₆ conversion increased to full conversion. H₂ was the major product.
Figure 3.3: $\text{C}_3\text{H}_6$ multi-pulse experiment over a 21.2 mg (0.1 mmol) pre-oxidised ceria at 580 °C, (A) product and reactants evolution versus pulse number, (B) product and reactants evolution versus hypothetical reduced ceria layers, and (C) Carbon and oxygen balance versus pulse number.
and the formation of CO declined with time in stage III. In stage V (pulse number 8000 - end), both C₃H₆ conversion and H₂ production declined. The H₂ production and C₃H₆ conversion remained persistent although at a low level and no CO was observed.

Some carbon (Figure 3.3C) started to deposit on the surface from stage II (determined from the carbon balance). Significant amounts of carbon depositions were observed when the CO formation started to decline, while H₂ formation persisted (stage IV). C₃H₆ shows full conversion during stage I and IV, corresponding to 0 to 0.25 and 1.5 to 2.7 hypothetical reduced ceria layers, respectively, as shown in Figure 3.3B.

The oxygen atom consumption and carbon atom deposition during the C₃H₆ multi-pulse experiment at 580 °C were calculated to be 1.5·10¹⁹ oxygen atoms (2.6 hypothetical ceria layers) and 4.1·10¹⁹ carbon atoms (2.9 wt.%), respectively, as shown in Table 3.2. Figure 3.4 shows the C₃H₆ conversion versus pulse number in a temperature window between 500 and 580 °C. Similar C₃H₆ reactivity profiles were observed, although the overall reactivity of C₃H₆ decreased, when reaction temperature declined. No significant
C₃H₆ activity and reduction of ceria were observed below 500°C. Table 3.2 summarises the oxygen consumption (hypothetical reduced ceria layers) and carbon deposits for the 500 to 580°C temperature window.

### 3.3.4. Reduction by C₃H₈

Figure 3.5 shows the result of C₃H₈ pulses experiment at 580°C. As compared to C₃H₆, C₃H₈ in stage I did not have a full conversion. Figure 3.5A shows the product and reactant evolution versus pulse number during C₃H₆ pulses. In stage II (pulse number 80-1000), a short period of a higher activity (up to 40% conversion) was observed, where predominantly total oxidation products, \(\text{i.e.}, \text{CO}_2\) and \(\text{H}_2\text{O}\), were formed. The \(\text{H}_2\) formation was observed from the start of the experiment, while CO production was initially zero, both \(\text{H}_2\) and CO production increased during this stage II. The C₃H₈ conversion declined during stage II and increased during stage III (up to 60% conversion). In stage III and IV, partial oxidation took place and CO and \(\text{H}_2\) were observed, while C₃H₆, the dehydrogenation product of C₃H₈, was only observed during stage III. The level of C₃H₈ conversion was substantially lower as compared to that of C₃H₆.

During the partial oxidation time interval (stage III, IV, and V), CO and \(\text{H}_2\) were observed as the main products. The reaction rate increased with pulse number during stage III and IV. During stage III the C₃H₆ production, resulting from the dehydrogenation of C₃H₈, increased progressively but vanished towards the end of stage III. A maximum in CO production was observed when the activity for the dehydrogenation reaction vanished. In this the partial oxidation time interval, in contrast to the C₃H₆ multi-pulse experiment, the C₃H₈ conversion was never 100%. Initially, the C₃H₈ conversion was around 10% and reached a maximum conversion of 60% at the point of maximum CO production (Figure 3.6). Following the maximum in the CO production, the C₃H₈ conversion and \(\text{H}_2\) production also reached their maximum level (stage IV, Figure 3.5). In stage V, the C₃H₈ conversion and CO and \(\text{H}_2\) production declined. CO evolution stopped after pulse number 22000, while C₃H₈ conversion and \(\text{H}_2\) production remained persistent at a low level. At a temperature of 500°C and lower, the reactivity of C₃H₈ was negligible or none (not shown).
Table 3.2: Summary of the number of deposited carbon and extracted oxygen atoms in the ceria (21.2 mg) reduction experiments and the number of converted NO molecules during NO re-oxidation experiments.

<table>
<thead>
<tr>
<th>Reduction by reactants</th>
<th>Deposited carbon</th>
<th>Extracted oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atoms</td>
<td>wt.%</td>
</tr>
<tr>
<td>580 °C C$_3$H$_6$</td>
<td>$3.1 \cdot 10^{19}$</td>
<td>2.9</td>
</tr>
<tr>
<td>560 °C C$_3$H$_6$</td>
<td>$3.4 \cdot 10^{19}$</td>
<td>3.2</td>
</tr>
<tr>
<td>540 °C C$_3$H$_6$</td>
<td>$3.3 \cdot 10^{19}$</td>
<td>3.1</td>
</tr>
<tr>
<td>500 °C C$_3$H$_6$</td>
<td>$1.9 \cdot 10^{19}$</td>
<td>1.8</td>
</tr>
<tr>
<td>580 °C C$_3$H$_8$</td>
<td>$1.5 \cdot 10^{19}$</td>
<td>1.4</td>
</tr>
<tr>
<td>540 °C C$_3$H$_8$</td>
<td>$1.1 \cdot 10^{19}$</td>
<td>1</td>
</tr>
<tr>
<td>580 °C CO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>500 °C CO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>400 °C CO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>560 °C H$_2$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Re-oxidation by NO at 540 °C

<table>
<thead>
<tr>
<th>The number of converted NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Over CO pre-reduced at 540 °C</td>
</tr>
<tr>
<td>Over C$_3$H$_8$ pre-reduced at 540 °C</td>
</tr>
<tr>
<td>Over C$_3$H$_6$6 pre-reduced at 540 °C</td>
</tr>
</tbody>
</table>

$^1$ hypothetical reduced ceria layer
3. The difference in reductant pre-treatment of ceria

Figure 3.5: C$_3$H$_8$ multi-pulse experiment over a pre-oxidised ceria (21.2 mg, 0.1 mmol) at 580°C: (A) product and reactants evolution with (A) pulse number, (B) product and reactants evolution versus hypothetical reduced ceria layers.
3.3. Result

As shown in Table 3.2, the amounts of deposited carbon ranged from 1.4 to 0.9 wt.% for temperatures from 580°C to 540°C, which is less than that of propene. C₃H₈ was able to reduce the catalyst as far as 2.7 hypothetical reduced ceria layers, which was the same as that for C₃H₆ at 580°C, but the required number of pulses, however, was around twice that of C₃H₆.

In Figure 3.6, the C₃H₈ conversion was plotted versus pulse number at 580 and 540°C, respectively. In the initial total oxidation period, approximately 40% and 30% C₃H₈ conversion were achieved at 580 and 540°C, respectively. The incremental C₃H₈ conversion in stage II and III was sensitive to the temperature, which shifted to higher pulse numbers with decreasing temperature and its maximum C₃H₈ conversion decreased from 65 to 30%, when the temperature decreased from 580 to 540°C. Compared to C₃H₆ conversion at 540°C, as indicated dotted grey line in Figure 3.6, C₃H₈ was less active and it took around two times pulses than that of C₃H₆ to reach the final state. As shown in Table 3.2, the amount of deposited carbon by C₃H₈ at 540°C was around three times less than that for C₃H₆ at the same temperature, even the pulses of C₃H₈ is twice that of C₃H₆.
3.3.5. Operando Raman experiment of C\textsubscript{3}H\textsubscript{6} flow over ceria

Operando Raman spectroscopy was used to characterise the deposited carbon formed over ceria during C\textsubscript{3}H\textsubscript{6} flow at 580°C. D-band and G-band of carbon were observed during the C\textsubscript{3}H\textsubscript{6} flow as shown in Figure 3.7. The G-band corresponded to graphitic in-plane vibrations with E\textsubscript{2g} symmetry. The D-band is generally assigned to the presence of defects in and disorder of carbon.

3.3.6. Re-oxidation of reduced ceria by NO

In order to investigate the effect of the reduction degree as well as the amount of deposited carbon on the NO reduction into (di)nitrogen (N\textsubscript{2}) over (pre-reduced) ceria, NO was used in the re-oxidation ceria pre-reduced with CO, H\textsubscript{2} (not shown), C\textsubscript{3}H\textsubscript{8}, and C\textsubscript{3}H\textsubscript{6} at 540°C, as illustrated in Figure 3.8. For the CO (and H\textsubscript{2}) pre-treated samples, full NO conversion was obtained till pulse number 2340, corresponding with around 6.8\cdot10^{18} NO molecules converted. For the propane pre-treated ceria, complete NO conversion maintained approximately till pulse number 1200. The total number of NO converted was around 2.9\cdot10^{19} molecules. For the C\textsubscript{3}H\textsubscript{6} pre-treated ceria sample, however, NO shows full conversion up to pulse number 5600,
3.4. Discussion

3.4.1. Reduction of ceria by CO and H₂

The CO multi-pulse experiments over ceria resulted in an overall catalyst reduction of around on average one hypothetical reduced ceria layer in the 400 to 580 °C temperature window (Table 3.2), indicating that a complete surface layer of ceria can be reduced by CO. The extraction of one oxygen resulted in the reduction of two Ce⁴⁺ ions into two Ce³⁺ ions. The oxidation of CO to CO₂ can be described as Equation 3.5:

\[ CO + 2Ce^{4+} + O^{2-} \rightarrow CO_2 + 2Ce^{3+} + \text{■} \]  

(■ : oxygen vacancy)

The CO₂ production was due to the oxidation of CO by oxygen species (originating) from the ceria lattice since there was no gas-phase O₂ present during followed by a conversion decline to 76% at pulse number 9000. Subsequently, the NO conversion for the C₃H₆ increased to full conversion till pulse number 40000. NO conversion declined after pulse number 97300. The total amount of NO being converted was around 7.6·10¹⁹ molecules.

Figure 3.8: NO pulse conversion over ceria pre-reduced at 540 °C by CO and hydrocarbons.
the CO multi-pulse experiment. The full CO₂ conversion dropped at the point corresponding to 0.5 hypothetical reduced ceria layers Figure 3.1B, which indicated that the oxygen species generated from surface lattice oxygen had a high activity for the CO oxidation into CO₂. The observed decline in CO activity between 0.5 to 1 hypothetical reduced ceria layers Figure 3.1B implied that only surface oxygen participated in the CO oxidation.

Significant participation of the disproportionation of CO into carbon and CO₂ (2CO → C + CO₂) can be excluded, because neither hardly any deposited carbon was observed nor could be quantified through the calculated carbon balance (Figure 3.1A). The total reduction degree of ceria by CO was not significantly affected by temperatures in the range of 400-580 °C. The reactivity of CO, however, declined as the temperature decreased, since more CO pulses were needed in order to obtain the same reduction degree at the low temperatures of 400 °C, compared to 580 °C (Appendix A).

The limitation for the reduction of only one hypothetical reduced ceria layer by CO cannot be attributed to the oxygen diffusion since the reduction degree of ceria was not significantly influenced by a temperature between 400 and 580 °C. The role of ceria in the reduction of CO₂ to CO had been widely studied in the field of solar cells [12–14]. CO₂ can also re-oxidise reduced ceria, thereby forming CO. The coexistence of CO and CO₂ in the 0.5 to 1 hypothetical reduced ceria layer range suggested the presence of an equilibrium between CO, CO₂, Ce³⁺, and Ce⁴⁺, which may limit the obtainable degree of reduction for ceria during CO multi-pulse experiments (Figure 3.1B).

For the H₂ multi-pulse experiments, a high activity towards H₂ was observed from the start of the experiment (Figure 3.2) in the absence of any water desorption. This indicated that water or its precursor species were initially retained on the catalyst's surface. This activity towards H₂ activity dropped immediately after the initial pulses to a conversion of about two-third, further continuously declining until hardly any conversion was observed when one hypothetical reduced ceria layer was reached. Similar to the CO multi-pulse experiments, when the ceria surface became reduced, the reduced ceria tended to use water or an intermediate to re-oxidise itself [15]. The coexistence of H₂ and H₂O during a whole H₂ multi-pulse experiment suggested the presence of an equilibrium between H₂, H₂O, Ce³⁺, and Ce⁴⁺,
3.4. Discussion

Figure 3.9: C₃H₆ activation steps for the formation of CO₂ and H₂O over oxidised ceria surface and the formation of CO and H₂ over reduced ceria surface.

which may limit a deeper reduction of ceria by H₂.

3.4.2. Reduction by hydrocarbons

3.4.2.1. Reduction by C₃H₆

The reduction of ceria by C₃H₆ led overall to 2.7 hypothetical reduced ceria layers at 580 °C (Table 3.2). Unlike CO and H₂ pre-treatment, the C₃H₆ interaction with the catalyst can be characterised by two types of reactions: complete C₃H₆ oxidation and subsequently C₃H₆ cracking/partial oxidation (Figure 3.3).

The initial high conversion to total oxidation products (stage I): CO₂ and H₂O, was most probably due to the high concentration of active surface oxygen species, which were formed through an oxygen activation chain as given in Equation 3.6 [16–18]:

\[
O_{2(ad)} + e^{-1} \rightleftharpoons O_2^- \rightleftharpoons O_2^{2-} \leftrightarrow 2O^- + 2e^{-1} \rightleftharpoons 2O^{2-} \quad (3.6)
\]

These active surface oxygen species reacted with C₃H₆ resulting mainly in
the formation of H₂O and CO₂ as described in Figure 3.9. The adsorbed C₃H₆ was activated by the active oxygen species from oxygen activation chain (equation 6), forming the C₃H₅· and H·. Then H· will react with active oxygen species, forming ·OH. Another H· will be further abstracted from C₃H₅· and to form H₂O from ·OH. The remaining hydrocarbon fragment (CₓHᵧ) will react with active oxygen species, forming oxygen-containing hydrocarbon intermediates (CₓHᵧO), and finally oxidation of some part of CₓHᵧO to CO₂, the remained CₓHᵧO will be deposited as "coke" as illustrated in Figure 3.9.

The C₃H₆ conversion dropped (stage II), accompanied by a decline in total oxidation products and the start of C₃H₆ cracking/partial oxidation reaction. The fall of C₃H₆ conversion during stage II was likely caused by the lower availability of the active surface oxygen species that were largely consumed during stage I. As described in Figure 3.9, the adsorbed C₃H₆ will be activated by the active oxygen species, forming the C₃H₅· and H·. This H· will react with active oxygen species, forming ·OH. More H will be further abstracted from C₃H₅·. However, on the reduced catalyst surface (less active surface oxygen), H surface species have more chance to associate to each other to form H₂. The remaining hydrocarbon fragment (CₓHᵧ) will react with active oxygen species, forming oxygen-containing hydrocarbon intermediates (CₓHᵧO). Some part of CₓHᵧO will be converted to CO, the remaining CₓHᵧO will be deposited as coke. The Figure 3.9 was also applied to the C₃H₆ cracking reaction during the stage III. C₃H₆ conversion increased during stage III accompanied by an increased H₂ and CO formation, indicating mainly cracking/partial oxidation/dehydrogenation were taking place on the reduced ceria surface.

The CO formation arrived at a maximum at 1.5 hypothetical reduced ceria layers, while CO₂ and H₂O were not observed beyond 1 hypothetical reduced ceria layer. This observation indicated that for the formation of CO oxygen from the bulk of ceria was used, resulting in a deeper degree of catalyst reduction by C₃H₆, as compared to the CO and H₂ treatment. The CO formation declined after 1.5 hypothetical reduced ceria layers and ceased at 2.7 hypothetical reduced ceria layers. This will indicate that the deposited carbon oxidation to CO started to become limited when the catalyst reduced to 1.5 hypothetical reduced ceria layers. This can be explained by the scarcity
of active surface oxygen species either due to slow bulk oxygen diffusion or the activation of bulk oxygen to active oxygen species. The formation of CO implied the additional extraction of oxygen from ceria bulk, i.e., a reduction of the ceria up to 2.7 hypothetical reduced ceria layers (stage V).

Also the increase of \( \text{C}_3\text{H}_6 \) conversion during stage III was likely due to the regeneration of active oxygen species from the bulk by diffusion to surface, which led to increased CO formation but to less carbon deposition as compared to stage II, based on the carbon balance calculations. The CO formation, however, declined beyond 1.5 hypothetical reduced ceria layers, while still a full \( \text{C}_3\text{H}_6 \) conversion and persistent \( \text{H}_2 \) formation was observed (stage IV). The full \( \text{C}_3\text{H}_6 \) conversion (\( \text{C}_3\text{H}_6 \) cracking) during stage IV cannot be ascribed to the increased active oxygen species availability. Otherwise, the CO formation rate would increase as well. Another type of species started to play a role in \( \text{C}_3\text{H}_6 \) cracking/partial oxidation (deeper dehydrogenation).

The total amount of carbon deposition till the point of 1.5 hypothetical reduced ceria layers was around \( 2 \cdot 10^{18} \) carbon atoms. Assuming that the carbon structure will be graphene-like structure, the coverage of ceria by carbon corresponded to roughly 4% of the available surface area (Detailed calculation is shown in Appendix A). Carbonaceous deposited (coke) that formed on the metal oxides can be regarded as the real catalyst site for (oxidative) dehydrogenation [19–22]. The formation of deposited carbon was observed from the operando Raman spectroscopy (Figure 3.7). The catalytic site on the coke will be the quinone/hydroquinone group on the surface of the coke [19–22], as evidence the formation of D-band and G-band (Figure 3.7). The full \( \text{C}_3\text{H}_6 \) conversion with persistent \( \text{H}_2 \) formation is attributed to the deposited carbon and will play a role in the deeper \( \text{C}_3\text{H}_6 \) dehydrogenation. The oxygen transport from ceria bulk will become the catalytically active site on the coke (\( \text{C}_x\text{H}_y\text{O} \)), and CO was formed by the oxidation of coke (\( \text{C}_x\text{H}_y\text{O} \)). When the number of available lattice oxygen declined, the CO formation declined as well. The deeper dehydrogenation of \( \text{C}_3\text{H}_6 \) will lead to more and more deposited carbon.

Till stage V, \( \text{C}_3\text{H}_6 \) conversion dropped, and simultaneously the \( \text{H}_2 \) formation declined as well from 2.2 hypothetical reduced ceria layers, indicating that the deeper dehydrogenation reaction largely slowed down. The slow-down of the bulk oxygen diffusion to surface when the ceria was 2.2 hypothetical
layers reduced caused the depletion of reducible oxygen on the ceria surface, which may explain the final lost in the C\textsubscript{3}H\textsubscript{6} conversion and hardly any CO formation.

In addition, C\textsubscript{3}H\textsubscript{6} conversion were persistent in a lower level after 14000 C\textsubscript{3}H\textsubscript{6} pulses, as shown in Figure 3.3. The total number of deposited carbon on the ceria surface after 14000 C\textsubscript{3}H\textsubscript{6} pulses was around 3.1 \cdot 10^{19} carbon atoms (Figure 3.7), which accounted for about 2.9 wt.%. Assuming that the carbon structure will be single-sheet graphene-like and the ceria surface will be flat, the coverage of ceria by carbon will correspond to roughly 60\% of the available surface area. There would be still about 40\% of the surface area available. In reality, the catalyst particles are aggregated together, as evidenced by TEM (Figure 4.1 in Chapter 4). Therefore, the surface of ceria will be a network of pores. The carbon deposition may completely cover the surface, considering the some pores are blocked by the carbon particles. The blocking of the pores in combination with a slow-down of the oxygen diffusion from the bulk to the ceria surface and the deposited carbon may be main reasons for the final lost in the C\textsubscript{3}H\textsubscript{6} conversion.

Similar C\textsubscript{3}H\textsubscript{6} reactivity profiles were also observed in the 500 to 580°C temperature window, although more pulses were needed. The maximum observed C\textsubscript{3}H\textsubscript{6} conversion during the cracking reaction period (stage III) shifted to higher pulse numbers in the 580 to 500°C temperature range, as shown in Figure 3.4. This observation indicated that more time (more pulses) was needed bulk oxygen diffusion and activation when temperature decreasing.

Such phenomenon also pointed out that the reactivity of C\textsubscript{3}H\textsubscript{6} during stage III was likely controlled by the availability of active oxygen species on the surface regenerated by bulk oxygen diffusion. At 400°C, only complete oxidation to CO\textsubscript{2} and H\textsubscript{2}O was observed (no carbon deposition). No cracking reaction was observed was observed during the experiment time of 24 h C\textsubscript{3}H\textsubscript{6} pulses.

The total amount of reducible oxygen during C\textsubscript{3}H\textsubscript{6} oxidation was highly depended on temperature, as shown in Table 3.2. The number of oxygen atoms extracted in the C\textsubscript{3}H\textsubscript{6} multi-pulse experiments declined from 1.5 \cdot 10^{19} to 0.9 \cdot 10^{19}, i.e., from 2.6 to 1.7 hypothetical reduced ceria layers when the
temperature decreased from 580 to 500 °C. The total amount of deposited carbon during the C₃H₆ multi-pulse experiment at 580 °C is twice that of the multi-pulse experiment at 500 °C. At 400 °C, carbon was hardly deposited, and no cracking/partial oxidation/dehydrogenation activities were observed.

3.4.2.2. Reduction by C₃H₈

C₃H₈ (Figure 3.5), shows the same trend as C₃H₆, although C₃H₈ conversion was lower than that of C₃H₆ during stage I and IV. This indicated that the reaction mechanisms were similar for both saturate and unsaturated hydrocarbons. C-H bond cleavage was easier for the unsaturated C₃H₆ as compared to the saturated C₃H₈ due to either the interaction with the surface through hydrogen bonding or Van der Waals forces for C₃H₈ and more strong electron-rich n orbital interactions on Lewis acid sites for C₃H₆ [23]. The lower reactivity, that C₃H₈ displayed towards oxygen species, did not affect the total amount of oxygen extracted during the whole C₃H₈ multi-pulse experiment, but affected strongly the amount of carbon deposited on the surface and the time to achieve the same degree of ceria reduction. Since the carbon deposition took predominantly place during stage IV, the lower C₃H₈ reactivity led to less carbon deposition. Comparing C₃H₆ and C₃H₈ pre-treatment at 580 °C, the amount of carbon deposited for the C₃H₆ pre-treatment was twice that for C₃H₈, as shown in Table 3.2.

The C-H bond cleavage is regarded as the first step in the activation of saturated hydrocarbons (C₃H₈). Due to the initial high concentration of active surface oxygen species in stage II, complete oxidation was observed with the formation of both H₂O and CO₂, similar as illustrated in Figure 3.9. The conversion of C₃H₈ decreased during stage II was due to the depletion of active oxygen species on the surface. A gradual increase in the amount of the C₃H₆ dehydrogenation product Figure 3.5 was observed from stage III, where the C₃H₈ conversion was enhanced. Similar to the C₃H₆ multi-pulse experiments (Figure 3.3), the C₃H₈ reactivity (Figure 3.5) increased during stage III was due to the reformation of surface active oxygen species by the diffusion of oxygen from the bulk of the ceria. Dehydrogenation of C₃H₈ to C₃H₆ was observed from initial of stage III and declined from the end of stage III. C₃H₆ evolution completely vanished from stage IV. The dehydrogenation selectivity of C₃H₈ to C₃H₆ in stage III can be explained by a
The difference in reductant pre-treatment of ceria

particular type of reformed active oxygen species, e.g., $O^-$. $C_3H_6$ formation declined around 1.3 hypothetical reduced layers, indicating that these oxygen species, e.g., $O^-$ [24], were less present from 1.3 hypothetical reduced layers.

Similar as in the $C_3H_6$ multi-pulse experiments, the formation of CO during $C_3H_8$ multi-pulse experiment consumed oxygen from the catalyst bulk, i.e., a deeper reduction. Deposited carbon started to play a role in $C_3H_8$ dehydrogenation during stage IV, where $C_3H_8$ conversion was around 60%.

The maximum conversion during the $C_3H_8$ cracking / partial oxidation / dehydrogenation reactions (stage III) shifted to a higher pulse number when the temperature was changed from 580 to 540 °C, as shown in Figure 3.6. Similarly to the observation in the $C_3H_6$ multi-pulse experiments, the reactivity of $C_3H_8$ during stage III was controlled by the availability of active oxygen species on the surface reformed by a temperature dependent oxygen diffusion. The observed $C_3H_8$ conversion drop can be explained with the same reasoning as discussed above for $C_3H_6$.

The total amount of reducible oxygen during $C_3H_8$ oxidation was significantly influenced by the temperature, as shown in Table 3.2. The number of oxygen atoms extracted in the $C_3H_8$ multi-pulse experiments declined from $1.5 \cdot 10^{19}$ to $0.9 \cdot 10^{19}$, i.e., from 2.7 to 1.7 hypothetical reduced ceria layers as the temperatures were lowered from 580 to 540 °C.

### 3.4.3. Re-oxidation of reduced ceria with NO

The pre-treatment of ceria by CO, $H_2$, $C_3H_8$, and $C_3H_6$ at 540 °C led to a degree of catalyst reduction corresponding to 1, 1, 1.7, and 1.8 hypothetical reduced ceria layers, respectively. The pre-treatment with $C_3H_6$ and $C_3H_8$ additionally resulted in the deposition of $3.3 \cdot 10^{19}$ and $1.1 \cdot 10^{19}$ carbon atoms, respectively.

The differences observed in the reduction of NO into $N_2$ over ceria by using either CO, $C_3H_8$ or $C_3H_6$ pulses at 540 °C was shown in Figure 3.8. CO and $H_2$ pre-treatments shows only a short time interval, where NO was reduced into $N_2$. The reduction of NO to $N_2$ started with oxygen from NO filling an oxygen defect site, followed by N-O bond scission and the recombination, after surface diffusion and migration of N species into dinitrogen ($N_2$) [9, 10].
3.5. Conclusions

When all oxygen defects were refilled, the NO reduction was ended. Both C$_3$H$_6$ and C$_3$H$_8$ pre-treated reduced ceria were able to convert considerable more NO into N$_2$ (much longer time interval) as compared to CO and H$_2$ pre-reductions. The pre-treatment of C$_3$H$_6$ and C$_3$H$_8$ resulted in a deeper catalyst reduction and more deposited carbon. These carbon deposits acted as reductant buffer. The oxidation of deposited carbon by active oxygen species from ceria lattice recreated the oxygen defect sites that can be again used for additional NO conversion [10]. C$_3$H$_6$ pre-treatment provided higher capacity for NO reduction into N$_2$ than C$_3$H$_8$ pre-treatment due to a three times larger carbon deposition.

The CO and H$_2$ pre-treatments resulted only in the reduction of surface oxygen and hardly any or no deposited carbon. Therefore, CO and H$_2$ pre-treatments are less effective than a hydrocarbon pre-treatment. Deposited carbon, acting as a reductant buffer, extended the period in which NO can be reduced into N$_2$. C$_3$H$_6$ will be preferred over C$_3$H$_8$ due to its higher reactivity and increased carbon deposit formation.

**3.5. Conclusions**

- The degree of ceria reduction obtained by C$_3$H$_6$ and C$_3$H$_8$ reduction, corresponded with up to 2.7 hypothetical reduced ceria layers. As compared to H$_2$ and CO, at 580 °C the obtainable reduction degrees with these hydrocarbons were around 3 times higher (Table 3.2). Pre-treatment by C$_3$H$_6$ due to its higher reactivity, resulting in three times more carbon deposited, is preferred over that of C$_3$H$_8$.

- Hydrocarbon pre-treatment led to carbon deposits on the reduced ceria surface. These carbon deposits will, however, act as a reductant reservoir, leading to a higher number of NO converted molecules (selective re-oxidation of reduced ceria) into nitrogen [9, 10].

- The deeper degree of reduction of ceria during reduction by hydrocarbons will be due to the oxidation of deposited (hydro)carbon intermediated by additional lattice oxygen on the reduced ceria to CO. For H$_2$ and CO pre-treatment, the apparent existence of H$_2$, H$_2$O, Ce$^{3+}$ and Ce$^{4+}$ (or CO,
The difference in reductant pre-treatment of ceria \( \text{CO}_2, \text{Ce}^{3+} \text{ and Ce}^{4+} \) equilibrium will limit the ceria reduction of to only one monolayer.

For practical application of ceria-based catalysts in Di-Air system, it might be beneficial to add promoters (for example noble metals) that allow these catalysts to convert hydrocarbons introduced by high frequent fuel injections at lower temperatures.
References


Fundamental understanding of the Di-Air system II: The role of ceria in NO reduction

Care and diligence bring luck.

Thomas Fuller
4. The role of ceria in NO reduction
The temporal analysis of products (TAP) technique was used to study the NO reduction to N₂ over H₂- and C₃H₆-reduced La-Zr doped ceria at 560°C. (La-Zr doped) ceria is found to be capable of fuel oxidation and NO reduction. NO dissociates on oxygen anion vacancies, thereby refilling these vacancies with oxygen anions and forming N₂. The carbonaceous deposits formed upon catalyst reduction by C₃H₆, are oxidized by oxygen species originating from the ceria lattice. This recreates oxygen anion vacancies, which enables substantial additional NO reduction. These findings may open a new perspective on the understanding of DeNOₓ by hydrocarbons.

This chapter is based on the following publications:

Y. Wang, J. Posthuma de Boer, F. Kapteijn, M. Makkee, ChemCatChem 8, 102 (2016)
Y. Wang, J. P. de Boer, F. Kapteijn, and M. Makkee, Topics in Catalysis 59, 854 (2016)
4.1. Introduction

NO$_x$ abatement of the more fuel economic lean-burn engine remains a challenge. Future Euro 7 automotive legislation is anticipated to involve a further reduction of NO$_x$ emissions compared to the current Euro 6 standards Figure 1.6 (Chapter 1). In addition, the more realistic Worldwide harmonized Light vehicles Test Procedures (WLTP) is expected to replace the outdated and unrealistic New European Driving Cycle (NEDC) of 1990. In order to comply with the anticipated Euro 7 standard, for a typical diesel exhaust composition, approximately 200 ppm NO has to be reduced to 10 ppm NO in competition with an excess of 5% O$_2$, 5% CO$_2$, and 5-10% H$_2$O. Extremely efficient exhaust emission after-treatment technologies will be required to meet future more stringent NO$_x$ regulation. The Di-Air (Diesel NO$_x$ after treatment by Adsorbed Intermediate Reductants) system, developed by Toyota, opts to meet these future NO$_x$-emission standards [1, 2]. The scheme of the Di-Air system is shown in Figure 1.14 (Chapter 1).

Short fuel rich periods are created by the direct injection of fuel into the exhaust upstream of an NSR (NO$_x$ storage reduction) catalyst (Pt/Rh/Ba/K/Ce/Al$_2$O$_3$) at temperatures above 350°C. By using the same amount of fuel, high-intensity injections were shown to be more efficient in the reduction of NO$_x$ as compared to low intensity or continuous fuel injection and/or post injection directly into the engine. How this system works remains a mystery. Currently, the DeNO$_x$ mechanism remains controversial [3]. The reported key step is either: (a) the dissociative adsorption of NO on reduced catalytic sites [4], or (b) NO$_2,\text{ad,r}$ -NCO and -CN intermediate formation [5, 6]. In the Di-Air system, several catalyst components are involved, this makes the elucidation of which catalyst component(s) play(s) a major role in the reduction of NO$_x$ a difficult task. What the role of each catalyst component is and why the Di-Air system can achieve its performance both remain unresolved.

In order to further develop and optimize this system, a detailed investigation with regard to the catalyst composition and final operation in practice is required. The Di-Air system has a complex reaction network with several interacting components and intermediates. The occurrence of mass-transport limitations and non-isothermal effects make meaningful bench-scale reactor tests and the data interpretation a non-trivial task. The dynamic nature of the Di-Air system makes it an ideal system to be explored by a pulse-
response technique, *e.g.*, Temporal Analysis of Products (TAP). TAP is a vacuum pulse-response technique developed to investigate gas-solid interactions with the aim to reveal the complex mechanism of catalytic reactions [7]. A more detailed description of the used TAP set-up, procedural details, can be found in Chapter 2.

A commercial Zr-La doped ceria catalyst (BASF Company) was used as a model for the ceria component. The enhanced thermal stability provided by Zr doping [8] is believed to be vital in obtaining consistent and reliable results. For undoped ceria, a significant decrease in the surface area was observed between 550 and 750 °C under air, vacuum or reducing environments [9]. In separate experiments with undoped ceria, we observed sintering of the ceria as a function of time on stream. Furthermore, the addition of Zr is reported to increase the lattice oxygen mobility and reactivity [10]. The addition of La into the ceria structure is also believed to enhance lattice oxygen diffusion [11].

### 4.2. Experimental

#### 4.2.1. Catalyst characterisation

##### 4.2.1.1. N₂ adsorption

Tristar II 3020 Micromeritics was used to determine the textural properties like specific BET surface area and pore volume. The catalyst samples were degassed at 473 K for 16 h in a vacuum (0.05 mbar) before the nitrogen adsorption at liquid nitrogen temperature.

##### 4.2.1.2. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Approximately 50 mg of samples were destructed in 4.5 mL 30% HCl + 1.5 mL 65% HNO₃ using the microwave. The destruction time in the microwave was 120 min at max. power (90 W). After destruction, the samples were diluted to 50 mL with Millipore-Q (purified demi) water. The samples were analysed with ICP-OES (PerkinElmer Optima 5300).
4.2.1.3. X-Ray photoelectron spectroscopy (XPS)

XPS measurements were recorded on a K-alpha Thermo Fisher Scientific spectrometer using monochromated Al Kα X-ray source. A flood gun was applied for charge compensation. Lorentz function was used to analyse the peak intensities. Binding energies were calibrated with C(1s) at 285 eV as a reference.

4.2.1.4. X-ray diffraction (XRD)

The Powder X-Ray diffraction (XRD) was recorded by a Bruker-AXS D5005 with a Co Kα source. The data was three times collected by varying the 2θ angle from 5° to 90° with a step size of 0.02.

4.2.1.5. Transmission electron microscope (TEM)

Transmission Electron Microscopy (TEM) images were recorded on a JEM-2100P electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples dispersed in ethanol and deposited onto a carbon-coated copper grid, shortly dried in air and then quickly moved into the vacuum system of the microscope.

4.2.2. Catalytic testing

4.2.2.1. TAP pulses experiments

All experiments were performed with the same catalyst Zr-La doped ceria sample, of which 21.2 mg was packed between two quartz particle (150-212 μm) beds. In all experiments a starting pulse size of approximately $1.6 \times 10^{15}$ molecules was used, the pulse size gradually decreases during an experiment as the reactant is pulsed from the closed and calibrated volume of the pulse-valve line. Prior to a ceria reduction, the catalyst was firstly re-oxidized at the same temperature at which the reduction was to be performed, using pulsing of 80 vol.% O₂ in Ar until a stable O₂/Ar signal ratio was obtained. The reduction of ceria was carried out by pulsing reductant quantities of 80 vol.% C₃H₆ in Ne, 80 vol.% CO in Ar or 67 vol.% H₂ in Ar until a stable reactant and product to internal standard signal ratio indicated that the catalyst was stablised. NO pulse experiments were performed using
4.3. Result and discussion

Table 4.1: Bulk and surface composition of La-Zr-doped ceria

<table>
<thead>
<tr>
<th>Metal atom fraction</th>
<th>Ce</th>
<th>La</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>0.64</td>
<td>0.15</td>
<td>0.21</td>
</tr>
<tr>
<td>Surface</td>
<td>0.63</td>
<td>0.03-0.04</td>
<td>0.34</td>
</tr>
</tbody>
</table>

80 vol.% NO in Ar or $^{15}$N (without internal standard) and were continued until the product distribution did not change any more. The reactor’s inertness was confirmed by pulsing all employed reactants and major products over a quartz packed reactor at 580°C, no detectable conversion into products, e.g., N$_2$, CO, CO$_2$, H$_2$O, and H$_2$ was observed.

4.2.2.2. Operando Raman

Operando Raman spectra (Renishaw, 2000) were recorded using a temperature controlled operando Raman cell (Linkam, THMS 600). Ten scans were collected for each spectrum in the 100 - 4000 cm$^{-1}$ range using a continuous grating mode with a resolution of 4 cm$^{-1}$ and scan time of 10 s. The spectrometer was calibrated daily using a silicon standard with a strong band at 520 cm$^{-1}$. The ceria was firstly pre-treated by C$_3$H$_6$ (1000 ppm in N$_2$, flow rate 200 mL/min) for 2 h. N$_2$ was used to flush the cell for 20 min. Subsequently, NO (1000 ppm NO in N$_2$, the flow rate of 200 mL/min) was admitted to the cell.

4.2.2.3. Flow reactor

100 mg catalyst was placed in a 6 mm inner-diameter quartz reactor tube. A feed composition of NO (with He for balance) was used with a flow rate of 50 mL/min. The reactor effluent was online analyzed by quadrupole Mass Spectrometry (MS, Leiden probe microscopy, TPM T100 Gas Analyser).
Table 4.2: BET area and pore volume of ceria exposed to different conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET (m²/g)</th>
<th>Pore volume (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh sample</td>
<td>65</td>
<td>0.37</td>
</tr>
<tr>
<td>Aged sample¹</td>
<td>65</td>
<td>0.38</td>
</tr>
<tr>
<td>Spent sample²</td>
<td>63</td>
<td>0.33</td>
</tr>
</tbody>
</table>

4.3. Result and discussion

4.3.1. Catalyst characterization

The bulk and surface composition of La-Zr-doped ceria (afterward note as doped ceria), determined by ICP-OES and XPS, respectively, shows that the surface contains hardly any La and enriches with Zr (Table 4.1) as compared to the bulk the surface. The doped ceria sample was thermally stable, as evidenced by the BET area (Table 4.2).

The TEM image (Figure 4.1A) indicated that the crystal size of this sample was approximately 5.0 ± 0.6 nm. The XRD pattern of the doped ceria sample (Figure 4.1B) showed the fluorite cubic structure (JCPD number: 43-1002), with dominant exposed (111) planes. The crystallite size of the doped ceria sample was calculated to be 5.0 ± 0.1 nm based on the Scherrer equation (Equation 4.1):

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

With:

- \( D \): crystallite size
- \( \lambda \): X-ray wavelength 0.1789 nm
- \( K \): the particle shape factor 0.94
- \( \beta \): the full width at half height of the (111) reflection

The particle size calculated from Scherrer equation fitted well with the TEM result. A perfect ceria with (111) crystal plane exposure was created as

1 The aged sample is thermal treated in the static air environment at 650 °C for 24 h
2 The spent sample is obtained after several reaction cycles of \( \text{C}_6\text{H}_6 \) oxidation and NO reduction at 580 °C for 10 days
4.3. Result and discussion

a model of Zr-La doped ceria, as shown in Figure 4.2. As the (111) crystal plane is a stoichiometric O-Ce-O tri-layer (0.316 nm) stacked along the [111] direction, assuming a perfect cubic crystal structure, the number of O-Ce-O tri-layer was determined to be 16 (111) layers in one single crystal, using the Equation 4.2:

\[ n = \frac{\text{crystalsize}}{0.316 \text{ nm}} \]  \hspace{1cm} (4.2)

The hypothetical ceria layers concept is introduced in order to obtain insight in the reactivity of the actual surface as a function of the degree of reduction (surface oxidation state). We regard one O-Ce-O tri-layer on the (BET) surface as one hypothetical ceria layer.

The total number of hexagonal surface units on the (BET) surface (Figure 4.2) is calculated to be \(3.6 \times 10^{18}\) using the Equation 4.3:

\[ N = \frac{S_{\text{BET}} \times W_{\text{sample}}}{S_{\text{hexagonal unit}}} \]  \hspace{1cm} (4.3)

\(S_{\text{BET}}\): 65 m\(^2\)/g

\(W_{\text{sample}}\): 21.2 mg

\(S_{\text{hexagonal unit}}\): 0.38 nm\(^2\)

The total number of O atoms in each hypothetical ceria layer can be calculated to be \(2.2 \times 10^{19}\) using the Equation 4.4:

\[ N_{\text{Total O}} = N \times n \]  \hspace{1cm} (4.4)

where \(n\) represents the number of oxygen atoms in one hexagonal unit. The number of oxygen atoms in one hexagonal unit is 6.

Assuming that Zr and La are Ce, a maximum of 25% of the number of O ions in each crystal layer can be reduced, according to the Equation 4.5:

\[ \text{CeO}_2 \leftrightarrow \text{CeO}_{1.5} + \frac{1}{2} \text{O} \]  \hspace{1cm} (4.5)

The number of reducible oxygens in one hypothetical ceria layer is calculated to be \(5.4 \times 10^{18}\) atoms.
4. The role of ceria in NO reduction

Figure 4.1: TEM image of Zr-La doped ceria, and (B) XRD pattern of a fresh Zr-La doped ceria.

Figure 4.2: (a) top view of the (111) crystal plane, (b) side view of the (111) crystal plane (red: O, light yellow: Ce).
Figure 4.3: Reactant and product evolution during the NO pulse experiment over H$_2$ pre-reduced doped ceria at 560 °C.

Table 4.3: Summary of H$_2$ and hydrocarbon pre-treatment and NO re-oxidation.

<table>
<thead>
<tr>
<th></th>
<th>Reduction stage</th>
<th></th>
<th>Re-oxidation stage</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$ (560 °C)</td>
<td>C$_3$H$_6$ (560 °C)</td>
<td>NO (560 °C)</td>
<td>NO (560 °C)</td>
</tr>
<tr>
<td>Oxygen extraction(atoms)</td>
<td>5.2·10$^{18}$</td>
<td>1.1·10$^{19}$</td>
<td>6·10$^{18}$</td>
<td>1.1·10$^{19}$</td>
</tr>
<tr>
<td>Hypothetical reduced ceria layers</td>
<td>1</td>
<td>1.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carbon deposited (atoms, wt% on ceria)</td>
<td>-</td>
<td>3·10$^{19}$ (3.3 wt%)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
4.3.2. Catalytic Testing

4.3.2.1. NO pulses over H\textsubscript{2} re-reduced doped ceria

Nover (pre- or re-) oxidized doped ceria did not show any reactivity. The product evolution observed for NO reduction over the H\textsubscript{2} reduced catalyst is shown in Figure 4.3. The pre-reduction by H\textsubscript{2} led to a (clean) reduced doped ceria from which $5.2\cdot10^{18}$ oxygen atoms were extracted, corresponding to 1 hypothetical reduced ceria layer. Subsequent NO pulses showed full NO conversion with N\textsubscript{2} as the only observed product for 1 to 0.5 hypothetical reduced ceria layers. At this stage, approximately 25% of the converted NO was not released as N\textsubscript{2} but had accumulated on the surface.

After that stage, an enhanced N\textsubscript{2} production was observed for each NO pulse. The N mass balance of the whole NO pulse experiment closed within 98%, indicating that all accumulated N was converted to N\textsubscript{2}. There was no evidence of any N\textsubscript{2}O or NO\textsubscript{2} formation. In total $6.0\cdot10^{18}$ oxygen atoms were incorporated into the catalyst, which is within experimental error (oxygen mass balance closed within 90%) equal to the number of oxygen atoms extracted during H\textsubscript{2} reduction (Table 4.3). This observation suggests that NO conversion is favored on a reduced surface, whereas an oxidized surface is hardly active.

An attractive mechanism to explain the current observations is the direct dissociation of adsorbed NO on oxygen anion vacancies, in which the O side of NO fills the oxygen anion vacancy, and the N species recombine to form N\textsubscript{2} [4, 12, 13].

4.3.2.2. NO pulses over C\textsubscript{3}H\textsubscript{6} re-reduced doped ceria

In the Di-Air system, the high-frequency direct fuel injection upstream of the catalyst will create a local reducing environment. In order to simulate such an environment, C\textsubscript{3}H\textsubscript{6} pulses were used to pre-reduce the catalyst. This C\textsubscript{3}H\textsubscript{6} pulse experiment resulted in the extraction of $1.1\cdot10^{19}$ oxygen atoms, corresponding to 1.8 hypothetical reduced ceria layers. In addition, this C\textsubscript{3}H\textsubscript{6} reduction led to the deposition of $3.4\cdot10^{19}$ carbon atoms (3.3 wt.% carbon). The results of the subsequent NO pulse experiment are shown in Figure 4.4.
Figure 4.4: Reactant and product evolution during the NO pulse experiment over C$_2$H$_6$ pre-reduced Zr-La doped ceria at 560°C (A) with pulse number; (B) with the number of hypothetical reduced ceria layers during stage I of (A).
In stage I of Figure 4.4A, corresponding with 1.8-0.5 hypothetical reduced ceria layers (Figure 4.4B), full NO conversion was observed with \( \text{N}_2 \) as the main observed product (hardly any \( \text{CO} \) formed). This finding was confirmed by an isotopic \( ^{15}\text{N} \) pulse experiment, in which \( 15\text{N}_2 \) (mass 30) was observed as the major product with hardly any \( \text{CO} \) or \( \text{CO}_2 \) formation (Figure 4.5A). The oxygen balance indicated that \( 8.7 \cdot 10^{18} \) oxygen atoms accumulated during this stage, which is around 80% of the oxygen atoms extracted from the ceria lattice in the previous \( \text{C}_3\text{H}_6 \) pulse experiment. This indicates that at this point the catalyst had been largely re-oxidized by NO. Similar as in the \( \text{H}_2 \) pretreatment, not all converted NO emerged directly as \( \text{N}_2 \), approximately 40% of the N species had accumulated. In stage II, the evolution of \( \text{CO}_2 \) was observed. This evolution of \( \text{CO}_2 \) was closely followed by a temporary decrease in the NO conversion. The NO conversion increased again during stage III. In stage IV full NO conversion was observed, while \( \text{N}_2 \) and \( \text{CO}_2 \) were the only observed products, per 2 converted NO molecules approximately 1 \( \text{CO}_2 \) and 1 \( \text{N}_2 \) molecule was formed. In stage V, a progressive decrease in the NO conversion was observed, which dampened when it approached zero conversion. The \( \text{N}_2 \) and \( \text{CO}_2 \) production followed the same trend as the NO conversion. No or hardly any \( \text{N}_2\text{O} \) or \( \text{NO}_2 \) were formed and no traces of -CN or -CNO were observed.

The observed accumulation of N species diminished with increasing pulse number. Up to stage IV, 13% of the N species had accumulated on the surface. The N mass balance of the whole NO pulse experiment closed within 94%, indicating that the N species arising from NO dissociation were almost entirely released as \( \text{N}_2 \). For the \( \text{C}_3\text{H}_6 \) reduction pre-treatment N accumulation was 1.6 times higher as compared to the \( \text{H}_2 \) reduction pre-
treatment. The accumulation of N may be related to that either (a) the recombination of N is affected by the presence of deposited carbon; or (b) more oxygen defect sites were present, e.g. ionic N species [13] are located in these oxygen defect sites. As this accumulation of N species was also evidenced in the NO pulse experiment over the H₂ reduced catalyst, it is unlikely that these accumulated N species were present in the form of -CNO or -CN as proposed by Toyota [1]. Detailed studies of the accumulated N species and their roles in the reduction of NO will be the subject of future articles (part of it will be discussed in Chapter 5).

The absence of oxidation products CO and CO₂ in stage I indicates that the carbonaceous residues, left on the surface after C₃H₆ pre-reduction, were not directly participating in the reduction of NO to N₂. NO dissociated on oxygen anion vacancies, as was also found for the H₂ reduction pre-treatment. NO dissociation resulted in a progressive re-oxidation of the catalyst with increasing NO pulse number (Figure 4.4B), thereby decreasing the number of oxygen anion defect sites. The start of CO₂ formation at the point at which the catalyst was largely re-oxidized suggests that at a specific catalyst oxidation state the La-Zr doped ceria catalyst becomes active in the oxidation of these deposited carbonaceous residues. The oxidation of these carbonaceous deposits creates two oxygen anion vacancies per formed CO₂ molecule, allowing the formation of one N₂ molecule from 2 NO molecules. This delayed CO₂ formation starts to counteract the depletion of oxygen anion vacancies that caused the temporary decline in NO conversion.

That oxygen species originating from lattice oxygen are responsible for the oxidation of carbon [14] was evidenced by an ¹⁸O₂ pulse experiment (Figure 4.5B), in which the initial exclusive formation of C¹⁶O and C¹⁶O₂ indicated that gas-stage oxygen was not directly involved in the oxidation of these carbon deposits. In summary, NO re-oxidizes the catalyst and is not directly involved in the oxidation of carbonaceous deposits. The oxidation of carbonaceous deposits to CO₂ by oxygen species originating from lattice oxygen recreates oxygen anion defect centres responsible for additional NO dissociation. Therefore, these carbonaceous deposits can be seen as a delayed or stored reductant.
4.3.2.3. Operando Raman

As TAP is a vacuum technique, operando Raman (at atmospheric pressure) is applied to confirm the results obtained from TAP. NO reduction is performed over C\textsubscript{3}H\textsubscript{6} pre-treated La-Zr doped ceria both at 560 °C and is shown in Figure 4.6. The band at 460 cm\textsuperscript{-1} is attributed to the symmetric stretch mode of the Ce-O\textsubscript{8} crystal unit, which is characteristic for the reduced fluorite ceria structure [15]. This peak disappears during the C\textsubscript{3}H\textsubscript{6} pre-treatment, while under NO flow the increase in the intensity of the band at 460 cm\textsuperscript{-1} indicates that the pre-reduced La-Zr doped ceria catalyst is re-oxidised by NO. The bands at 1575 and 1350 cm\textsuperscript{-1} are assigned to G band and D band of carbon in the form of graphene or graphite [16]. The G band is usually assigned to zone centre phonons of E\textsubscript{2g} symmetry of the perfect graphite structure, and the D peak is a breathing mode of A\textsubscript{1g} symmetry, this mode is forbidden in a perfect graphite structure and only becomes active in the presence of structural defects and disorders [16]. The intensity of D band and G band of graphene/graphite remains constant during the first 270 min of NO/N\textsubscript{2} flow, indicating that the oxidation of carbon commences much later than the re-oxidation of the ceria. This observation also points out that the oxidation of carbon is via an oxygen species originating from the lattice and not from gas stage NO, in line with previous findings in the oxidation of soot on ceria-based catalysts [14].
Figure 4.6: *Operando* Raman spectra of C$_6$H$_6$ reduced ceria upon exposure to NO (1000 ppm) at 560 °C. Raman spectra of the band at (A) 460 cm$^{-1}$ and (B) 1575 and 1350 cm$^{-1}$; (C) Raman bands intensity of 460, 1575, and 1350 cm$^{-1}$ responses versus time.
The inventors of the Di-Air system attributed the exceptional behaviour of their system to the formation of hydrocarbon -CN and -CNO type intermediates. In the current study, in which the presence of hydrocarbons and NO are decoupled, we found a similar behaviour for the hydrogen reduced and the hydrocarbon reduced (Zr-La doped) ceria. Hydrocarbon pre-reduced outperforms $H_2$ pre-reduced La-Zr doped ceria by a factor of 15, due to the deeper degree of reduction and the presence of carbon deposits. Also CO pre-reduced ceria was less effective by a factor of 13. We found no evidence that hydrocarbon residues or carbonaceous residues play a direct role in the NO conversion. However, these carbonaceous residues extend the effectiveness of the catalyst in the decomposition of NO under fuel lean conditions by recreating new oxygen anion vacancies. Toyota’s observation, that large hydrocarbon pulses are beneficial [1, 2] can be explained by the formation of these carbon deposits, which are preferentially oxidized to $CO_2$ by oxygen species originating from lattice oxygen.

4.4. Conclusions

La-Zr doped ceria is a promising catalyst for a Di-Air system. Oxygen anion vacancies in La-Zr doped ceria are responsible for the decomposition of NO to $N_2$, thereby re-oxidizing these centers. The delayed oxidation of carbon deposits by oxygen species originating from lattice oxygen will in practice maintain a reduced surface state during fuel lean conditions. These carbon deposits can, therefore, be seen as a stored reductant with a delayed function. Our work, therefore, provides an alternative view on the role of hydrocarbons in the reduction of NO to $N_2$. Additional catalyst composition optimization may be considered in order to enhance the hydrocarbon activation capability at lower temperatures ($< 500 \, ^\circ C$).
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Evaluation the role of noble metals in $\text{NO}_x$ reduction in the Di-Air De$\text{NO}_x$ system

Success is no accident. *It is hard work, perseverance, learning, studying, sacrifice and most of all, love of what you are doing or learning to do.*

Pele
5. The role of noble metals
Oxygen vacancies of reduced ceria are extremely selective sites in the catalytic conversion of NO into N₂ for the Di-Air deNOₓ system, that will surpass by far commercially applied lean burn engine DeNOₓ systems. The noble metals Pt and Rh promote the ceria reduction by hydrocarbons C₃H₆ and C₃H₈, at lower temperatures than without these metals. Rh was a more active promoter in ceria reduction and carbon deposition than Pt. During the NO reduction the pre-reduced ceria support becomes gradually oxidized and after filling 70-80% of the oxygen vacancies the NO starts to appear in the product mixture. In the presence of carbon deposit the lattice oxygen of the ceria reacts with the carbon keeping the ceria in a reduced form, sustaining the NO decomposition process as long as the carbon is present. The reduction of NO over pre-reduced noble metal/ceria showed a selective formation N₂, while N₂O and NO₂ formation were never observed. During the NO reduction process some unidentified N-species remain on the catalyst, the amount depending on the catalyst, but finally all nitrogen is released as N₂. More importantly, the presence of noble metal leads to a faster N₂ formation rate than over the bare ceria.

This chapter is based on the following publication:
Y.Wang, F. Kapteijn, and M.Makee, Evaluation the role of noble metals in NOₓ reduction in the Di-Air DeNOₓ system (underreview)
5. The role of noble metals

5.1. Introduction

Nitrogen oxides (NO\textsubscript{x}) are harmful gasses which caused every year premature deaths of millions of people [1, 2]. Around 40% of the total NO\textsubscript{x} released into the atmosphere originated from road transport [1, 3]. The actual average of NO\textsubscript{x} emissions from the cars on the road is six to eight times more than the actual emission requirement [4]. Therefore, as of September 2017, the European Commission will proclaim that the real driving emission (RDE) will partially replace the current laboratory test in order to introduce new car models into the market [5]. However, up to 2.1 times higher NO\textsubscript{x} emission (0.168 g/km), relatively to the current Euro 6 NO\textsubscript{x} emission standard (0.08 g/km), is allowed under the RDE testing by September 2017 [5]. The fact that a higher NO\textsubscript{x} emission by the new rule in 2017 is allowed indicating that currently available technologies: Urea- Selective Catalytic Reduction (SCR)\[6–8\], NO\textsubscript{x} Storage and Reduction (NSR) \[9–11\] and combinations thereof still need to be significantly improved. In future, it can be anticipated that the NO\textsubscript{x} emission will become even more stringent. Therefore, more efficient or alternative exhaust emissions after-treatment technologies will be required. Di-Air system \[12\], developed by Toyota Motor Company, showed promise to meet the future NO\textsubscript{x} emission standards under real driving test conditions. The Di-Air system retains high NO\textsubscript{x} conversion levels (above 80%) even up to 800 °C and high gas hourly space velocities (GHSV) up to 120.000 L/L/h. Short fuel rich and long fuel lean periods are created by the directly injecting hydrocarbons (HC’s) at a high frequency downstream of the engine in the exhaust system upstream of a complex NSR catalyst (Pt/Rh/Ba/K/Ce/Al\textsubscript{2}O\textsubscript{3}) \[12, 13\]. Investigation on the role of each catalyst component is essential for understanding how the system works and its further improvement.

Ceria was a critical catalyst ingredient in the Di-Air system due to its redox properties and it can act as an oxygen buffer \[14\]. The lattice oxygen released during ceria reduction can react with hydrocarbon, CO, and H\textsubscript{2} under rich (fuel injection) conditions \[15, 16\]. HC’s injection is essential to create a deep reduction of ceria and deposition of carbon on ceria \[15\]. Oxygen vacancies (reduced ceria) were found able to selectively convert NO into (di)nitrogen (N\textsubscript{2}) \[14\], even in the presence of an excess of oxygen \[17\] and CO\textsubscript{2} (Chapter 7). The deposited carbon was oxidised by oxygen species...
from the lattice oxygen of ceria under oxidative conditions, recreating new oxygen anion vacancies, thereby increasing substantially the NO reduction capacity.

The temperature required for the reduction of the applied unpromoted ceria composite by hydrocarbon (HCs), however, needed to exceed 500 °C for C₃H₆ and 540 °C for C₃H₈ used as reductant. The reactivity of oxygen in the ceria lattice is too low to activate the C₃H₆ and C₃H₈ at temperatures below 500 °C [15]. Considering automotive conditions, especially during the cold start, the reduction of ceria may be difficult. For practical application of ceria-based catalysts it may be beneficial to add promoters, e.g., noble metals that could assist ceria reduction at lower temperatures. After hydrocarbon treatment of ceria at 300 °C Yao and Yao [16] found no oxygen storage capacity (OSC) and a limited capacity at 400 °C, meaning that HCs cannot reduce surface oxygen of ceria at temperatures below 300-350 °C. After addition of Pt, Pd, or Rh to ceria, however, a substantial OSC even at 300 °C was evidenced. Much research has been performed on ¹⁸O/¹⁶O isotope exchange, a common method used to study the adsorption/desorption properties of oxygen and the participation of lattice oxygen from ceria in oxidation reactions, either by using ¹⁸O₂ or C¹⁸O₂ over the ceria and noble metal loaded ceria [18, 19]. The presence of noble metals was found to accelerate the exchange rate of oxygen from either ¹⁸O₂ or C¹⁸O₂ in the lower temperature range as compared to bare ceria. Although improved oxygen exchange phenomena are no direct evidence for affecting reduction, it is an indication that the presence of noble metals may affect the reactivity of oxygen from the ceria lattice with HCs or carbonaceous deposits in the absence of gas-phase O₂.

The aim of this study is to investigate the role of noble metals on ceria for its reduction by HCs and performance in subsequent NO reduction. For this purpose, C₃H₆ and C₃H₈ were used as a model of fuel. Temporal Analysis of Products (TAP) was mainly used for the quantification of the degree of reduction of the ceria support and the NO reduction mechanism. Additionally, operando Raman spectroscopy performed in a fixed bed reactor was applied to support the TAP results.

A commercial Zr- and La-doped ceria is used as a model ceria system mainly for its high hydrothermal stability and enhanced oxygen lattice diffusion [14,
5. The role of noble metals

5.2. Experimental

5.2.1. Materials preparation

Pt/ceria and Rh/ceria, aimed at 0.5wt.% loading were prepared via an incipient wetness impregnation method on Zr-La doped ceria (a gift of Engelhard, now BASF, further denoted as ceria). The bulk atomic ratio of Ce, La and Zr is 0.64 : 0.15 : 0.21. Tetra-ammine platinum (II) nitrate and rhodium(III) nitrate hydrate purchased from Sigma-Aldrich, were used as precursors. Subsequently, the samples (thin layer in a crucible) were dried at 110°C overnight and calcined at 550°C for 5h in a static air furnace.

5.2.2. Characterisation

5.2.2.1. N$_2$ adsorption

N$_2$ adsorption at 77 K (Tristar II 3020) Micromeritics was used to determine the textural properties like BET area and pore volume. The catalyst samples were pretreated by degassing at 473 K for 16h in vacuum (0.05 mbar).

5.2.2.2. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Approximately 50 mg of samples were digested in 4.5 mL 30% HCl + 1.5 mL 65% HNO$_3$ using microwave irradiation for 120 min at max. power (900 W). After the destruction, the samples were diluted to 50 mL with Millipore-Q (purified demi) water. The samples were analysed with ICP-OES (PerkinElmer Optima 5300).

5.2.2.3. X-Ray photoelectron spectroscopy (XPS)

XPS measurements were recorded on a K-alpha Thermo Fisher Scientific spectrometer using mono-chromated Al Kα X-ray source. A flood gun was applied for charge compensation. Lorentz function was used to analyse the peak intensities. Binding energies were calibrated with C(1s) at 285 eV as a reference.
5.2.2.4. X-ray diffraction (XRD)

The Powder X-Ray diffraction (XRD) was recorded by a Bruker-AXS D5005 with a Co Ka source. The data was collected three times by varying the 2θ angle from 5° to 90° with a step size of 0.02.

5.2.2.5. Transmission electron microscope (TEM)

Transmission Electron Microscopy (TEM) images were recorded on a JEM-2100P electron microscope operating at 200 kV. Prior to transfer the samples into the TEM analysis chamber, the samples were dispersed in ethanol and deposited onto a carbon-coated copper grid, shortly dried in air and, subsequently, inserted into the vacuum system of the microscope.

5.2.2.6. Raman microscopy

Raman spectra of samples were collected by a Renishaw in Via Reflex confocal Spectrometer. The excitation wavelength was 325 nm. The power of each laser line was kept at about 2.5 mW to prevent local heating. The resolution of the spectrometer was 1 cm⁻¹.

5.2.2.7. Temperature programmed reaction (TPR)

TPR (H₂) of all the samples were carried out in a fixed bed reactor system connected to a thermal conductivity detector (TCD) to monitor the consumption of hydrogen by the catalyst. Catalyst samples (200 mg) were packed between SiC layers (300 - 425 μm). The sample was then reduced in a 10% H₂/Ar flow of 30 mLSTP/min by increasing temperature from room temperature to 1000 °C with a heating rate of 5 °C/min. TCD was calibrated by using CuO as a reference. A permaphure tubular drier was used to remove the water produced during the reduction step upstream of the TCD detector.

5.2.3. TAP pulse experiments between 450 °C to 500 °C

The pulse experiments were performed in an in-house developed and constructed TAP (Temporal Analysis of Products) reactor. Series of small gas pulses, typically in the order of 1·10¹⁵ molecules, were introduced in a small volume upstream of the catalyst packed bed reactor. The produced pressure
gradient over the catalyst packed bed thereby causes the molecules to be transported through the packed bed to the ultra-low vacuum at the opposite side of the packed bed. Depending on the actual amount of molecules pulsed, the transport will be in the pure Knudsen diffusion regime. In other words, the molecules interact only with the ‘walls’ (catalyst surface and reactor walls) of the system and not with each other. Upon interaction with the catalyst, molecules can be converted into different products. The evolution of the reactant and product molecules is tracked (one mass $m/e$ unit per pulse) with a high time resolution of 10 kHz using a quadrupole mass spectrometer. A careful calibration of the MS ensured a quantitative analysis, and overall mass balances could be closed within 5-15% accuracy. Details about TAP can be found elsewhere [14] and in Chapter 2.

### 5.2.3.1. Multi-pulse TAP experiment

10 mg Rh/ceria and Pt/ceria were used in the TAP reactor at 450°C. In all experiments a starting pulse size of approximately $2 \cdot 10^{15}$ molecules was used (including reactants and internal standard gas), the pulse size gradually decreases during an experiment as the reactant was pulsed from a closed and calibrated volume of the pulse-valve line. Prior to a reduction, the catalyst was firstly (re-)oxidised at the same temperature at which the reduction was performed, using pulses of 80 vol.% $O_2$ in Ar until a stable $O_2/Ar$ signal ratio downstream of the reactor was obtained. The reduction was carried out by injecting reductant pulses of either 80 vol.% $C_3H_8$ in Ne, 80 vol.% $C_3H_8$ in Ne, 80 vol.% CO in Ar, or 66.7 vol.% $H_2$ in Ar until a stable reactant and product to an internal standard signal ratio was obtained, indicating that the catalyst was ‘equilibrated’. $^{15}NO$ and $^{18}O_2$ pulse experiments were performed using 80 vol.% $^{15}NO$ in Kr, and 5 vol.% $^{18}O_2$ in He, respectively.

The consumption of the oxygen species from the catalyst and the carbon species deposited during $C_3H_8$, and $C_3H_6$ multi-pulse experiments were calculated using the Equation 5.1 and 5.2:

$$n_{O, consumed} = n_{H_2O, obs} + n_{CO, obs} + 2n_{CO_2, obs}$$  (5.1)
\[ n_{C,\text{deposited}} = 3n_{C_3H_6,\text{in}(C_3H_8,\text{in})} - 3n_{C_3H_6,\text{obs}(C_3H_8,\text{obs})} - n_{\text{CO,obs}} - n_{\text{CO}_2,\text{obs}} \]  

(5.2)

Where \( n \) is the number of molecules or atoms of the specified species observed (\text{obs}), consumed or introduced (\text{in}).

Similarly, the amount of oxygen accumulation and carbon consumption during \(^{15}\text{NO} \) pulses experiments were calculated using the Equation 5.3, 5.5 and 5.4:

\[ n_{O,\text{accumulated}} = n_{(NO,\text{in})} - n_{\text{CO,obs}} - 2n_{\text{CO}_2,\text{obs}} - n_{N_2O,\text{obs}} - 2n_{\text{NO}_2,\text{obs}} \]  

(5.3)

\[ n_{c,\text{consumed}} = -n_{\text{CO,obs}} - n_{\text{CO}_2,\text{obs}} \]  

(5.4)

\[ n_{N,\text{consumed}} = n_{(NO,\text{in})} - n_{\text{NO,obs}} - 2n_{N_2,\text{obs}} - 2n_{N_2O,\text{obs}} - n_{\text{NO}_2,\text{obs}} \]  

(5.5)

5.2.3.2. Pump-probe TAP experiments

Pump-probe TAP experiments were performed using two pulse valves to consecutively inject \(^{15}\text{NO} \) and \(^{14}\text{NO} \), respectively. Rh/ceria and ceria were used at 450 and 500 °C, respectively. Before the pump-probe experiment, multi-pulse experiments were conducted to reduce the catalysts by \( \text{H}_2 \), then \(^{15}\text{NO}/\text{Kr} \) and \(^{14}\text{NO}/\text{Ar} \) mixtures were subsequently injected in an alternating sequence, and the m/e intensity of \(^{15}\text{N}_2,^{15}\text{N}^{14}\text{N},^{14}\text{N}_2,^{14}\text{NO} \), and \(^{15}\text{NO} \) were measured during each pulse for a time interval of 5 s. The injection time was \( t = 0 \) for \(^{15}\text{NO}/\text{Kr} \) and \( t = 5 \) s for \(^{14}\text{NO}/\text{Ar} \).

5.2.3.3. Single pulse TAP experiments

Single pulse TAP experiments were performed to investigate the interaction of \( \text{N}_2 \) with the catalyst bed using one single pulse of \( \text{N}_2 \) over the catalyst. The study of \( \text{N}_2 \) interaction with oxidised catalyst was conducted by pulsing \( \text{N}_2 \) over a pre-oxidised catalyst at 450 °C. For the study over a reduced catalyst, 10000 pulses of \( \text{H}_2 \) were used to reduce the catalysts prior to the \( \text{N}_2 \) single pulse.
5.2.4. *Operando* Raman spectroscopy

The Raman spectroscopy measurements were performed under reaction conditions by using an AvaRaman-PRB-FC Raman probe. The catalyst sample (200 mg) was placed in a 6 mm inner diameter quartz reactor tube and downstream equipped with a mass spectrometer (MS, Hiden Analytical, HPR-20 QIC) and infrared (IR) spectroscopy (Perkin-Elmer, Spectrum One), both for gas analysis. For the IR analysis a gas cell with KBr windows with a path length of \( \sim 5 \text{ cm} \) was used. The spectra were recorded in a continuous mode using the Perkin-Elmer ‘Time-Base’ software between \( 4000 - 700 \text{ cm}^{-1} \) wavenumbers with a spectral resolution of \( 8 \text{ cm}^{-1} \) and an acquisition of 8 scans per spectrum, resulting in a time interval of 23 s between each displayed spectrum. Raman data were collected using a Kaiser Optical Systems RXN spectrometer with a diode laser operating at 532 nm and output power of 10 mW. AvaRaman-PRB-FC Raman probe was used to focus the laser beam to a spot and to collect the scattered radiation behaviour. A CCD camera was used to record the data using the Thermo Galactic Grams AI v. 7.0 software. Spectra were acquired using 2 scans at a resolution of \( 0.3 \text{ cm}^{-1} \) in the range between 100 (detector cutoff) and 4350 cm\(^{-1}\).

A feed composition of 0.2% NO (He balance) was used with a GHSV of 67,000 L/L/h. Prior to feeding NO, the catalyst was pre-treated by 1.25% C\(_3\)H\(_6\) in He for 2 h and flushed with He (200 mL/min) for 30 min afterwards, both at 500 °C.

5.3. Result

5.3.1. Characterisation

5.3.1.1. Structure and chemical composition

Characterisation details of the ceria support were reported elsewhere [14, 22]. In brief, the typical fluorite structure of ceria was confirmed by Raman and XRD. The BET area was \( 65 \pm 2 \text{ m}^2/\text{g} \). The crystal size of ceria determined by the Scherrer’s equation and TEM measurements were on average \( 5.0 \pm 0.6 \text{ nm} \).

The BET surface areas of Pt/ceria and Rh/ceria were similar to that of the support (65±2 m\(^2\)/g). Measured by the ICP-OES, the mass loadings of Pt
and Rh were determined to be 0.5 wt%. Figure 1A shows the XPS spectrum of Pt (4f). 4f7/2,5/2 peaks of PtO were observed at 71.5 and 74.9 eV with the spin-orbit splitting around 3.5 eV. 4f7/2,5/2 peaks of PtO2 were found at 74 and 77.2 eV (Figure 5.1A). These binding energies for Pt were in good accordance with the literature values [23]. Figure 5.1B shows the XPS spectrum of Rh/ceria, corresponding to the electronic transitions Rh 3d3/2 and Rh 3d5/2, with binding energies at 313 eV and 306-310 eV [24]. 307 eV and 309 eV were assigned to be the presence of Rh0 and Rh3+ of Rh 3d5/2, respectively [24, 25].

Figure 5.2A shows the XRD patterns of Pt/ceria, Rh/ceria, and the ceria support. The patterns of noble metal loaded samples show the fluorite cubic structure of CeO2. Diffraction lines due to Rh and Pt metals or to any plat-
The role of noble metals

Figure 5.3: HR-TEM and STEM micrographs of oxidised Pt/CeO$_2$ (A and B) and Rh/CeO$_2$ (C and D), respectively.

In this study, platinum oxides or rhodium oxides are not observed (below the detection of the XRD apparatus due to the low noble metal loading and the high noble metal dispersion of the ceria). The presence of a peak at around 460 cm$^{-1}$ in the Raman spectra (Figure 5.2B) was due to the characteristic fluorite peak of ceria assigned to the F$_{2g}$ mode. This peak presented a shoulder between 500 and 700 cm$^{-1}$ including contributions of vacant sites of the ceria support and MO$_x$ (PtO$_x$ or RhO$_x$) species [24, 26, 27].

Figure 5.3 shows the TEM micrographs of Pt/ceria and Rh/ceria (TEM (Figure 5.3A and C) micrographs and STEM (Figure 5.3B and D) micrographs). Pt and Rh nanoparticles were circled in red in Figure 5.3A and C, respectively. The red arrows point the presence of Pt and Rh on ceria support in Figure 5.3B and D, respectively. However, the molar mass of noble metal and ceria, however, are very close and, therefore, their contrasts were low in the STEM micrograph (Figure 5.3B and D). In combination with the low mass loadings of Pt and Rh (0.5 wt.%), the noble metal particle size distributions could not be adequately obtained.

The reduction properties of Pt/ceria, Rh/ceria, and ceria were conducted
5.3. Result

by TPR(H₂), and the results are presented in Figure 5.4. Ceria shows two peaks centred at 430 and 550 °C. It is generally accepted that the low temperature (430 °C) process is attributed to the surface reduction and the high temperature (550 °C) accounted for the bulk reduction [16]. As compared to the ceria support, the surface and bulk reduction of noble metal loaded ceria significantly shifts to a lower temperature, the maximum reduction peak is given in Table 5.1. As shown in Table 5.1, the total H₂ consumption for ceria support, Pt/ceria, and Rh/ceria is 0.31, 0.36, and 0.43 mol H₂/mol Ce. However, hydrogen consumption cannot be related to the ceria reduction, due to that H₂ is incorporated into bulk CeO₂ above 200 °C [28].

5.3.2. Multi-pulses TAP experiments

5.3.2.1. Reduction of noble metal loaded ceria by reductants

The reduction of noble metal loaded ceria catalysts was investigated by using CO, H₂, C₃H₆, and C₃H₈ as reductant in TAP. As an example for a noble metal, Figure 5.5 shows the result of C₃H₆ pulses over the pre-oxidised Pt/ceria at 450 °C. Two types of C₃H₆ reactions were observed: complete C₃H₆ oxidation and C₃H₆ oxidative cracking/dehydrogenation, as described
Table 5.1: Summary of H₂-TPR (H₂ consumption unit: mol H₂/mol Ce).

<table>
<thead>
<tr>
<th></th>
<th>First peak</th>
<th></th>
<th>Second peak</th>
<th></th>
<th>Total H₂ consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T/°C</td>
<td>H₂ uptake</td>
<td>T/°C</td>
<td>H₂ uptake</td>
<td></td>
</tr>
<tr>
<td>Ceria</td>
<td>430</td>
<td>-</td>
<td>550</td>
<td>-</td>
<td>0.31</td>
</tr>
<tr>
<td>Pt/ceria</td>
<td>215</td>
<td>0.08</td>
<td>360</td>
<td>0.28</td>
<td>0.36</td>
</tr>
<tr>
<td>Rh/ceria</td>
<td>100</td>
<td>0.07</td>
<td>265</td>
<td>0.36</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Figure 5.5: C₆H₆ pulses over a pre-oxidised 0.5 wt.%Pt/ceria at 450 °C, (A) product and reactant evolution, and (B) carbon and oxygen balance versus pulse number.
5.3. Result

in the Equation 5.6 and 5.7, respectively. C₃H₆ experienced a full conversion till pulse number 500.

\[ C₃H₆_{\text{ceria}} \rightleftharpoons CO₂ + H₂O \quad (5.6) \]

\[ C₃H₆_{\text{ceria}} \rightleftharpoons CO + H₂ + C_{\text{deposited}} \quad (5.7) \]

During the complete C₃H₆ oxidation period (pulse number 0-50), the main oxidation products were CO₂ and H₂O. Moreover, a small amount of CO was observed. The H₂ formation considerably increased after pulse number 50, accompanied by a significant decline of the H₂O formation. CO formation increased after pulse number 90, where CO₂ formation significantly dropped with pulse number. During the pulse number from 50-1000 oxidative hydrocarbon cracking was the main reaction with the formation of CO and H₂. The oxygen and carbon balances at each C₃H₆ pulse are displayed in Figure 5.5B. The formation of CO₂, H₂O, and CO caused partial reduction of ceria from Ce⁴⁺ to Ce³⁺ (Table 5.2). Carbon deposition was observed during both the complete oxidation and cracking reactions. The pulses of C₃H₈ over Pt/ceria showed a similar product evolution as that for the C₃H₆ pulses, although the C₃H₈ showed full conversion till pulse number 150. Rh/ceria showed the same trends as Pt/ceria during the both C₃H₆ and C₃H₈ pulses at 450 °C, but carbon deposits for the Rh/ceria were significantly higher than that on Pt/ceria upon the C₃H₆ pulse exposure (Table 5.2).

Additionally, the pulse of CO over noble metal loaded ceria led to the CO₂ formation. Hardly any carbon was left over during the CO pulses. Moreover, the pulses of H₂ over the noble metal loaded ceria results in the formation of H₂O. The total amount of oxygen extraction during CO and H₂ exposures can be seen in Table 5.2.

5.3.2.2. NO reduction

The reduction of NO over H₂ reduced noble metals loaded ceria support was investigated in TAP by using ¹⁵NO. Figure 5.6 shows the products and reactant evolution during the ¹⁵NO pulses over H₂ reduced Pt/ceria and Rh/ceria at 450 °C. For the Pt/ceria (Figure 5.6A), the full ¹⁵NO conversion
Table 5.2: Summary of oxygen extraction (O) and carbon deposition (C) using different reductants (unit: $10^{17}$ atoms / mg\textsubscript{cat}) at 450°C.

<table>
<thead>
<tr>
<th></th>
<th>Pt/ceria</th>
<th>Rh/ceria</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}</td>
<td>2.1</td>
<td>2.2</td>
</tr>
<tr>
<td>CO</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{6}</td>
<td>6.3</td>
<td>8.2</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{8}</td>
<td>5.8</td>
<td>6.0</td>
</tr>
</tbody>
</table>

was observed with $^{15}$N\textsubscript{2} as the exclusive product from pulse number 0 to 700. Moreover, around 70% of oxygen vacancies were refilled by $^{15}$NO before the breakthrough of $^{15}$NO. There was no N\textsubscript{2}O and NO\textsubscript{2} formation in that time frame. Similar to Pt/ceria, Rh showed full $^{15}$NO conversion till pulse number 900, where 80% of oxygen vacancies were refilled by $^{15}$NO (Figure 5.6B). $^{15}$N\textsubscript{2} was the exclusive product and no N\textsubscript{2}O and NO\textsubscript{2} formation were observed. It is noted that some nitrogen temporarily accumulated on the samples.

The NO reduction into nitrogen over the hydrocarbons reduced noble metals loaded ceria support was investigated in TAP by using $^{15}$NO, to distinguish its products from CO and N\textsubscript{2} ($m/e = 28$) and CO\textsubscript{2} from N\textsubscript{2}O ($m/e = 44$). Figure 5.7 shows the products and reactant evolution and the carbon and oxygen balance during the $^{15}$NO pulses over the C\textsubscript{3}H\textsubscript{6} reduced Pt/ceria at 450°C. As illustrated in Figure 5.7, stage I and II were used to distinguish the full $^{15}$NO conversion time interval and the time intervals where NO started to breakthrough. Stage I was subdivided into stages Ia and Ib for the CO\textsubscript{2} formation during stage I. During stage Ia (from pulse number 0 to 1000, Figure 5.7A), full $^{15}$NO conversion was observed with $^{15}$N\textsubscript{2} as the main product (negligible amount of CO formed). The evolution of CO\textsubscript{2} was observed from pulse number 1000 (stage Ib, Figure 5.7A). $^{15}$NO showed
Figure 5.6: $^{15}$NO pulse experiment over an $\text{H}_2$ reduced Pt/ceria (A and B) and Rh/ceria (C and D) at 450 °C, respectively.

Figure 5.7: $^{15}$NO pulse experiment over $\text{C}_3\text{H}_8$ reduced Pt/ceria at 450 °C, (A) products and reactant evolution and (B) carbon and oxygen balance versus pulse number.
The role of noble metals

Figure 5.8: $^{15}$NO pulse experiment over $C_2H_4$ reduced Rh/ceria at 450°C, (A) products and reactant evolution, and (B) carbon and oxygen balance versus pulse number.

full conversion until pulse number 4000 (stage I, Figure 5.7A), where $^{15}$N$_2$ and CO$_2$ were the only products. From pulse number 4000 onwards (stage II, Figure 5.7A), a progressive decline to zero for the $^{15}$NO conversion was observed. The $^{15}$N$_2$ and CO$_2$ production followed the same trend as that of the NO conversion. Neither $^{15}$N$_2$O nor $^{15}$NO$_2$ were formed and no traces of cyanide or cyanate containing species were detected. The oxygen, carbon balances and nitrogen balance were plotted as shown in Figure 5.7B. During stage Ia (pulse number 0 to 1000, Figure 5.7B), oxygen incorporation into catalyst was observed with a negligible amount of carbon consumption. The majority of the carbon conversion was found from pulse number 1000 onwards (stage Ib), accompanied by an oxygen accumulation decline. Both oxygen accumulation and carbon consumption vanished after pulse number 6000. During stage I NO was fully converted, 80% of oxygen vacancies were refilled, and 50% of the deposited carbon was oxidised. 17% of $^{15}$N was accumulated during the first 2000 $^{15}$NO pulses, followed by the accumulated $^{15}$N release during pulse number between 2000 and 6000. The N-balance closed to 90%.

The result of $^{15}$NO pulses over a $C_3H_6$ reduced Rh/ceria (Figure 5.8) showed a similar trend as that over Pt/ceria. $^{15}$NO started to breakthrough from pulse number 12000 onwards, which was 3 times larger than that over Pt/ceria. However, a small amount of CO evolution was observed during stage Ia of Rh/ceria NO conversion. During stage I (a full NO conversion period), 80% of oxygen vacancies were refilled and 90% of carbon deposits
were oxidised. Neither $^{15}$N$_2$O nor $^{15}$NO$_2$ were formed and no traces of cyanide or cyanate containing species were detected during stage I and II. Hardly any $^{15}$N accumulation before pulse number 5000. After that $^{15}$N started to accumulate up to an N/O ratio of 1. Still a persistent $^{15}$N$_2$ formation was observed after $^{15}$NO started to breakthrough until the carbon deposit had been consumed. The overall $^{15}$N balance was closed to 90%.

5.3.2.3. $^{18}$O$_2$ pulses over C$_3$H$_8$ reduced Rh/ceria

Figure 5.9 shows the product evolution for the $^{18}$O$_2$ multi-pulse experiment over C$_3$H$_8$ reduced Rh/ceria at 450°C. All introduced $^{18}$O$_2$ was completely converted until a steep oxygen breakthrough profile was observed from pulse number 30000 onwards. C$^{16}$O evolved as the main product till pulse number 10000, where C$^{16}$O$_2$ started to evolve and gradually became the main product. After 13000 pulses C$^{18}$O$^{16}$O was observed and a small amount of C$^{18}$O$_2$ was detected after pulse number 15000. After 28000 pulses C$^{16}$O, C$^{16}$O$_2$, C$^{18}$O$^{16}$O, C$^{18}$O, and C$^{18}$O$_2$ decreased to zero, where $^{18}$O$_2$, $^{16}$O$_2$, and $^{18}$O$^{16}$O started to break through in a kind of exchange equilibrium. The observed C$^{18}$O ($m/e = 30$) during pulse number 13000 to end of the pulse sequence was due to the fragmentation from C$^{18}$O$_2$ and C$^{18}$O$^{16}$O. A small amount of C$^{18}$O was also observed before pulse number 13000, where the major product was C$^{16}$O. $^{16}$O$_2$ was the main product after the oxygen breakthrough.

5.3.3. Pump probe TAP experiments

In order to investigate the rate of N$_2$ formation from NO over H$_2$ reduced ceria and Rh/ceria, pump-probe TAP experiments were performed using alternating $^{15}$NO and $^{14}$NO pulses at 450°C. The pulse size of $^{15}$NO and $^{14}$NO were both $1.5 \cdot 10^{15}$ molecules/pulse. Figure 5.10A and B shows the flux of $^{14}$N$_2$, $^{14}$N$^{15}$N, and $^{15}$N$_2$ at the exist of the reactor over a H$_2$ pre-reduced Rh/ceria. The pulse of $^{15}$NO at $t = 0$ s in the first injection cycle led to the exclusive $^{15}$N$_2$ formation with a peak position at $t = 0.056$ s and peak height at $5.5 \cdot 10^{15}$ molecules/s. The total number of $^{15}$N$_2$ molecules formed during the time interval of 5 s was calculated to be $7 \cdot 10^{14}$ molecules. The pulse of $^{14}$NO at $t = 5$ s in the 1st injection cycle resulted in the formation of a major product of $^{14}$N$_2$ with peak position at $t = 5 + 0.056$ s and $7 \cdot 10^{14}$ $^{14}$N$_2$
molecules formation during the time interval of 5 s. The peak height of $^{14}$N$_2$ was identical to the $^{15}$N$_2$ during the time period of 0-5 s. A small fraction of $^{14}$N$^{15}$N molecules, around 2-3% of $^{14}$N$_2$, were observed from $t = 5$ to 10 s. After the first injection cycle, also a small fraction of $^{14}$N$^{15}$N (2-3% of $^{15}$N$_2$) was observed during pulse of the $^{15}$NO pulses, as indicated for the 70th injection cycle (Figure 5.10B).

Figure 5.10C and D shows the flux of $^{14}$N$_2$, $^{14}$N$^{15}$N, and $^{15}$N$_2$ during the $^{15}$NO and $^{14}$NO injections for the H$_2$ pre-reduced ceria at 500 °C. The pulse of $^{15}$NO at $t = 0$ s during first injection cycle led to the exclusive $^{15}$N$_2$ formation. The total number of $^{15}$N$_2$ molecules formed during the time interval of 5 s was calculated to be $3.3 \cdot 10^{14}$ molecules. The maximum peak position of $^{15}$N$_2$ was at $t = 0.063$ s with peak height of $1.3 \cdot 10^{15}$ molecules/s. The pulse of $^{14}$NO at $t = 5$ s during the 1st injection cycle led to the formation of both $^{14}$N$_2$ and $^{14}$N$^{15}$N. During the time from $t = 5$ to 10 s, the number of $^{14}$N$_2$ and $^{14}$N$^{15}$N was calculated to be $3.7 \cdot 10^{14}$ and $2 \cdot 10^{14}$ molecules, respectively. $^{14}$N$^{15}$N was also observed during the $^{15}$NO pulses after the first injection cycle. Moreover, an increase in the intensity of $^{14}$N$_2$ and $^{14}$N$^{15}$N, and $^{15}$N$_2$ were observed during the 40th injection as compared to 1st in-

---

Figure 5.9: Product and reactant evolution versus pulse number during $^{18}$O$_2$ pulse experiment over C$_3$H$_8$ reduced Rh/ceria at 450°C.
Figure 5.10: The flux of $^{14}\text{N}_2$, $^{14}\text{N}^{15}\text{N}$, and $^{15}\text{N}_2$ during the experiment of $^{15}\text{NO}$ and $^{14}\text{NO}$ alternate pulsing over the H$_2$ pre-reduced (A and B)Rh/ceria at 450 °C and (C and D) ceria at 500 °C, measured at the exist of the reactor. The blue arrow indicated the start of a pulse of $^{15}\text{NO}$ (t=0) and the black arrow for $^{14}\text{NO}$ (t=5 s). Pulse size: $1.5\cdot10^{15}$ molecules of $^{15}\text{NO}$ or $^{14}\text{NO}$ per pulse.
Injection cycle. During 40th injection cycle, $8.8 \times 10^{14}$ molecules of $^{15}\text{N}_2$ and $8 \times 10^{14}$ molecules of $^{14}\text{N}^{15}\text{N}$ were observed during $^{15}\text{NO}$ injection from $t = 0$ to $t = 5$ s, and $5.7 \times 10^{14}$ molecules of $^{14}\text{N}_2$ and $8 \times 10^{14}$ molecules of $^{14}\text{N}^{15}\text{N}$ were observed during $^{14}\text{NO}$ injection from $t = 5$ to 10 s.

### 5.3.4. $\text{N}_2$ pulses experiments over Rh/ceria and ceria

In order to explore the interaction of dinitrogen with ceria and Rh/ceria, $^{14}\text{N}_2$ pulses experiments were performed over different oxidation state of ceria and Rh/ceria. The Ar response was used as a standard reference response curve. Figure 5.11A shows the $\text{N}_2$ and Ar response shape over the ceria at 500 °C. The $\text{N}_2$ response showed peaks at $t = 0.0672$ s both over the oxidised and $\text{H}_2$ reduced ceria. Moreover, the Ar peak located at the time of $t = 0.0803$ s. Both Ar and $\text{H}_2$ showed the same response shape but with a shift of the peak position due to the difference in molar mass affecting the Knudsen diffusion coefficient [27]. Figure 5.11B shows the $\text{H}_2$ and Ar response shape over the Rh/ceria at 450 °C. The $\text{H}_2$ response showed a peak at $t = 0.0674$ s both over the oxidised and $\text{H}_2$ reduced ceria, while the Ar peak position was at $t = 0.0805$ s.
5.3.5. **Operando** Raman study of NO reduction C\textsubscript{3}H\textsubscript{6} oxidation and NO reduction over Rh/ceria

Figure 5.12 shows *operando* Raman spectra during 1.25% C\textsubscript{3}H\textsubscript{6}/He flow at 500 °C over Rh/ceria. The broad band from 100 to 500 cm\textsuperscript{-1} was attributed to the quartz tube. The sharp intensity centered at 460 cm\textsuperscript{-1} was attributed to the symmetric stretch mode of the Ce-O\textsubscript{8} crystal unit, which was characteristic for the fluorite ceria structure \[29\]. Its intensity started to drop after the first minute of C\textsubscript{3}H\textsubscript{6} exposure and disappeared two minutes after C\textsubscript{3}H\textsubscript{6} exposure. Subsequently, two bands at 1575 and 1350 cm\textsuperscript{-1} started to appear and grew during the prolonged C\textsubscript{3}H\textsubscript{6} exposure. The bands at 1575 and 1350 cm\textsuperscript{-1} were assigned to the G band and D band of carbon \[30\]. The G band was usually assigned to zone center phonons of E\textsubscript{2g} symmetry of the perfect graphite structure and the D peak was assigned to a breathing mode of A\textsubscript{1g} symmetry, which is forbidden in a perfect graphite structure and only became active in the presence of structural defects and disorders.

Figure 5.13 shows *operando* Raman spectra for the NO reduction over C\textsubscript{3}H\textsubscript{6} reduced Rh/ceria at 500 °C. As shown in the Figure 5.13A, the sharp feature centered at 460 cm\textsuperscript{-1} was initially hardly visible and its intensity slightly increased during the first 20 min upon NO exposure. Moreover, it increased significantly after 60 min on NO stream. Subsequently, the intensities at 1575 and 1350 cm\textsuperscript{-1} strongly disappeared only after 90 min of NO exposure.
Figure 5.13: Raman spectra of the band at (A) 460 cm\(^{-1}\) and (B) 1575 and 1350 cm\(^{-1}\), (C) MS and (D) FT-IR of NO exposure over a C\(_3\)H\(_6\) reduced Rh/ceria at 500 °C.
During the *operando* Raman experiment, the gas evolution downstream the reactor was monitored with an MS and FT-IR spectrometer (Figure 5.13C and D, respectively). Full NO conversion was observed till 60 min. Only \( m/e = 28 \) was monitored, attributed from both \( \text{N}_2 \) and CO. The FT-IR data showed that CO was only formed in the initial stage of NO exposure, declining after 20 min. After 20 min, \( m/e = 44 \) assigned to \( \text{CO}_2 \) started to form. \( \text{N}_2\text{O} \) (detection limit < 1 ppm) was not observed in the FT-IR detector (Figure 5.13D). Therefore, the \( m/e = 44 \) was contributed to \( \text{CO}_2 \). Since the CO almost vanished around 30 min, the observed \( m/e = 28 \) response from 20 to 60 min was mainly attributed to \( \text{N}_2 \).

**5.4. Discussion**

**5.4.1. Reduction of noble metal loaded ceria**

Ceria is an important catalyst ingredient in the Di-Air system, since it is capable of fuel (HCs) oxidation and NO reduction. The oxygen from the ceria lattice can react with hydrocarbon, CO, and \( \text{H}_2 \), thus creating oxygen vacancies and reducing \( \text{Ce}^{4+} \) to \( \text{Ce}^{3+} \). Oxygen vacancies in reduced ceria are the catalytic sites for selectively converting NO into (di)nitrogen (\( \text{N}_2 \)), even in the presence of an excess \( \text{O}_2 \) and \( \text{CO}_2 \) (Chapter 7)[15]. However, the reduction of ceria with \( \text{C}_3\text{H}_6 \) and \( \text{C}_3\text{H}_8 \) required a temperature above 500 °C and 540 °C, respectively. Lowering the temperatures of ceria reduction by fuel is essential for an industrial application of this Di-Air DeNO\(_x\) system.

The TPR(\( \text{H}_2 \)) (Figure 5.4 and Table 5.1) shows that the noble metal loading onto the ceria support lowered the reduction temperature of the ceria support as compared to the ceria support. This shift in reduction temperature may be associated with the \( \text{H}_2 \) splitting on the noble metal and the existence of strong metal-support interaction, increasing the reactivity of lattice oxygen [31]. The high intensity in the range of 500 and 700 cm\(^{-1}\) on Rh/ceria from Raman spectroscopy (Figure 5.2B) indicated a stronger interaction between noble metal and ceria.

As shown in Figure 5.5, \( \text{C}_3\text{H}_6 \) and \( \text{C}_3\text{H}_8 \) experienced full conversion over Pt/ceria for a pulse number of 100 and 50, respectively. A complete oxidation to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) was observed during both \( \text{C}_3\text{H}_6 \) and \( \text{C}_3\text{H}_8 \) pulses, followed by a cracking reaction to \( \text{CO}, \text{H}_2, \) and carbon deposition. The total number of
The role of noble metals

Oxygen extraction from Pt/ceria by C_3H_6 and C_3H_8 was around 6.3 \times 10^{17} and 5.8 \times 10^{17} oxygen atoms/mgcat (Table 2), respectively. Additionally, 2.8 \times 10^{17} and 1.3 \times 10^{17} carbon atoms/mgcat were deposited after using C_3H_6 and C_3H_8 as reductant, respectively. So C_3H_6 pulsing led to around 2 times higher carbon deposition than C_3H_8 pulsing. Apparently, the reduction by C_3H_6 or C_3H_8 of an oxidised noble metal loaded ceria followed a similar process, but resulted in different carbon deposits. Dehydrogenation and cracking of C_3H_6 was easier than that of C_3H_8 due to the strong electron-rich π-orbital interactions on Lewis acid sites \[20\], resulting in more carbonaceous deposit.

Pulsing C_3H_6 and C_3H_8 over Rh/ceria showed similar trends over Pt/ceria, which experienced both complete oxidation and cracking reaction. The total number of oxygen extraction from Rh/ceria by C_3H_6 and C_3H_8 were similar to that of Pt/ceria. However, the amounts of deposited carbon over Rh/ceria was around 3 times larger than on Pt/ceria when using C_3H_6 as a reductant. Furthermore, the operando Raman experiment of passing 1.25% C_3H_6/He gas stream over Rh/ceria at 500 °C (Figure 5.13) showed that the reduction of the ceria support occurs firstly, followed by the subsequent deposition of carbon.

The ceria support was not reactive for C_3H_8 and only slightly active for C_3H_6 at 450 °C. The addition of noble metals to the ceria support significantly enhanced the reactivities to C_3H_6 and C_3H_8, i.e., the degree of ceria support reduction and the amounts of carbon deposition (Table 5.2). This agrees with the finding that noble metals were able to promote the oxygen mobility, surface migration, and reactivity, especially at the interface of noble metals and support \[18\].

5.4.2. Study of NO reduction

5.4.2.1. NO reduction routine and its selectivity to N_2

NO_2 and N_2O are common side products in the NO reduction technologies especially when using noble metal as an active ingredient in the catalyst composition \[32–35\]. Therefore, the study on NO reaction processes over noble metal/ceria is essential.

^{15}N_2 was the exclusive product of ^{15}NO reduction over the H_2 reduced
5.4. Discussion

Pt/ceria and Rh/ceria (Figure 5.6). After around 70-80% of oxygen vacancies was refilled by oxygen from $^{15}$NO, $^{15}$NO started to break through, while no N$_2$O and NO$_2$ was formed. This was also observed for the ceria support [14]. The presence of Pt or Rh did not affect the NO reaction selectivity, i.e., NO was selectively reduced into N$_2$. Moreover, when NO reduction was carried out over hydrocarbon reduced Pt/ceria and Rh/ceria then in the initial stage of $^{15}$NO pulsing no oxygenate gas products were observed at 450°C (Figure 5.7 for Pt/ceria). The absence of CO and CO$_2$ indicated that the carbonaceous residues, left on the surface after C$_3$H$_6$ pre-reduction, did not directly participate in the reduction of $^{15}$NO into $^{15}$N$_2$. The formation $^{15}$N$_2$ indicated that $^{15}$N-O was dissociated either on the reduced Pt or reduced ceria sites, with O filling the oxygen vacancies and $^{15}$N species associated to form $^{15}$N$_2$. The absence of $^{15}$N$_2$O indicated that $^{15}$NO was selectively reduced into $^{15}$N$_2$ on the reduced Pt/ceria over the whole range of oxidation states of the catalyst. The $^{15}$NO started to break through when 80% of the oxygen vacancies were refilled and 50% of deposited carbon was consumed (Figure 5.7B). The direct reaction between $^{15}$NO and deposited carbon can be ruled out since there was no CO$_2$ formation before pulse number 1000. Approximately, the ratio between N$_2$ and CO$_2$ was around 2 during pulse number from 1000 to 4000, clearly demonstrated that the formation of one CO$_2$ allowed two NO to be reduced into one N$_2$. Around 17% of nitrogen species accumulated on the catalyst before pulse number 2000. However, the accumulated 13% of N was released as N$_2$ from pulse number 2000 to 6000. Therefore, the deposited carbon acted as a reductant buffer. Lattice oxygen of ceria was used for the oxidation of deposited carbon to CO and CO$_2$. $^{15}$N$_2$O and $^{15}$NO$_2$ were never detectable. The direct reaction of $^{15}$NO molecules to $^{15}$NO$_2$ over reduced Pt/ceria can be eliminated as well since carbon is an excellent reductant of NO$_2$ to NO [36, 37].

The overall performance of Rh/ceria (Figure 5.8) was similar. $^{15}$NO started to break through much later than over Pt/ceria. The longer duration of the full $^{15}$NO conversion was attributed to 3 times larger carbon deposition on Rh/ceria using C$_3$H$_6$ as a reductant. This clearly demonstrated that deposited carbon acted as reductant buffer for NO reduction. NO reduction to N$_2$ ended when there was no carbon left and the catalyst was (re)oxidised. A small amount of CO was observed before the evolution of CO$_2$ started during $^{15}$NO over the C$_3$H$_6$ reduced Rh/ceria (phase I1, Figure 5.8A) in compari-
The role of noble metals

son with the case of Pt/ceria (Figure 5.7A). However, the major initial $^{15}$NO oxidation activity resulted in filling the oxygen vacancies, as evidenced by the oxygen balance and carbon balance (Figure 5.8B). Regarding the N balance, hardly any $^{15}$N accumulation before pulse number 5000. This was also demonstrated at the N$_2$ response shape I during NO pulses (Figure 5.10A and B), where 98% of injected NO was converted to N$_2$ in the time interval of 5s. Upon further oxidation of the sample the N and O accumulation in a ratio of 1:1 suggested some NO adsorption until the carbon deposit was completely removed and NO broke through.

An experiment of $^{18}$O$_2$ pulses over the C$_3$H$_8$ reduced Rh/ceria at 450°C (Figure 5.9) was performed to confirm that lattice oxygen was responsible for the oxidation of deposited carbon during stage Ib (Figures 5.7 and 5.8). The results showed hardly any C$^{18}$O and C$^{18}$O$_2$ formation prior to pulse number 13000. C$^{18}$O$^{16}$O started to evolve after pulse number 13000. The initial exclusive formation of unlabelled C$^{16}$O and C$^{16}$O$_2$ indicated that gas-stage oxygen was not directly involved in the oxidation of the carbon deposit. Lattice oxygen was the main source for the oxidation of deposited carbon.

Operando Raman (at ambient pressure flow reactor) was applied to confirm further the results obtained from TAP (ultra-vacuum system, 10$^{-9}$-10$^{-9}$ mbar) using Rh/ceria at 500°C in flow reactor coupled with Raman probe, as shown in Figure 5.13. The band at 460 cm$^{-1}$ (Figure 5.13A), attributed to the symmetric stretch mode of Ce-O$_8$ crystal unit in the oxidised catalyst [29], disappeared during the C$_3$H$_8$ reduction pre-treatment (Figure 5.12A), while it re-appeared and its intensity increased during the exposure to 0.2% NO/He. The changes of intensity at 460 cm$^{-1}$ indicated that the reduced ceria was re-oxidised during 0.2% NO/He flow. The intensities at 1575 and 1350 cm$^{-1}$, assigned to G band and D band of carbon, remained almost constant during the first 20 min of 0.2% NO/He flows (Figure 5.13B), and afterwards, these two bands completely vanished. The operando Raman results confirmed the TAP’s finding: NO mainly re-oxidised the reduced ceria, and after a sufficient degree of re-oxidation the deposited carbon started to react with the oxygen from the ceria lattice. Apparently in the flow set-up upon the C$_3$H$_8$ exposure firstly the catalyst was reduced and in second instance carbon was deposited. Upon NO exposure of the C$_3$H$_8$ pre-treated catalysts (ceria and Rh/ceria) initially the reduced catalyst was
oxidised and thereafter the carbon deposits were oxidised. This reduction-oxidation process could be completely repeated several times.

Like in the TAP reactor (Figure 5.8) CO formation was observed during the first 20 min, followed by the formation of CO₂ till 60 min (Figure 5.13C and D). N₂O and NO₂ formation was not observed. All results of this operando study (Figure 5.13) pointed out that NO was still selectively reduced into N₂ at these ambient pressure conditions. NO was dissociated on the active sites, being reduced ceria or reduced Rh sites, thereby filling the oxygen vacancies of ceria. In case of reaction on the noble metal the oxygen must have been transmitted to the ceria since this was eventually completely re-oxidised.

The investigation of NO reduction under both ultra-high vacuum TAP system and ambient pressure flow reactor pointed out that the presence of noble metal/ceria system can selectively reduce NO into N₂ [14, 15]. The conversion of NO into NO₂ was not observed on a reduced catalyst. Even NO₂ will be completely converted into N₂ when the catalyst was reduced [38]. Under all investigated (oxidative or reductive) circumstances no N₂O was detected (detection limit <1 ppm) on ceria and noble metal supported ceria. The presence of Rh and Pt on ceria can reduce the ceria at 450°C C₃H₆ and C₃H₈, but unpromoted ceria was hardly reduced by C₃H₆ and C₃H₈ at 450°C [22]. During NO reduction over the H₂ or C₃H₆ pre-reduced unpromoted ceria, up to 25% and 40% of N-species accumulation was observed, respectively. The Pt promoted ceria showed only 17% of N-species accumulation and Rh promoted ceria showed hardly (1%) N-species accumulation during the oxidation of the carbon deposit. The N/O atomic accumulation ratio in this period suggested the some kind of NO chemisorption took place (Figure 5.8B). The lower N-accumulation on Rh- and Pt/ceria indicated that these metals accelerate the N₂ release.

5.4.2.2. The effect of noble metal on N₂ formation rate

In the formation of N₂ the following steps can be distinguished: (1) NO adsorption, (2) NO dissociation, (3) N diffusion and association, and (4) N₂ desorption. Pump-probe TAP experiments with alternating ¹⁴NO and ¹⁵NO pulse were performed to explore this N₂ formation rate over ceria and Rh/ceria.
Over H\textsubscript{2} reduced ceria formation of only $^{15}$N\textsubscript{2} was observed during the first $^{15}$NO pulse (Figure 5.10C). However, the $^{15}$N\textsubscript{2} response was much broader and lower in intensity than that for the H\textsubscript{2} reduced Rh/ceria (Figure 5.10A). The same holds for the $^{14}$N\textsubscript{2} response during the $^{14}$NO injection. Both the $^{15}$N\textsubscript{2} and $^{15}$N\textsubscript{2} responses over the H\textsubscript{2} reduced ceria indicated a slow process of dinitrogen formation upon the NO pulses. This process of N\textsubscript{2} formation was so slow that some N-species were still sticking on the surface after the pulse detection time range (5 s). The observation of the mixed isotope $^{14}$N$^{15}$N during the subsequent $^{15}$NO injection suggested that stored $^{15}$N, during the $^{15}$NO injection, met $^{14}$N created after the following $^{15}$NO injection (Figure 5.10D), and recombined to $^{14}$N$^{15}$N, and vice versa for the reversed sequence. The formation of $^{14}$N$^{15}$N further proved the accumulation of N ($^{14}$N and $^{15}$N) species on the ceria surface that continue to slowly associate forming dinitrogen. The mixed isotope response is much broader and its maximum appeared also later than the dinitrogen stemming directly from the pulsed NO isotope, both evidencing a slower recombination process for these ‘dwelling’ nitrogen species.

Over the H\textsubscript{2} reduced Rh/ceria a smaller fraction of $^{14}$N$^{15}$N was observed (Figure 5.10A and B). This suggested that more N accumulated on the H\textsubscript{2} reduced ceria than H\textsubscript{2} reduced Rh/ceria. The N-balance in Figure 5.6 also suggested that less N accumulated during the NO reduction to N\textsubscript{2}. Almost all NO was converted and directly formed N\textsubscript{2} during the MS detection time range (5 s) over the H\textsubscript{2} reduced Rh/ceria before pulse number 200.

The N\textsubscript{2} formation includes NO adsorption, NO dissociation, N diffusion and association, and N\textsubscript{2} desorption. Regarding the NO adsorption, there was no $^{15}$NO or $^{14}$NO observed by the MS in the first $^{15}$NO or $^{14}$NO injection, i.e., all the $^{15}$NO or $^{14}$NO molecules were completely and irreversibly adsorbed over both H\textsubscript{2} pre-reduced Rh/ceria and ceria. Therefore, the adsorption of $^{15}$NO or $^{14}$NO could not be the cause for the slow process of $^{15}$N\textsubscript{2} or $^{14}$N\textsubscript{2} formation over H\textsubscript{2} reduced ceria. The possibility of $^{15}$N\textsubscript{2} or $^{14}$N\textsubscript{2} desorption as a limiting step could be ruled out by the experiments of pulsing N\textsubscript{2} over ceria and Rh/ceria in fully reduced or oxidized state as shown in Figure 5.11, where N\textsubscript{2} peak is at the same time position as the internal standard Ar response [39]. So once formed, the desorption of $^{15}$N\textsubscript{2}, $^{14}$N\textsubscript{2} or $^{14}$N$^{15}$N was not a limiting step. Then, either the NO dissociation or N diffusion and recombin-
tion, or a combination of these steps determine the slower $^{15}\text{N}_2$ formation process over the ceria. Lööf et al., also observed an enhanced $\text{N}_2$ formation by addition of ceria to noble metal/Al$_2$O$_3$. Oxygen spillover from the noble metal to reduced ceria was attributed to the enhanced $\text{N}_2$ formation, which reduced the inhibition by the produced oxygen [40]. Mullins and Overbury also investigated the NO dissociation over reduced Rh/CeO$_x$ and CeO$_x$ using soft X-ray photoelectron spectroscopy (SXPS) [41]. They observed NO dissociation with no $\text{N}_2$ desorption at 175°C over oxidised Rh/CeO$_2$, which suggested that the desorption of $\text{N}_2$ may be limited by the recombination of N on the surface. The faster $\text{N}_2$ formation over Rh/ceria than over ceria at least indicated that over Rh/ceria the N recombination was faster.

5.5. Conclusions

The addition of noble metals to ceria was essential for the selective NO reduction. The noble metals Pt and Rh promote the ceria reduction by hydrocarbons $\text{C}_3\text{H}_6$ and $\text{C}_3\text{H}_8$, at lower temperatures than without these metals. At 450°C, Pt/ceria and Rh/ceria can be reduced by using $\text{C}_3\text{H}_8$ or $\text{C}_3\text{H}_6$ over Pt/ceria and Rh/ceria, while unpromoted ceria can hardly be reduced. Rh was a more active promoter in ceria reduction and carbon deposition than Pt. $\text{C}_3\text{H}_8$ or $\text{C}_3\text{H}_6$ lead to 3-4 times deeper reduction as compared to the CO and H$_2$.

The reduction of NO over pre-reduced noble metal/ceria showed a selective formation $\text{N}_2$, while $\text{N}_2\text{O}$ and NO$_2$ formation were never observed (detection limit 1 ppm). More importantly, the presence of noble metal leads to a faster $\text{N}_2$ formation rate than over the ceria. During the NO reduction the pre-reduced ceria support became gradually oxidized and after filling 70-80% of the oxygen vacancies the NO starts to appear in the product mixture. In the presence of carbon deposit the lattice oxygen of the ceria reacted with the carbon keeping the ceria in a reduced form, sustaining the NO decomposition process as long as the carbon is present. Gas-phase oxygen did not directly react with the carbon. During the NO reduction process some unidentified N-species remain on the catalyst, the amount depending on the catalyst, but finally all nitrogen is released as $\text{N}_2$. 
References


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Oxygen Vacancies in Reduced Rh- and Pt-ceria for Highly Selective and Reactive Reduction of NO into N$_2$ in excess of O$_2$

*A good decision is based on knowledge and not on numbers*

Plato
Commercial DeNO\textsubscript{x} catalysts exhibit a poor performance in the selective conversion NO into N\textsubscript{2}, especially at high temperature and high gas hourly space velocities. In this study, oxygen vacancies of reduced ceria and Pt/ or Rh/ceria are found to be the efficient and selective catalytic sites for NO reduction into N\textsubscript{2}. Even at low concentration of NO can compete with excess O\textsubscript{2} at high temperature of 600\textdegree C and high GHSV of 170.000 L/L/h, where SCR and NSR DeNO\textsubscript{x} system are not working properly. N\textsubscript{2}O is not detected over the whole range of conditions, while NO\textsubscript{2} is only formed when the catalyst is oxidised, when both NO and O\textsubscript{2} start to breakthrough. For consideration of the fuel economy, the working temperature should be between 250 and 600\textdegree C. Above 600\textdegree C, most of the injected fuel was used for combustion with O\textsubscript{2}. Below 250\textdegree C, ceria support will not be reduced by fuel and the oxidation rate of the deposited carbon by oxygen from the ceria lattice will be too low.

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6.1. Introduction

Nitrogen Oxides (NO\textsubscript{x}) are a family of poisonous, highly reactive gasses, that have an adverse effect on our environment and human health. Each year around 2.6 million people' premature deaths are related to NO\textsubscript{x} pollution, according to the World Health Organization [1]. The NO\textsubscript{x} concentration in the air of most European countries is above the 40 µg/m\textsuperscript{3}, which is the safety limit value according to Air Quality Standards of European Emission [2]. Above 40% of the NO\textsubscript{x} emissions are contributed by the on-road transportation [3]. The current Euro 6 emission standard has led to the development of highly efficient lean-burn turbo-charged diesel engines and catalytic deNO\textsubscript{x} systems (Urea-Selective Catalytic reduction (SCR) and Lean NO\textsubscript{x} Traps (NSR) or a combination thereof), aiming at ≤ 0.08 g/km NO\textsubscript{x} emission. However, the real NO\textsubscript{x} emission during the real driving is actually on average 6 times higher than the NO\textsubscript{x} emission regulation standards [4]. This huge variation is among others, caused by the difference between the mild test conditions in the laboratory and the very dynamic acceleration and deceleration during the real driving. Therefore, from September 2017 the European Commission will partly replace the current laboratory test by the real driving emission (RDE) standard, aiming at 0.168 g/km NO\textsubscript{x} emission, which is still even 2.1 times the current Euro 6 limit. In future, test conditions will be more stringent and with lower NO\textsubscript{x} level. The current available technologies, including SCR [5–7], NSR [8–10], and combinations thereof, need to be significantly improved now and in the near future.

Recently, Bisaiji et al. (Toyota company) developed the Di-Air system in which short fuel-rich and long fuel-lean periods are created by the direct hydrocarbons (HC’s) injection with a high frequency downstream of the engine in the exhaust system upstream of a complex NSR catalyst (Pt/Rh/Ba/K/Ce/Al\textsubscript{2}O\textsubscript{3}) [11]. The Di-Air system is a promising technology to meet the future NO\textsubscript{x} emission standards under real driving test conditions (dynamic operations, high exhaust temperature, and high gas hourly space velocities (GHSV)) (Chapter 1).

However, detailed research is required to develop further and optimise this catalytic system before it can be commercialised at a large scale. Oxygen of O\textsubscript{2}. ChemCatChem, 9, 2935-2939
6. Reduction of NO into N\textsubscript{2} in excess of O\textsubscript{2}

Vacancies in reduced ceria have been found to act as the vital sites for NO reduction into N\textsubscript{2}. Both these oxygen vacancies and deposited carbon created during the direct fuel injection in the exhaust can explain the high effectiveness of the Di-Air system [12]. However, the reactivity of NO towards oxygen vacancies could be an issue in a typical diesel gas exhaust stream, where approximately 200 ppm NO has to compete with 5% O\textsubscript{2}, 5% CO\textsubscript{2}, and 5-10% H\textsubscript{2}O. In addition, NO\textsubscript{2} and N\textsubscript{2}O, both to be avoided for environmental and human health reasons, are common side products in the NO reduction technologies especially when using noble metal as an active ingredient in the catalyst composition [13–16]. Therefore, the studies on reactivity and selectivity in NO reduction processes are essential. In order to investigate whether NO can be reduced into N\textsubscript{2} under real conditions, i.e., trace amounts of NO in excess O\textsubscript{2} at high GHSV and high temperature, we have studied the selectivity and reactivity of NO reduction over ceria and noble metal loaded ceria in a fixed bed flow reactor.

6.2. Experimental

6.2.1. Catalyst preparation

Pt/Zr-La doped ceria and Rh/Zr-La doped ceria, aimed at 0.5 wt % noble metal loading, were prepared via incipient wetness impregnation method on Zr-La doped ceria (onwards denoted as ‘ceria’, a gift from Engelhard, now BASF). Tetra-ammine platinum (II) nitrate (Pt(NH\textsubscript{3})\textsubscript{4}(NO\textsubscript{3})\textsubscript{2}) and rhodium(III) nitrate hydrate (Rh(NO\textsubscript{3})\textsubscript{3}·xH\textsubscript{2}O, 36% Rh loading), both purchased from Sigma-Aldrich, were used as the precursor. Subsequently, the samples were dried at 110 °C overnight and calcined at 550 °C for 5 h both in a crucible in static air.

6.2.2. Catalyst characterisation

6.2.2.1. N\textsubscript{2} adsorption

Tristar II 3020 Micromeritics was used to determine the textural properties like BET area and pore volume [17]. The catalyst samples were degassed at 473 K for 16 h in a vacuum (0.05 mbar) before the nitrogen adsorption at liquid nitrogen temperature.
6.2.2.2. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Approximately 50 mg of samples were destructed in 4.5 mL 30% HCl + 1.5 mL 65% HNO$_3$ using the microwave. The destruction time in the microwave was 120 min at max power (900 W). After destruction, the samples were diluted to 50 mL with Millipore-Q (purified demi) water. The samples were analysed with ICP-OES (PerkinElmer Optima 5300).

6.2.2.3. X-Ray photoelectron spectroscopy (XPS)

XPS measurements were recorded on a K-alpha Thermo Fisher Scientific spectrometer using monochromated Al $K\alpha$ X-ray source. A flood gun was applied for charge compensation. A Lorentz function was used to analyse the peak intensities. Binding energies were calibrated with C(1s) at 285 eV as a reference.

6.2.2.4. X-ray diffraction (XRD)

The Powder X-Ray diffraction (XRD) was recorded by a Bruker-AXS D5005 with a Co $K\alpha$ source. The data was three times collected by varying the 2θ angle from 5° to 90° with a step size of 0.02.

6.2.2.5. Transmission electron microscope (TEM)

Transmission Electron Microscopy (TEM) images were recorded on a JEM-2100P electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples dispersed in ethanol and deposited onto a carbon-coated copper grid, shortly dried in air and then quickly moved into the vacuum system of the microscope.

6.2.2.6. Temperature Programmed Reduction (TPR)

TPR ($H_2$) of all the samples was carried out in fixed bed-reactor system connected to a thermal conductivity detector (TCD) to monitor the consumption of hydrogen by the catalyst. Samples of 200 mg catalyst were packed between SiC layers (300 - 425 μm). The samples were then reacted with the 10% $H_2$/Ar flow at a flow rate of 30 mL$_{STP}$/min, with temperature from
room temperature to 1000 °C at a heating rate of 5 °C/min. The TCD was calibrated by using CuO as a reference. A Permapure tubular drier was used to remove the water produced during the reduction upstream of the TCD detector.

6.2.2.7. Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) in the synthetic air of the ceria and Pt/ceria samples on which carbon was deposited were carried out in a Mettler Toledo TGA/SDTA851e instrument. Ceria and Pt/ceria samples were pre-treated with 0.5% C₃H₆ (in He) at a reaction temperature of 600 °C for 2 h and cooled down to room temperature in the environment of 0.5% C₃H₆ in a flow reactor.

6.2.3. Catalytic Testing

A flow reactor was used to study the reactivity and selectivity of NO into N₂ in the presence of excess O₂. A series of experiments were performed by using ¹⁵NO (and/or ¹⁴NO) co-fed with an excess of O₂ over ceria, Pt/ceria, and Rh/ceria at 400 °C, 450 °C or 600 °C. To mimic the fuel injection in the Di-Air system, C₃H₆ (1.25%) was used as a model fuel to pre-treat the catalyst at 400 °C, 450 °C, and 600 °C, respectively. ¹⁵NO was used to distinguish ¹⁴N₂ and CO (both at m/e = 28) as well as CO₂ and ¹⁴N₂O (both at m/e = 44).

In a typical experiment, 200 mg catalyst was loaded in a 6 mm inner-diameter quartz reactor tube. A feed composition of 0.2%, 0.01% or 0.05% of ¹⁴NO (or ¹⁵NO) in the presence of 5% O₂ (He balance) was used with gas hourly space velocities (GHSV) from 33.000 to 170.000 L/L/h. The exit gasses were online analysed by mass spectrometry (MS, Hiden Analytical, HPR-20 QIC) and Fourier Transform infrared (FT-IR) spectroscopy (Perkin–Elmer, Spectrum One).

A gas cell with KBr windows and a path length of ~5 cm⁻¹ was used for the FT-IR analysis. The spectra were measured in a continuous mode using the Perkin-Elmer ‘Time-Base’ software between 4000-7000 cm⁻¹ wavenumbers with a spectral resolution of 8 cm⁻¹ and an acquisition of 8 scans per spectrum, resulting in a time interval of 23 s between each spectrum.
6.3. Result and discussion

6.3.1. Catalyst characterization

Detailed characterisations of ceria and Rh/ceria were reported in Chapter 4 and 5. Briefly, the crystal size of ceria with typical fluorite structure was on average 5 nm as determined by the Scherrer’s equation and TEM micrograph analyses. The BET areas of Rh/ceria, Pt/ceria, and ceria were all 65 ± 2 m$^2$/g. For both the Pt/ceria and Rh/ceria, the noble metal loading was 0.5 wt %, as measured by ICP-AES.

6.3.2. Catalytic testing

6.3.2.1. NO reduction in the presence of O$_2$ at 600°C

Figure 6.1A shows the $^{15}$NO, O$_2$, and $^{15}$N$_2$ evolution at 600°C under 0.2% $^{15}$NO + 5% O$_2$ over C$_3$H$_6$ reduced Rh/ceria at a GHSV of 125,000 L/L/h. After switching to the reaction mixture, $^{15}$N$_2$ was observed until 70 s and no $^{15}$N$_2$O or $^{15}$NO$_2$ were detected by MS during this time interval. $^{15}$NO and O$_2$ started to break through from 35 s, followed by the formation of $^{15}$NO$_2$, detected by FT-IR (Figure 6.1B). The absence of $^{15}$NO$_2$ in the MS analysis is attributed to the instability of NO$_2$ and its easy decompositon into NO by high energy electrons in the mass spectrometer filament.

The formation of CO and CO$_2$, shown in Figure 6.1A, started to decline after...
Figure 6.2: Reactant and product evolution upon 0.2% $^{15}$NO + 5% O$_2$ in He exposure over at 600 °C C$_3$H$_6$ reduced Pt/ceria (A) and ceria (B) in a flow reactor with GHSV of 67,000 L/L/h at 600 °C. The insets of (A) and (B) present the $^{15}$N$_2$ and $^{15}$NO evolutions versus time.

35 s and vanished after 70 s. The formation of CO and CO$_2$ was owing to the reaction of deposited carbon with oxygen from the ceria lattice [12], which re-created the oxygen vacancies and kept the ceria surface reduced. Therefore, the deposited carbon acted as buffer reductant. The decline in CO and CO$_2$ formation after 35 s indicated that the deposited carbon was almost entirely consumed and Rh/ceria started to be oxidised from 35 s onwards. The formation of $^{15}$N$_2$, as the exclusive N-containing product during the first 35 s, demonstrates the selective reduction of NO in the presence of excess O$_2$ in which Rh/ceria was in a largely reduced state at 600 °C. The simultaneous breakthrough of $^{15}$NO and O$_2$ indicates that $^{15}$NO and O$_2$ had the same reactivity towards oxygen vacancies at 600 °C. Hence, only 2% of the oxygen vacancies were filled by NO.

The $^{15}$NO reduction in the presence of O$_2$ was also performed over Pt/ceria at 600 °C at GHSV of 67,000 L/L/h. The result was shown in Figure 6.2A. The $^{15}$NO and O$_2$ started to breakthrough at the same time ($t = 60$ s). The inset of Figure 6.2A shows that $^{15}$N$_2$ was the exclusive product of $^{15}$NO reduction during full $^{15}$NO conversion time interval. The same selectivity and reactivity of NO and O$_2$ were also observed over C$_3$H$_6$ reduced ceria at 600 °C at GHSV of 67,000 L/L/h (Figure 6.2B). $^{15}$N$_2$ was also the exclusive product of $^{15}$NO reduction during full $^{15}$NO conversion time interval (Figure 6.2B inset).

Figure 6.3A shows the result of $^{15}$NO reduction in the presence of O$_2$ over
Pt/ceria at 600 °C at GHSV of 170.000 L/L/h, where SCR and NSR DeNOₓ systems are not working properly. The result for the reduced ceria shows that ⁴⁵NO and O₂ started to breakthrough at the same time (t = 20 s). The inset of Figure 6.3A shows that ⁴⁵N₂ was still the exclusive product during the full ⁴⁵NO conversion time interval. Similar experiments over the reduced ceria shows the same breakthrough time for NO and O₂ (Figure 6.3B). The inset of Figure 6.3B shows ⁴⁵N₂ was the exclusive product of ⁴⁵NO reduction. It can be concluded that even up to high GHSV 170.000 L/L/h, ⁴⁵NO was still selectively reduced into ⁴⁵N₂ over both noble metal loaded ceria and ceria at high temperature and gas hourly space velocities where SCR and NSR DeNOₓ system are not working.

Experiments using ¹⁴NO were performed to further confirm the selectivity of NO, especially over noble metal loaded ceria. ¹⁴NO with O₂ gas mixtures were used besides ⁴⁵NO with O₂ gas mixture to distinguish IR bands of CO (2174 and 2116 cm⁻¹) from those of ¹⁴N₂O (2235 and 2208 cm⁻¹). The ⁴⁵N₂O bands were isotopically shifted to 2174 and 2116 cm⁻¹ [18], the same as for CO. The results of 0.2% ¹⁴NO + 5% O₂ over the ceria and Pt/ceria (Figure 6.4A and B) again shows no N₂O formation during the whole experiment and NOₓ was only formed, when NO and O₂ started to breakthrough and the ceria was fully re-oxidised. Therefore, it can be concluded that even in the presence of 25 times more O₂, the NO was selectively converted into N₂ on the reduced ceria surface at 600 °C. NO will be oxidised to NOₓ when the reduced ceria-based catalysts are 90% re-oxidised.

Figure 6.3: Reactant and product evolutions for 0.2% ¹⁵NO + 5% O₂ exposure in He over at 600 °C C₃H₆ Pt/ceria (A) and ceria (B) GHSV of 170.000 L/L/h at 600 °C.
Figure 6.4: FT-IR of reactant and product evolutions for 0.2% NO + 5% O₂ exposure in He over at 600 °C C₃H₆ reduced ceria (A) and Pt/ceria (B); GHSV of 67.000 L/L/h at 600 °C downstream of flow reactor.
6.3. Result and discussion

Figure 6.5: NO and O₂ breakthrough time during exposure of C₃H₆ reduced ceria and Pt/ceria to a gas flow with 0.2% NO + 5% O₂ in He at 600 °C as a function of the GHSV. Both ceria and Pt/ceria were pre-treated by 1.25% C₃H₆ in He at 600 °C.

Figure 6.5 shows the summaries of NO and O₂ breakthrough time during 0.2% NO + 5% O₂ flow over C₃H₆ reduced ceria and Pt/ceria at 600 °C for a GHSV between 33.000 L/L/h and 170.000 L/L/h. The results shows that NO and O₂ breakthrough time was an inversely proportional with GHSV. Since the reduction of ceria support was performed at the same conditions, the number of oxygen vacancies and deposited carbon were identical, i.e., the same oxygen vacancies capacities based on assuming that all deposited carbon will be oxidised to CO₂. The NO and O₂ breakthrough time was largely depended on the space velocity, i.e., the amount of NO and O₂ per time unit. The higher space velocities, the more NO and O₂ were fed per time unit, the earlier the breakthrough time of NO and O₂. The same was also observed for 0.2% NO + 5% O₂ exposure over C₃H₆ reduced Pt/ceria at 600 °C GHSV ranging from 33.000 L/L/h to 170.000 L/L/h, where NO and O₂ breakthrough times was again inversely proportional to GHSV. Apparently, even at GHSV of 170.000 L/L/h, the Di-Air system was not suffered for any kinetic limitation. For SCR and NSR, kinetic limitation will appear at GHSV of 50.000 L/L/h.

NO reactivity studies were further investigated over reduced ceria, Pt/ceria,
Table 6.1: The NO and O\textsubscript{2} breakthrough time using 0.05% + 5% O\textsubscript{2} over C\textsubscript{3}H\textsubscript{6} reduced samples with GHSV of 67.000 L/L/h.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T/\degree C</th>
<th>( t ) (NO) / s</th>
<th>( t ) (O\textsubscript{2}) / s</th>
<th>( t ) (NO) - ( t ) (O\textsubscript{2}) / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/ceria</td>
<td>600</td>
<td>60</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>Pt/ceria</td>
<td>400</td>
<td>215</td>
<td>5</td>
<td>210</td>
</tr>
<tr>
<td>Rh/ceria</td>
<td>600</td>
<td>65</td>
<td>65</td>
<td>0</td>
</tr>
<tr>
<td>Rh/ceria</td>
<td>400</td>
<td>253</td>
<td>10</td>
<td>245</td>
</tr>
<tr>
<td>Ceria</td>
<td>600</td>
<td>70</td>
<td>70</td>
<td>0</td>
</tr>
</tbody>
</table>

and Rh/ceria using NO concentrations 100 times lower than that of O\textsubscript{2}. Table 6.1 summarises the NO and O\textsubscript{2} appearance times under 0.05% NO+5% O\textsubscript{2} over C\textsubscript{3}H\textsubscript{6} reduced ceria-based catalysts at a GHSV of 67.000 L/L/h. As shown in Table 6.1, NO and O\textsubscript{2} had same breakthrough time for all catalyst at 600 °C. Therefore, the number of oxygen vacancies is fairly similar, and the reactivity of NO towards these oxygen vacancies at this temperature is much higher than O\textsubscript{2} and still be reduced at low concentration in an excess of O\textsubscript{2}.

6.3.2.2. NO reduction in the presence of O\textsubscript{2} at 450 °C

The reduction of \(^{15}\)NO in the presence of O\textsubscript{2} was also performed at lower temperature at 400 °C and 450 °C. Figure 6.6A shows the \(^{15}\)NO, O\textsubscript{2}, and \(^{15}\)N\textsubscript{2} evolution at 450 °C during 0.2% \(^{15}\)NO + 5% O\textsubscript{2} over C\textsubscript{3}H\textsubscript{6} reduced Rh/ceria at GHSV of 67.000 L/L/h.

The selective reduction of \(^{15}\)NO into \(^{15}\)N\textsubscript{2} was observed, where \(^{15}\)N\textsubscript{2}O was not observed (detection limit of 1 ppm) and \(^{15}\)NO\textsubscript{2} started to become detectable after \(^{15}\)NO breakthrough (Figure 6.6B). \(^{15}\)NO started to break through 50 s later than that of O\textsubscript{2}. So, NO was more effective than O\textsubscript{2} in refilling the oxygen vacancies and the oxidation of the deposited carbon at 450 °C. 30% of oxygen vacancies had been filled by NO, where the concentration of
6.3. Result and discussion

Table 6.2: Summary of H₂-TPR

<table>
<thead>
<tr>
<th>Surface reduction</th>
<th>Bulk reduction</th>
<th>Total reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/°C</td>
<td>H₂ (mmol/g&lt;sub&gt;cat&lt;/sub&gt;)</td>
<td>T/°C</td>
</tr>
<tr>
<td>Ceria</td>
<td>430</td>
<td>-</td>
</tr>
<tr>
<td>Pt/ceria</td>
<td>215</td>
<td>0.3</td>
</tr>
<tr>
<td>Rh/ceria</td>
<td>100</td>
<td>0.3</td>
</tr>
</tbody>
</table>

oxygen from O<sub>2</sub> was 50 times higher than that of O<sub>2</sub>.

NO reactivity studies were further investigated over reduced ceria, Pt/ceria, and Rh/ceria using NO concentrations 100 times lower than that of O<sub>2</sub> at 400 °C. Table 6.1 shows the NO and O<sub>2</sub> appearance time under 0.05% NO + 5% O<sub>2</sub> over C<sub>3</sub>H<sub>6</sub> reduced ceria-based catalysts at a GHSV of 67.000 L/L/h. As shown in Table 6.1, O<sub>2</sub> appeared much earlier than NO over Pt/ceria and Rh/ceria at 400 °C. Clearly, NO can compete even at low concentration under an excess of O<sub>2</sub> for filling the oxygen vacancies. Around 30% of oxygen vacancies were refilled by NO.

Experiments using <sup>14</sup>NO were performed to further confirm the selectivity of NO over Rh/ceria. Figure 6.7 shows the FT-IR spectra during 0.05% <sup>14</sup>NO + 5% O<sub>2</sub> exposure over C<sub>3</sub>H<sub>6</sub> reduced Rh/ceria at 400 °C. The CO absorbance at 2174 and 2116 cm<sup>-1</sup> was observed from the start and vanished after 90 s. In addition, a broad band at 2350 cm<sup>-1</sup>, assigned to CO<sub>2</sub>, appeared initially and vanished after 90 s. Absorbances at 1908 and 1850 cm<sup>-1</sup> were observed from 255 s onwards, both assigned to <sup>14</sup>NO. During the whole time interval, no absorbance of <sup>14</sup>N<sub>2</sub>O at 2235 cm<sup>-1</sup> (detection limit of 1 ppm) was observed. The rise of 1601 and 1628 cm<sup>-1</sup> bands after 285 s is attributed to the formation of <sup>14</sup>NO<sub>2</sub>. <sup>14</sup>NO<sub>2</sub> was only observed when both <sup>14</sup>NO and O<sub>2</sub> had broken through. Oxidised ceria and Rh/ceria are well known catalysts to promote NO oxidation into NO<sub>2</sub> [13].
Figure 6.6: Gas evolution during exposure of Rh/ceria $\text{C}_4\text{H}_6$ reduced at 450 °C to a 0.2% $^{15}\text{NO} + 5\% \text{O}_2$ containing He flow at a GHSV of 125.000 L/L/h at 450 °C. (A) MS signals and (B) FT-IR responses.
6.3. Result and discussion

Figure 6.7: FT-IR of reactant and product evolutions for 0.05% NO + 5% O₂ exposure over at 400 °C C₆H₆ reduced Rh/ceria, GHSV of 67.000 L/L/h at 400 °C downstream of flow reactor.

Figure 6.8: TPR(H₂) profiles for ceria (blue), Pt/ceria (magenta), and Rh/ceria (red).
6.3.2.3. Operational temperature window of Di-Air

In TPR with H₂ bare ceria support shows two reduction peaks centred at 430 and 550 °C. It is generally accepted that the low temperature (430 °C) reduction is attributed to the surface reduction and the high temperature (550 °C) accounts for the bulk reduction [19]. Compared to the bare support, surface and bulk reduction of noble metal loaded ceria shifted to lower temperature, as summarised in the Table 6.2. Therefore, as evidenced by TPR(H₂) (Figure 6.8, Table 6.2), the bulk oxygen reduction for noble metal loaded ceria was around 300 °C.

The ceria reduction by deposited carbon oxidation to CO and CO₂ by oxygen from ceria lattice provided new oxygen vacancies for NO reduction. Therefore, the oxidation of deposited carbon by ceria was essential for the rejuvenation of active catalyst sites (oxygen vacancies). TGA was applied to study the oxidation of deposited carbon in synthetic air. Ceria and Pt/ceria samples were firstly pre-reduced by using 0.5% C₃H₆ (in He) at a reaction temperature of 600 °C for 2 h and cooled down to room temperature in 0.5% C₃H₆ in He in a flow reactor. Around 10 mg of the samples were taken out for TGA analysis. The results in Figure 6.9 shows that the carbon oxidation effectively started from around 250 °C onwards over both ceria and Pt/ceria. Our previous experiments proved that oxygen from ceria lattice was used for the oxidation of deposited carbon over ceria and noble metal loaded ceria (Chapter 4 and 5) [12]. Therefore, the TGA results suggested that the reduction of ceria by the oxidation of deposited carbon started from 250 °C.

Therefore, as displayed in Figure 6.10, the operational temperature window for the Di-Air system will be from 250 to 600 °C. Below 250 °C, the reduction of ceria by fuel and oxidation of deposited carbon by oxygen from ceria will become the rate limiting steps. Above 600 °C, most of the deposited carbon will be primarily used for the reaction with O₂ and not for the NO reduction.

Due to the experimental limitations, dynamic injection of fuel onto the catalyst was not aimed for. In this study, C₃H₆ pre-treatment in 2 h was used to mimic the consequence of fuel injection, e.g., ceria reduction and carbon deposition. In reality, the fuel, especially diesel will have a higher reactivity in ceria reduction and carbon deposition than the applied C₃H₆. Therefore, the reactivity of NO and O₂ can possibly be tuned over an even broader
6.3. Result and discussion

The prominent advantage of the Di-Air system is maintaining a high NO conversion at high reaction temperatures ≥ 600 °C, and ≥ GHSV, 170,000 L/L/h, where NSR and SCR techniques are not effective at all [11]. The NSR system relies on the NO\textsubscript{x} storage components, that can hardly work at 600 °C, causing the NSR system to fail in the high-temperature regime. NO\textsubscript{x} storage will also fail when storage demands cannot be compensated at higher GHSV (above 40,000 L/L/h) due to kinetic limitation. The same GHSV kinetic limitations are applicable for SCR. The excellent performance of the Di-Air system at high reaction temperatures and high GHSV can be explained by the presence of oxygen vacancies and carbon deposits. The reduced ceria is extremely active and selective for NO conversion into N\textsubscript{2} even in excess oxygen. The existence of a reductant buffer (deposited carbon during fuel injection) extends the NO reduction capacity. Unlike the NSR system that relies on the capacity of and storage rate of NO\textsubscript{x} storage materials, in the Di-Air system highly reactive oxygen vacancies and the reductant buffer (deposited carbon) can effectively be re-created by periodical fuel injection.

Figure 6.9: TGA profile in air of ceria (black) and Pt/ceria (red) pre-treated in a 0.5% C\textsubscript{2}H\textsubscript{6} (in He) flow at 600 °C for 2 h. Heating rate 5 K/min.
6.4. Conclusions

Noble metal supported ceria catalyst are promising starting materials for the development of the Di-Air system. The fuel injection direct onto the catalyst led to a reduced ceria and carbon deposition. Oxygen vacancies of reduced ceria and Pt/ or Rh/ceria are found to be the efficient and selective catalytic sites for NO reduction into N₂. Even at low concentration of NO can compete with excess O₂ at high temperature of 600°C and high GHSV of 170,000 L/L/h. N₂O is not detected over the whole range of experimental conditions, while NO₂ is only formed when the catalyst is oxidised, where both NO and O₂ start to breakthrough. Oxygen vacancies indirect reduction with fuel and indirectly from the lattice oxygen reduction by deposited carbon are the active sites for the selective and reactive reduction of NO into N₂ in the presence of oxygen. For consideration of the fuel economy, the working temperature should be between 250 and 600°C.
References


The influence of CO$_2$ on NO reduction to N$_2$ over reduced ceria - based catalyst

*It’s not what you look at that matters, it’s what you see.*

Henry David Thoreau
7. The influence of CO\textsubscript{2} on NO reduction to N\textsubscript{2}
Oxygen vacancies in reduced ceria are the catalytic sites for the NO reduction into N\textsubscript{2} in the Toyota Di-Air DeN abatement technology. Traces of NO (several hundred ppm) have to compete with other oxidants present in excess, e.g., 5% CO\textsubscript{2} and 5% O\textsubscript{2}, in an exhaust gas of a lean burn (diesel) engine. The reactivity of CO\textsubscript{2} and NO over a reduced ceria and noble metal loaded ceria has been investigated under ultra-high vacuum system in TAP and under atmosphere pressure in operando Raman and flow reactor. The results showed that CO\textsubscript{2} was a mild oxidant able to oxidize the oxygen vacancies but hardly oxidised deposited carbon over both ceria and noble metal loaded ceria. NO was a stronger oxidant and more efficient in refilling the oxygen vacancies and able to convert the deposited carbon, which acted as buffer reductant to extend the NO reduction time interval. NO was selectively and completely converted into N\textsubscript{2}. The presence of excess CO\textsubscript{2} hardly affected the NO reduction process into N\textsubscript{2}.

This chapter is based on the following publication:
Y.Wang, M.Makee, (2018). The influence of CO\textsubscript{2} on NO reduction to N\textsubscript{2} over reduced ceria - based catalyst. Applied Catalysis B: Environmental, 221,196-205
7.1. Introduction

For diesel powered vehicles due to the more stringent NO$_x$ emission standard and emission test certifications, more effective and advanced exhaust emission after-treatment technologies are required. The by EU commission in 2017 introduced realistic driving emission (RDE) significantly forces the improvement of the current DeNO$_x$ technologies, i.e., NO$_x$ Storage and Reduction (NSR) [1], Selective Catalytic Reduction (SCR) [2], and their combination thereof [3]. Recently, Bisaiji et al., (Toyota Company) developed a new emission control technology, the Di-Air system (Diesel deNO$_x$ System by Adsorbed Intermediate Reductants). In this system, short rich and lean periods are created by high frequency direct diesel fuel injection downstream of the engine into the exhaust upstream of a NSR catalyst (an unspecified complex mixture of Pt/Rh/Ba/K/Ce/Al$_2$O$_3$ coated onto a monolith) [4, 5]. These pulses will reduce the catalyst and create carbon deposits on the catalyst [6]. The Di-Air system promises to meet future emission standards under realistic driving test conditions. Oxygen vacancies of a reduced ceria have been identified to be the catalytic sites for the conversion of NO into N$_2$ [6]. Deposited carbon on the reduced ceria created during diesel fuel injection acts as a buffer reductant. The oxidation of deposited carbon via the ceria lattice oxygen species will recreate new oxygen vacancies in the ceria lattice. These recreated ceria oxygen vacancies provide additional NO conversion capacity [6].

In the exhaust gas of a lean burn engine, the concentration of O$_2$ and CO$_2$ (around 5%) are much higher than that of NO (in the order of hundred ppm). In a previous article we have demonstrated that even in the excess of oxygen NO is completely converted into N$_2$ (100% NO conversion with 30% efficiency with respect to oxygen at an O$_2$ to NO ratios of $= 100$) at 450 $^\circ$C for bare ceria and noble metal loaded ceria [7]. CO$_2$ will also be capable to oxidize these sites of reduced ceria [8], which has been commonly reported in the field of solar fuel cells [9]. Metal and/or metal oxide interaction or boundary regions are reported to further assist in the CO$_2$ dissociation over the noble metal loaded ceria [10, 11]. Although the universal mechanism of CO$_2$ activation into CO and (atomic or molecular) oxygen is still unresolved [12, 13], the CO$_2$ activation via dissociation was extensively reported both by DFT modelling study and some experimental work. To best of our knowl-
edge, no work has been published on the efficiency and reactivity of CO\textsubscript{2} versus the number of oxygen vacancies in ceria. Especially, the relative reactivity of CO\textsubscript{2} versus NO will be crucial for the Di-Air system optimization. The oxidation of deposited carbon by CO\textsubscript{2} should be minimized in order to maximize the function of deposited carbon as buffer reductant for the NO reduction. Furthermore, the study of NO reactivity and selectivity in the presence of CO\textsubscript{2} are essential, as the common side products especially over noble metal catalysts, \textit{e.g.}, N\textsubscript{2}O and NO\textsubscript{2}, have an even worse effect on our environment and human health.

Therefore, the Temporal Analysis Products (TAP, ultra-high vacuum) technique was applied to study the reactivity of CO\textsubscript{2} and NO versus the number of oxygen vacancies and deposited carbon over ceria and noble metal loaded ceria. \textit{Operando} Raman (atmosphere pressure) and fixed bed flow reactor experiments were performed to confirm the TAP results. More importantly, the competition of small amount of NO with an excess of CO\textsubscript{2} was performed in a fixed-bed flow reactor in order to mimic of the selectivity and reactivity of NO reduction under more realistic conditions.

Commercially available Zr and La-doped ceria (a gift of BASF, further denoted as ceria) is used as a model of ceria due to its high hydrothermal stability \cite{6, 14, 15}. The concept of the hypothetical ceria layer is introduced to describe the oxidation state of the catalyst. Each one O-Ce-O tri-layer is regarded as one hypothetical ceria layer. The number of reducible oxygen vacancies on one hypothetical reduced ceria layer was calculated to be \(2.6 \times 10^{17}\) oxygen atoms/mg	extsubscript{cat} for an agglomerate of ceria crystallites (5 nm) with a BET area of 65 m\textsuperscript{2}/g \cite{6, 16}.

### 7.2. Materials and methods

#### 7.2.1. Materials preparation

0.5 wt.% Rh/ceria and Pd/ceria were prepared via an incipient wetness impregnation method on dried ceria. Rhodium(III) nitrate hydrate and Palladium(II) nitrate hydrate (purchased from Sigma Aldrich) were used as precursors in purified demi water. Subsequently, the samples were dried at 110 °C overnight and calcined at 550 °C for 5 h.
7.2.2. Characterisation

7.2.2.1. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Approximately 50 mg catalyst was digested in 4.5 mL 30% HCl + 1.5 mL 65% HNO₃ in a microwave for 120 min. at max. power of 900 W. After destruction the samples were diluted to 50 mL with Millipore-Q (purified demi) water. The samples were analysed with ICP-OES (PerkinElmer Optima 5300).

7.2.2.2. N₂ adsorption

Tristar II 3020 Micromeritics was used to determine the textural properties like BET area and pore volume at -196 °C. The catalyst samples were degassed at 200 °C for 16 h in vacuum (0.05 mbar) prior to the nitrogen adsorption.

7.2.2.3. X-ray diffraction (XRD)

The powder X-ray diffraction (XRD) was recorded on a Bruker-AXS D5005 with a Co Kα source. The data was 3 times collected by varying the 2θ angle from 5° to 90° with a step size of 0.02.

7.2.2.4. Temperature Programmed Reaction (TPR)

TPR (temperature programmed reaction with hydrogen) for the ceria, Rh/ceria, and Pd/ceria were carried out in home-made fixed bed reactor system connected to a thermal conductivity detector (TCD) to monitor the consumption of hydrogen by the catalyst sample. 200 mg of sample was packed between SiC layers (300-425 μm). The sample was then reduced with H₂ (10%)/Ar flow with a flow rate of 30 mL/STP/min at a constant heating rate of 5 °C /min to 1000 °C. TCD was calibrated by using CuO as a reference. A Perma Pure tubular drier was used to remove the water produced during the reduction upstream of the TCD detector.
7.3. Catalytic testing

7.3.1. TAP experiments under ultra-high vacuum condition

The pulse experiments were carried out in an in-house developed TAP (Temporal Analysis of Products) reactor. Small gas pulses, typically in the order of $1 \cdot 10^{15}$ molecules, were introduced in a small volume (1 mL) upstream of the catalyst packed bed reactor. The produced pressure gradient over the catalyst packed bed thereby caused the molecules to be transported through the packed bed to the ultra-low vacuum at the opposite side of the reactor bed. Depending on the actual amount of molecules pulsed, the transport can be purely Knudsen diffusion. In other words, the molecules will only interact with the ‘walls’ (catalyst surface and reactor walls) of the system and not with each other. Upon interaction with the catalyst, the molecules can be converted into different products. The evolution of the reactant and product molecules is tracked (one mass at a time) in time with a high resolution of 10 kHz by means of a mass spectrometer. More details about TAP can be found in Chapter 2 [6].

21.2 mg of ceria, 10 mg of Rh/ceria, and 10 mg of Pd/ceria (100-250 μm) were used and loaded as a fixed-bed reactor in the TAP equipment. For all measurements, the gas pulses contained either 20 vol.% Ne or 20 vol.% Ar or 20 vol.% Kr as an internal standard. In all experiments, the catalyst was initially oxidised by admitting $O_2$/Ar pulses until the $O_2$ signal approached a stable level. Reductions of ceria or noble metal loaded ceria were subsequently performed using reductant pulses of either 80 vol.% $C_3H_6$ in Ne or 80 vol.% CO in Ar. The re-oxidation was conducted using oxidant pulses of either 80 vol.% $CO_2$ or 80 vol.% NO both in Ar, or 80 vol.% $^{15}$NO both in Kr. In all experiments a starting pulse size of approximately $1.6 \cdot 10^{15}$ molecules was used, the pulse size gradually decreased during an experiment since the reactant was injected from the closed volume of a pulse-valve line.

The oxygen and carbon mass balances during the $CO_2$ or NO pulsing over the CO and $C_3H_6$ pre-reduced catalyst were calculated by Equation 7.1 and 7.2, respectively.

$$O_{\text{balance}} = NO_{\text{in}}(2 \times CO_{\text{in}}) - 2CO_{\text{out}} - CO_{\text{out}} - NO_{\text{out}} \quad (7.1)$$
The influence of CO on NO reduction to N₂

\[ C_{balance} = CO_{2in} - CO_{2out} - CO_{out} \]  

A positive O-balance meant that oxygen accumulates in/on the catalyst, while a negative C-balance indicated the consumption of deposited carbon from the catalyst.

7.3.2. Operando Raman

Operando Raman spectra (Renishaw, 2000) were recorded using a temperature controlled operando Raman cell (Linkam, THMS 600). Ten scans were collected for each spectrum in the 100-4000 cm\(^{-1}\) range using continuous grating mode with a resolution of 4 cm\(^{-1}\) and scan time of 10 s. The excitation wavelength was 325 nm. The power of each laser line was kept at about 2.5 mW to prevent local heating effects. The spectrometer was daily calibrated using a silicon standard with a strong absorption band at 520 cm\(^{-1}\). The (re-oxidised) ceria was pre-treated by C\(_3\)H\(_8\) (1000 ppm in N\(_2\), flow rate 200 mL/min) for 2 h. N\(_2\) was used to flush the cell for 20 min. Subsequently, CO\(_2\) (1000 ppm CO\(_2\) in N\(_2\), a flow rate of 200 mL/min) was admitted to the cell.

7.3.3. Flow reactor experiment under atmosphere pressure

The catalyst sample (200 mg) was placed in a 6 mm inner diameter quartz reactor tube and equipped downstream with mass spectrometry (MS, Hiden Analytical, HPR-20 QIC) and infrared (IR) spectroscopy (Perkin–Elmer, Spectrum One). For IR analysis a gas cell with KBr windows with an internal path length of \(~\)5 cm was used. The spectra were recorded in a continuous mode using the Perkin-Elmer 'Time-Base' software between 4000-700 cm\(^{-1}\) wavenumbers with a spectral resolution of 8 cm\(^{-1}\) and an acquisition of 8 scans per spectrum, resulting in a time interval of 23 s between each displayed spectrum.

In all experiments, the catalyst was initially (re-)oxidised by O\(_2\)/He until the O\(_2\) signal reached a stable level in MS. Reduction of catalyst was performed by flowing 1.25% C\(_3\)H\(_6\) (He) for 2 h with a flow rate of 200 mL/min and subsequently flushed with He (200 mL/min) for 30 min at 450°C. Feed compositions of either 0.2% NO/He or 0.2% CO\(_2\)/He or (0.2% NO + 5% CO\(_2\))/He were used at a GHSV of 67.000 L/L/h.
7.4. Results and discussion

7.4.1. Characterisation

7.4.1.1. Structure and chemical composition

Characterisation details of the ceria support were reported in more detail elsewhere [6, 16]. In brief, typical fluorite structure of ceria was detected by Raman and XRD. A 5.0 nm crystal size of ceria was determined by the Scherrer’s equation and confirmed by the analysis of the TEM micrographs. The bulk composition of ceria support was measured by ICP, which showed that the atomic ratio of Ce, Zr, and La was 0.64 : 0.15 : 0.21. The BET area of bare (fresh and spent) ceria was 65 m$^2$/g. The BET areas of Rh/ceria and Pd/ceria (fresh and spent) were similar to the bare ceria support (66 ± 2 m$^2$/g). The loadings of Rh and Pd were determined to be 0.5 wt.%, measured by ICP-OES (0.0486 mmol/g$_{cat}$ and 0.0470 mmol/g$_{cat}$ of Rh and Pd loading, respectively). Figure 7.1 shows the XRD patterns of ceria, Rh/ceria, and Pd/ceria. The patterns of both Rh/ceria and Pd/ceria showed a fluorite cubic structure of ceria. Diffraction lines due to Rh and Pd metals or any rhodium oxides and palladium oxides were not observed due to the low loading (0.5 wt.%) and high dispersion of these noble metals on the applied
The influence of CO\textsubscript{2} on NO reduction to N\textsubscript{2}

7.4.1.2. TPR\textsubscript{(H\textsubscript{2})}

The reduction properties of bare support and Rh- and Pd-loaded support were studied by TPR technique. The TPR\textsubscript{(H\textsubscript{2})} results are presented in Figure 7.2. The bare support showed two reduction steps centred at 430 and 550 °C. It was generally accepted that the low temperature (430 °C) process was attributed to the surface reduction, whereas the high temperature (550 °C) was accounted for the bulk reduction [17]. The total H\textsubscript{2} consumption was calculated to be 1.2 mmol/g\textsubscript{cat}, corresponding to 2.7 ceria layer reduction. The H\textsubscript{2} consumption up to temperatures of 500 °C (surface reduction) was calculated to be 0.4 mmol/g\textsubscript{cat}, corresponding to around 0.9 ceria layers reduction.

For Pd/ceria, the peak area at 50 °C with a H\textsubscript{2} consumption of 0.05 mmol/g\textsubscript{cat} was contributed from the reduction of PdO to Pd. The amount of H\textsubscript{2} consumption is almost equal to the Pd loading on the ceria. This was in agree-
Table 7.1: Summary of oxygen removal and deposited carbon (carbon atoms/mg<sub>cat</sub>) by CO and C<sub>3</sub>H<sub>6</sub> pre-treatment over ceria. Oxygen unit: oxygen atoms/mg<sub>cat</sub>, Carbon unit: oxygen atoms/mg<sub>cat</sub>

<table>
<thead>
<tr>
<th>T/°C</th>
<th>Oxygen removal</th>
<th>Deposited carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxygen</td>
<td>Reduction layers</td>
</tr>
<tr>
<td>CO</td>
<td>580 3·10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>540 3·10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>1</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>580 7.1·10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>560 5.9·10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>2.3</td>
</tr>
</tbody>
</table>

ment with the literature [18]. The reduction peak area at 350°C was related to the surface reduction of ceria support with H<sub>2</sub> consumption of 0.55 mmol/g<sub>cat</sub>, corresponding to around 1.2 ceria layers reduction. The total H<sub>2</sub> consumption up to temperatures of 500°C was calculated to be 1.3 mmol/g<sub>cat</sub>, corresponding to 2.9 ceria layers reduction.

For Rh/ceria, the peak area with H<sub>2</sub> consumption of 0.3 mmol/g<sub>cat</sub> at 100°C which was larger than the amount needed for the reduction of Rh<sub>2</sub>O<sub>3</sub> (or other type of RhO<sub>x</sub>) to Rh (0.05 mmol/g<sub>cat</sub> of Rh loading). Therefore, the hydrogen consumption was a combination reduction of Rh<sub>2</sub>O<sub>3</sub> to Rh and a partial reduction of CeO<sub>2</sub> into Ce<sub>2</sub>O<sub>3</sub>. The total H<sub>2</sub> reduction was calculated up to a temperature of 350°C to be 1.7 mmol/g<sub>cat</sub>, corresponding to 3.8 layers ceria reduction.

7.4.2. Catalytic testing

7.4.2.1. Investigation of CO<sub>2</sub> and NO reactivity over reduced ceria support by TAP

To investigate the reactivity of CO<sub>2</sub> and NO towards the oxygen vacancies of ceria, CO and C<sub>3</sub>H<sub>6</sub> were applied as reductants to pre-treat the catalyst samples. Table 7.1 summarises the result of CO and C<sub>3</sub>H<sub>6</sub> pre-treatment.
The influence of CO\(_2\) on NO reduction to N\(_2\). Over (re-oxidised) ceria [19]. All the CO\(_2\) experiments were performed at 580 °C and the NO experiments were carried out at 540 °C and 560 °C.

The conversion of CO\(_2\) over CO pre-reduced ceria at 580 °C was presented in Figure 7.3A and B. As shown in Figure 7.3A, the CO\(_2\) conversion was almost 100% during the first several CO\(_2\) pulses, accompanied by CO formation. Then the conversion quickly declined until to nearly zero conversion after 14000 CO\(_2\) pulses. CO\(_2\) was able to produce oxygen species and to re-oxidise reduced metal oxides [20], which made CO\(_2\) a promising oxygen source or oxidant in partial oxidation reactions such as methane reforming [?] and oxidative dehydrogenation (ODH) of alkanes [21, 22]. Our TAP CO\(_2\) pulses experiment over CO reduced ceria (Figure 7.3A and B) showed that CO\(_2\) molecules were able to convert to CO at 580 °C. The carbon balance during the CO\(_2\) pulses (Figure 7.3B) showed a maximum 13% of carbon was left during the CO\(_2\) pulse. Therefore, more than 85% of CO\(_2\) was converted into CO with O filling into oxygen vacancies of ceria. This missing carbon could due to the slow desorption of CO and CO\(_2\) from the ceria surface. It might be argued that the missing carbon can be formed as carbonate over
the ceria, since the exposure of ceria with CO$_2$ can cause the formation of carbonate over the ceria [23, 24]. However, over the reduced ceria surface, the formation of carbonate can be limited. A DFT calculation result had shown that CO$_2$ was favoured to chemisorb to the reduced ceria resulting in the formation of an activated mono-dentate carbonate species, which could further dissociate to form CO [25]. Regarding the activation of CO$_2$ over the reduced ceria, the assistance by hydroxyl groups could be largely eliminated, since CO$_2$ multi-pulse experiments were performed in ultra-high vacuum system. Oxygen anion vacancies and the associated electrons should be regarded as the active sites to activate CO$_2$ [25]. Therefore, the pathway of CO$_2$ activation via surface hydroxyl groups could be largely ruled out and had to proceed via a C=O bond activation. Charges had to be transferred from the reduced ceria to CO$_2$, resulting in the formation of CO$_2^-$ anion radical species [26]. Overall, the CO$_2$ activation over oxygen anion vacancies resulted in that one of CO$_2$’s O atoms was used to fill the oxygen anion defect site and, thereby, re-oxidising the reduced ceria in combination with the desorption of one CO molecule (Equation 7.3):

$$CO_2 + 2Ce^{3+} \leftrightarrow CO + 2Ce^{4+} + O^{2-} \quad \text{(7.3)}$$

Till 2000 pulses around half of the oxygen vacancies were filled. The NO pulses over the CO reduced ceria at 540°C showed that NO was completely converted into N$_2$ during the first 2000 NO pulses, followed by a breakthrough of NO (Figure 7.3C). Around 75% of the oxygen vacancies were refilled when the NO conversion dropped down (Figure 7.3D). N$_2$ was the exclusive product during the NO reduction. N$_2$O and NO$_2$ were not observed.

The different observations between CO$_2$ and NO pulses indicated that the reaction rate of CO$_2$ for the re-oxidation process of ceria was slow, i.e., CO$_2$ was not a very effective oxidant in refilling the oxygen vacancies. This could be either related to a slow desorption of CO or the negative driving force to the (quasi-) equilibrium between CO, CO$_2$, Ce$^{3+}$, and Ce$^{4+}$, according to Equation 7.3. The pulse of CO over the (pre-) oxidised ceria showed that CO could only reduce ceria up to 1 hypothetical ceria layer supported the existence of a (quasi-) equilibrium between CO, CO$_2$, Ce$^{3+}$, and Ce$^{4+}$. The inactivity of CO$_2$ could not be caused by the full coverage of CO on the surface according the carbon balance in Figure 7.3B.
In the Di-Air system, diesel fuel is used as reductant instead of CO and H₂. Therefore, the study on the performance in CO₂ over a fuel reduced ceria will be required. Propene was used to mimic diesel fuel used in the real practical operation. As displayed in Figure 7.4, stage I and stage II will be used to distinguish the full NO (CO₂) conversion (stage I) and NO (CO₂) started to breakthrough (stage II). The CO₂ conversion over C₃H₆ pre-reduced ceria is shown in Figure 7.4A and B. In contrast to the CO₂ conversion over a CO reduced ceria (Figure 7.3A and B), the CO₂ pulses over a C₃H₆ reduced ceria showed that CO₂ was completely converted till pulse number 6000 (stage I). CO was the only product. There is some more CO formation than was required for refilling the oxygen vacancies (Figure 7.4A). Apparently, some of the deposited carbon was consumed from the catalyst as indicated from the carbon balance in Figure 7.4B. According to the oxygen balance in Equation 7.1, oxygen vacancies in the ceria were refilled during the CO₂ pulses. As shown in Figure 7.4B, when CO₂ started to break through from pulse number 6000 onwards, the oxygen refilling rate declined. The CO₂ conversion dropped from 100% in stage I to around 20% in stage II. The quantity of oxygen accumulation during the stage I was around 50% of oxygen vacancies that created by the C₃H₆ pre-treatment. The total carbon consumption during stage I and stage II was around 2% of the deposited carbon formed during the C₃H₆ pre-treatment.

This full conversion time interval period (stage I, Figure 7.4A) was due to the deeper degree of ceria reduction (2.8 hypothetical reduced ceria layers). A higher degree of reduction of ceria drove the CO₂ conversion to CO (Equation 7.3). The formation of carbonate by CO₂ pulses could be eliminated here since carbon balance was negative, indicating that the CO₂ pulse will convert carbon deposits from the surface instead of carbon accumulation. The formation of CO during the CO₂ pulses will be a combination of CO₂ reduction and deposited carbon oxidation.

The majority of CO formation during stage I came from the reduction of CO₂ on the oxygen vacancies according to the carbon and oxygen balance in Figure 7.4B [20], as could be described by Equation 7.3. This observation confirmed the existence of a (quasi-) equilibrium between CO, CO₂, Ce³⁺, and Ce⁴⁺.

The oxidation of deposited carbon via lattice oxygen from ceria could be
described [6, 27], according to Equation 7.4:

\[
C + 2C_{\text{e}^4^+} + O^{2^-} \leftrightarrow CO + 2C_{\text{e}^3^+}
\] (7.4)

Therefore, the CO\(_2\) pulses during the stage I where CO\(_2\) was completely converted, led to oxygen accumulation in the ceria, thus re-filling the oxygen vacancies.

CO\(_2\) started to break through from pulse number 6000 onwards, where 50\% of oxygen vacancies in the one hypothetical mono-layer reduced ceria were present and 2\% of deposited carbon was oxidised (Figure 7.4B). One might argue that gas phase CO\(_2\) could react with surface deposited carbon, forming CO directly according to Equation 7.5:

\[
CO_2 + C \leftrightarrow 2CO
\] (7.5)

This reaction will be very unlikely since then for each converted CO\(_2\) molecule two CO molecules should be generated, which was not supported by the observation in Figure 7.4A. Also thermodynamically the gasification of carbon (stable graphite) to CO by CO\(_2\) at this temperature is not favoured [28].

Figure 7.4C and D show the results of NO pulse over a C\(_3\)H\(_6\) reduced ceria at 560 °C. The pulse of NO resulted in the formation of N\(_2\) and CO, followed by the formation of N\(_2\) and CO\(_2\). NO was completely converted during the stage I and started to breakthrough from pulse number 30000 (stage II). The oxygen and carbon balances during the NO pulses were displayed in Figure 4D. The quantity of oxygen vacancies refilling during stage I was around 84\%. The formation of CO and CO\(_2\) during NO pulses indicated the conversion of deposited carbon from ceria surface. Total carbon conversion during the stage I was around 90\% of deposited carbon. Apparently, NO conversion only dropped when most of the deposited carbon was consumed.

Oxygen anion defect centres in reduced ceria were responsible for the decomposition of NO into N\(_2\), thereby re-oxidizing these defect centres. The oxidation of the carbon deposits by oxygen species originating from lattice oxygen will prolong a reduced ceria surface state. NO conversion time interval will, thereby, be extended due to the oxidation of deposited carbon by the ceria lattice oxygen, which will re-create oxygen vacancies in the ceria for additional NO reduction [6].
Figure 7.4: CO\textsubscript{2} pulse responses in TAP at 580\textdegree C (A and B) and NO pulse responses at 540\textdegree C (C and D) over CO reduced ceria at 580\textdegree C and 540\textdegree C, respectively.
7.4. Results and discussion

![Figure 7.5: Operando Raman of CO₂ exposure over C₃H₆ reduced ceria at 560°C: A) D band and G band of carbon; and B) Ce-O₆ band of ceria.](image)

7.4.2.2. Investigation of CO₂ and NO reactivity over reduced ceria support by operando Raman

Operando Raman was applied to investigate the NO and CO₂ reaction reactivity over reduced ceria under atmosphere pressure. The band at 460 cm⁻¹ was attributed to the symmetric stretch mode of Ce-O₆ crystal unit (F₂g mode), which was characteristic for a reduced fluorite ceria structure [29]. As shown in the Figure 7.5A, band at 460 cm⁻¹ disappeared after the C₃H₆ pre-treatment and this band intensity re-appeared and its intensity increased during CO₂ exposure, indicating that pre-reduced ceria was re-oxidised by CO₂. The bands at 1575 and 1350 cm⁻¹ were assigned to G band and D band of carbon in either graphene or graphite form, respectively. The G band was usually assigned to zone centre phonons of E₂g symmetry of the perfect graphite structure, and the D peak was a breathing mode of A₁g symmetry. This mode was forbidden for a perfect graphite structure and only became active in the presence of structural vacancies and disorders [30]. The intensity of D band and G band of graphene/graphite hardly changed during CO₂ exposure for C₃H₆ reduced ceria (Figure 7.5A), while the band at 460 cm⁻¹ to some extent increased (Figure 7.5B), indicating that CO₂ was only able to re-fill oxygen vacancies.

In order to make a comparison between NO and CO₂ reactivity under atmosphere pressure, operando Raman spectroscopy was recorded during the NO flow over C₃H₆ reduced ceria at 560°C. In contrast to the CO₂ experiment, the band at 460 cm⁻¹ significantly increased during the NO exposure...
7.4.2.3. Investigation of CO$_2$ and NO reactivity over reduced noble metal loaded ceria by TAP

The presence of noble metals on CeO$_2$ systems will promote the migration/exchange of oxygen species between isotopic C$^{18}$O$_2$ and Pt/Ce$^{16}$O$_2$ [10]. The presence of Pt accelerated the exchange rate between 200 and 400 °C, mainly favouring the exchange of one of the oxygen atoms of C$^{18}$O$_2$ molecule [10]. The loading of noble metal over ceria might have an influence in either in assisting or inhibiting CO$_2$ reduction reactivity versus NO. Additionally, loadings of either Rh on Pd on ceria were able to promote the reduction of ceria surface and bulk to lower temperature by hydrogen, as evidenced by TPR in Figure 7.2. However, the reduction of bare ceria required the temperatures exceeded 500 °C for C$_3$H$_6$ and 540 °C for C$_3$H$_8$ [19]. Here, to investigate the reactivity of CO$_2$ and NO towards the oxygen vacancies of noble metal loaded ceria, C$_3$H$_6$ was used as reductant to pre-treat the noble metal loaded ceria samples. Table 7.2 summarises the result of CO and C$_3$H$_6$ pre-treatment over Rh/ceria and Pd/ceria.

The results of CO$_2$ pulses over C$_3$H$_6$ reduced Rh/Ceria are shown in Figure 7.7A and B. CO$_2$ was completely converted during stage I (pulse number 0-2000, Figure 7.7A), more CO formation than the quantity of pulsed CO$_2$
Figure 7.7: CO₂ pulse over at 450 °C C₃H₆ reduced Rh/ceria (A and B) and Pd/ceria (C and D). (A) and (C) gas evolution during the CO₂ pulses, and (B) and (D) oxygen and carbon balances.
molecules was observed. CO\textsubscript{2} started to break through from pulse number 2000. According to Equation 7.1 and 7.2, the oxygen balance and carbon balance were plotted, as shown in Figure 7.7B. The oxygen balance showed that the quantity of oxygen accumulation during stage I was around 40\% of oxygen vacancies that were created by the C\textsubscript{3}H\textsubscript{6} pre-treatment. The oxygen accumulation dropped at the same point as the CO\textsubscript{2} reactivity dropped. The carbon balance indicated that around 2\% of deposited carbon was oxidised. Initially the oxygen from the pulsed CO\textsubscript{2} was used for refilling the oxygen vacancies and those re-oxidised ceria vacancies were immediately partially used for the oxidation of the deposited carbon. After this initial stage the CO\textsubscript{2} conversion dropped when still a large amount of deposited carbon on the Rh/ceria sample was present. The re-oxidation rate of the remaining oxygen vacancies was inhibited.

Similar to the experiment over Rh/Ceria, the experiment of CO\textsubscript{2} pulses over C\textsubscript{3}H\textsubscript{6} reduced Pd/Ceria at 450 \degree C was performed (Figure 7.7C and D). The CO\textsubscript{2} conversion was complete during stage I (0-1200 pulse number) and dropped during the stage II. The oxygen balance (Figure 7.7D) indicated that around of 30\% of the oxygen vacancies had been refilled by CO\textsubscript{2} and only 1\% of the deposited carbon was converted during stage I. In stage II the remaining deposited carbon inhibited the re-oxidation of the oxygen vacancies and subsequently also the conversion of the deposited carbon.

In order to make a comparison between CO\textsubscript{2} and NO reactivity over the noble metal loaded ceria, NO pulse experiments were also performed over Rh/ceria and Pd/ceria with the same pre-treatment as CO\textsubscript{2} pulse experi-

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T/\degree C</th>
<th>Oxygen removal</th>
<th>Deposited carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Oxygen Ceria reduction layers</td>
<td></td>
</tr>
<tr>
<td>Rh/ceria</td>
<td>450</td>
<td>8.2\cdot10\textsuperscript{17}</td>
<td>3</td>
</tr>
<tr>
<td>Pd/ceria</td>
<td>450</td>
<td>7.3\cdot10\textsuperscript{17}</td>
<td>2.8</td>
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Figure 7.8: CO$_2$ pulse over at 450°C C$_3$H$_6$ reduced Rh/ceria (A and B) and Pd/ceria (C and D). (A) and (C) gas evolution during the CO$_2$ pulses, and (B) and (D) oxygen and carbon balances.
ments in order to obtain the same reduction degree of ceria and the same amount of deposited carbon.

The pulse of NO over a C\textsubscript{3}H\textsubscript{6} reduced Rh/Ceria at 450°C showed that NO showed full conversion at a time interval of 12000 pulses (stage I, Figure 7.8A), followed by NO conversion dropped to zero during stage II. The oxygen balance indicated the refilling of oxygen vacancies in the Rh/ceria sample and during stage I approximately 80% of oxygen vacancies were refilled. At the same time the carbon balance indicated that 90% of the total deposited carbon was oxidised to either CO or CO\textsubscript{2} (Figure 7.8A).

Similarly to Rh/ceria, the NO pulse experiment over the C\textsubscript{3}H\textsubscript{6} reduced Pd/Ceria at 450°C showed that NO showed full conversion at a time interval of 7000 pulses (stage I, Figure 7.8B). During stage I, around 90% of oxygen vacancies were refilled and around 70% of deposited carbon was oxidised.

### 7.4.2.4. Investigation of CO\textsubscript{2} and NO reactivity over reduced Rh/ceria support by flow reactor

Similar to TAP experiments, C\textsubscript{3}H\textsubscript{6} (1.25%) in helium was used as the reductant to pre-treat the Rh/ceria for 2 h in the flow reactor at 450°C for the experiments of NO reduction in the presence of an excess of CO\textsubscript{2}. The pre-treatment of C\textsubscript{3}H\textsubscript{6} led to 8.2\cdot10^{17} carbon atoms/mgcat deposition and around 3 layers of ceria reduction.

Figure 7.9 shows the results of the exposure of 0.2% NO in He over the
C$_3$H$_6$ reduced Rh/ceria at 450 oC with GHSV of 67,000 L/L/h. Figure 7.9A showed the MS response of gasses from the exit of the reactor. $m/e = 28$ was observed, attributed to the formation of N$_2$ and CO. NO was not observed during the first 450 s, followed by a signal increased gradually in the MS response. A low intensity of $m/e = 44$ was observed, attributed to the formation of CO$_2$. FT-IR results confirmed the formation of CO and CO$_2$ and excluded the formation of N$_2$O and NO$_2$, as shown in Figure 7.9B. The formation of only N$_2$ during the NO reduction was also reported by using $^{15}$NO, as reported in our previous work [7]. The reduced ceria was fully re-oxidised and the total quantity of CO and CO$_2$ formed during the NO exposure was calculated to be 8·10$^{17}$ molecules, which was almost equal to the carbon deposition by C$_3$H$_6$ pre-treatment. The result of NO reduction in the flow reactor under atmosphere pressure in Figure 7.9 is consistent with the result from TAP. NO can selectively be reduced to N$_2$ and deposited carbon can be oxidised during the NO exposure at the applied conditions.

Figure 7.10 shows the results of the exposure of 0.2% CO$_2$ in He over the C$_3$H$_6$ reduced Rh/ceria at 450 °C with GHSV of 67,000 L/L/h. $m/e = 28$ and $m/e = 44$ were observed in the MS response (Figure 7.10A), attributed to CO and CO$_2$, respectively. CO$_2$ immediately broke through during the CO$_2$ feeding.

The FT-IR was also used to further quantify CO and CO$_2$ from the exit of reactor (Figure 7.10B). The reduced ceria was fully re-oxidised and the amount of carbon consumption was calculated to be 8.2·10$^{16}$ carbon atoms/mgcat,
which was around 10% of the total deposited carbon. The result of Figure 7.10 confirms that from TAP experiments, *i.e.*, CO₂ is a mild oxidant and the deposited carbon can hardly be oxidised (gasified) during the CO₂ exposure.

For a typical diesel exhaust composition, approximately several hundred ppm NO had to compete with an excess of 5% O₂, 5% CO₂, and 5-10% H₂O in order to meet the future automotive legislation emission standards. Although the results from TAP experiments showed that NO was able to be reduced on oxygen vacancies into N₂, it was still a question whether NO was able to reduce into N₂ in the presence of excess CO₂. Therefore, 0.2% of NO was used to compete with 5% CO₂ over C₃H₆ reduced Rh/ceria at 450°C. As shown in Figure 7.11A, NO started to breakthrough at the time of t = 410 s m/e = 28 was observed, related to the formation of N₂ and CO. m/e = 44 immediately appeared during the CO₂ exposure and stabilized around 5%. There was no N₂O and NO₂ formation as confirmed by FT-IR (Figure 7.11B). Both N₂ and CO were observed with no detection of N₂O and NO₂ (detection limit 1 ppm), indicating that NO was completely selectively reduced to N₂ in a CO₂ excess. The total quantity of converted NO and CO₂ was calculated to be 1.1·10¹⁸ NO molecules/mgcat and 5·10¹⁷ CO₂ molecules/mgcat, respectively. Although the CO₂ concentration was 25 times larger than that of NO, the number of converted NO molecules was around 2.2 times more than that of converted CO₂. More importantly, the reduction of CO₂ mainly occurred during the first 80 s, and CO₂ was hardly reactive during time from 80 s to 410 s, where still full NO conversion was observed. The carbon balance of Figure 7.11B was plotted in Figure 7.11C. The amount of carbon consumption during the first 80 s was calculated to be 8.8·10¹⁶, which was around 10% of total deposited carbon. Therefore, the majority of the deposited carbon was consumed by the NO reduction to N₂. The reduction of CO₂ to CO occurred mainly over the reduced sites of ceria, refilling the oxygen vacancies. Once the oxygen vacancies were refilled the CO₂ conversion was almost completely stopped.

### 7.4.3. CO₂ versus the NO reactivity evaluation

Although CO₂ was able to fill the oxygen vacancies in the CO pre-reduced ceria, the effectiveness of the CO₂ re-oxidation was low since the CO₂ conversion dramatically declined after only a few CO₂ pulses as shown in Figure
Figure 7.11: Reduction of NO in the presence of excess CO\textsubscript{2} over C\textsubscript{3}H\textsubscript{6} pre-reduced Rh/ceria in a flow reactor at 450 °C.
The influence of CO\textsubscript{2} on NO reduction to N\textsubscript{2}

7.3A and B. Up to 2000 CO\textsubscript{2} pulses, only 50% of oxygen vacancies were refilled. Regarding the C\textsubscript{3}H\textsubscript{6} pre-reduced ceria, it can be concluded that the CO\textsubscript{2} was mainly used for the re-filling oxygen vacancies. CO\textsubscript{2} pulses will hardly consume any deposited carbon (Figure 7.4A and B). The operando Raman experiments under atmosphere pressure (Figure 7.6A and B) also pointed out that CO\textsubscript{2} is a mild oxidant in oxidising the reduced ceria and it hardly oxidised the deposited carbon. Even with noble metal loading, both the TAP multi-pulse experiment (Figure 7.7) and the flow reactor (Figure 7.10) at atmospheric pressure suggest that CO\textsubscript{2} still hardly oxidised the deposited carbon. Further, from the perspective of thermodynamics, the gasification of carbon (stable graphite) to CO by CO\textsubscript{2} at this temperature is not favoured [28].

In contrast, NO pulses over C\textsubscript{3}H\textsubscript{6} reduced ceria sample showed that NO was completely reduced into N\textsubscript{2} (stage I, Figure 7.4C), where 84% of oxygen vacancies were refilled and 90% of the deposited carbon was oxidised (Figure 7.4D). The TAP multi-pulse experiments suggested that NO was the more efficient oxidant for refilling oxygen vacancies and oxidation of deposited carbon (through the lattice), as compared to CO\textsubscript{2}. Again, the flow reactor experiments under atmospheric conditions also confirmed that the NO can be reduced to N\textsubscript{2} and oxidise the deposited carbon.

Moreover, the CO\textsubscript{2} and NO competition experiment over the C\textsubscript{3}H\textsubscript{6} pre-reduced Rh/ceria in the flow reactor indicated that NO is the much more powerful oxidant in competing for the oxygen vacancies (Figure 7.11). Around 90% of deposited carbon was consumed by NO. NO is selectively reduced to N\textsubscript{2} in the absence and presence of CO\textsubscript{2}.

In the Di-Air system, total reduction capacity, including the oxygen vacancies of ceria and the deposited carbon, determined the quantity of NO molecules conversion in to N\textsubscript{2}. And fuel injection is used to create the oxygen defect capacity. The low reactivity of CO\textsubscript{2} towards oxygen vacancies and deposited carbon over both reduce ceria and noble metal ceria implies that the most of the fuel will be used for reduction NO, not converting CO\textsubscript{2}. 
7.5. Conclusions

- CO₂ is a mild oxidant in the oxidation of oxygen vacancies of ceria due to the existence of a (quasi-) equilibrium between CO, CO₂, Ce³⁺, and Ce⁴⁺. The deposited carbon, generated during C₃H₆ (fuel) pre-treatment, will hardly be converted during CO₂ exposure.

- The loading of noble metals, Rh and Pd on the ceria hardly changed the reactivity of CO₂ in the oxidation of oxygen vacancies and deposited carbon.

- Compared to CO₂, NO was a much stronger oxidant. The deposited carbon can be fully oxidised (gasified) during the NO exposure.

- Traces of NO were able to compete with an excess of CO₂ for oxygen vacancies over Rh/ceria. The presence of CO₂ in the exhaust gas streams of lean burn engines will not significantly affect the NO reduction efficiency.
References


Summary and Outlook
Nitrogen oxides (NO$_x$, including NO and NO$_2$) are a group of hazardous, toxic and harmful gasses, which have an adverse effect on both environment and human health, e.g., acid rain, photochemical smog, and affecting the human respiratory system. The NO$_x$ concentration in most of the EU cities exceeds the EU annual limit value (40 μg/m$^3$). Around 40% of the emitted NO$_x$ is attributed to transport related emissions. In currently applicable Euro 6, the real NO$_x$ emission from a diesel car is on average 400% than the Euro 6 regulation limit allows if measured under more realistic driving conditions. Although NSR and SCR DeNO$_x$ systems have been broadly investigated and commercially applied with the aim to reduce NO$_x$ emissions from lean burn engines, some common problems still exist, e.g., a narrow temperature window and a low gas hourly space velocity (up to 50,000 L/L/h) in order to convert the NO$_x$ selectively into N$_2$. Due to the in practice high NO$_x$ emission from September 2017 additional legislation will be in force to arrive at a more realistic determination of the highly dynamic NO$_x$ emission by among others the introduction of the real driving emission (RDE) test in the certification procedure. The Di-Air (Diesel NO$_x$ after treatment by Adsorbed Intermediate Reductants) system was developed by Toyota (2011-2012) and is still under development. This Di-Air system showed promise by yielding a high NO$_x$ conversion, especially at high temperature (up to 600 $^\circ$C) and high gas hourly space velocity (up to 125,000 L/L/h). This system opts to meet the future stringent NO$_x$ reduction requirements under RDE test conditions (Chapter 1).

However, little is known about this system. The Di-Air system operates with high frequent injection of fuel pulses, this means that the catalyst operates under transient conditions. This is an open opportunity for an investigation by a transient research technique, like Temporal Analysis of Products (TAP). In Chapter 2 this nano-pulse reactor system is described and the qualities of this home-built system are demonstrated. Especially important, with regard to this thesis, are the quantitative capabilities of this machine. Depending on the complexity of the mass fragmentation of the molecules under investigation, mass balances typically close from 85% to 100%.

The principle and fundamental understanding of the Di-Air system is a prerequisite for the optimisation and application of this system. Moreover, the first step towards resolving the reaction mechanism is to understand the
role of each catalyst component in their claimed complex catalyst formula-
tion (Rh, Pt, K, Ba, Ce on an alumina support) in the reaction network for
NO reduction into nitrogen. Therefore, the research leading up to this the-
esis started by investigating the specific role each Di-Air catalyst component
plays. The role of the main Di-Air catalyst components is summarised as
follows:

- **Al₂O₃**
  C₃H₆, C₃H₈, CO, CO₂, H₂, and NO molecules were found to have a very
  limited interaction with the Al₂O₃ surface, *i.e.*, adsorption and desorption.
  No reactions were found to take place in the temperature range between
  RT - 600 °C (not in this thesis).

- **Ceria**
  Ceria was found to be capable of both fuel oxidation and NO conversion
to either N₂ or NO₂.
  Oxidised ceria showed high activity in the oxidation of CO, H₂, and hydro-
carbons in the absence of gas-phase oxygen. The obtainable ceria
reduction degree was around 3 times higher when hydrocarbons (C₃H₆
and C₃H₈) were used as a reductant at 580 °C, as compared to H₂ and
CO. Hydrocarbons led to the formation of carbon deposits on the reduced
ceria surface. The higher reduction degree of ceria obtained by C₃H₆ and
C₃H₈ above 500 °C can explain Toyota’s observation that fuel injection led
to higher NOx conversion and efficiency than that of CO and H₂ at high
temperature (Chapter 3).
  Oxidised ceria showed hardly any activity in the reduction of NO to N₂.
  H₂ or CO or hydrocarbon pre-reduced ceria were found to be very active
in the selective reduction of NO to N₂. Oxygen anion vacancies in ceria
are responsible for the decomposition of NO to N₂, thereby re-oxidising
these defect centres. The delayed oxidation of carbon deposits by oxy-
gen species originating from lattice oxygen will in practice maintain a re-
duced surface state during lean fuel conditions. These carbon deposits
can, therefore, be seen as a stored reductant with a delayed function
(Chapter 4).

- **Noble metal (Rh, Pt, and Pd)**
  Noble metals on ceria enhance the rate and degree of ceria reduction by
hydrocarbon based fuels. Rh is the most active among the investigated noble metals. With regard to NO reduction, the noble metals accelerate the selective reduction of NO into N₂, since less N accumulation on the catalyst was observed in comparison with NO reduction over bare ceria. The formation of both N₂O and NO₂ was excluded over reduced noble metal/ceria (Chapter 5).

- Alkali and alkaline earth metals (K and Ba):

The addition of potassium to Rh/ceria resulted in a decrease in NO decomposition activity over time, i.e., decrease with an increase in the number of oxidation-reduction cycles. Potassium can adsorb NOₓ, but it requires a high temperature to desorb (700 °C), which in turn (NOₓ adsorption) inhibits the reduction of the ceria support by the fuel. Therefore, the addition of potassium and/or barium onto ceria can have a short term benefit for the first few cycles. However, on the long term, the addition of potassium and barium will have adverse effects (not in this thesis).

Other oxidants, e.g., O₂, CO₂, and H₂O, will also react with reduced ceria. The competition for oxygen vacancies between NO and other oxidants may be of critical importance. Therefore, the activity and selectivity of NO reduction in the presence of an excess of O₂ and CO₂ was investigated. It was found that small (trace) amounts of NO can decisively compete for oxygen vacancies, leading to the formation of N₂, with excess O₂ over both reduced ceria and noble metal loaded reduced ceria. Oxygen vacancies in ceria (directly) and deposited carbon (indirectly) are responsible for the high activity and selectivity over a broad temperature window (250 - 600 °C) and up to high GHSV (up to 170.000 L/L/h). No N₂O was observed, and NO₂ was only observed when NO and O₂ broke through when ceria is fully re-oxidised (Chapter 6). CO₂ was found to be a mild oxidant, able to oxidise oxygen vacancies, but was found to be largely incapable to oxidise the deposited carbon formed upon C₂H₆ pre-treatment in order to reduce ceria. In the competition for oxygen defect sites, the high NO decomposition activity and selectivity observed in (an excess) CO₂ indicated a strong preference for NO over CO₂. The presence of excess CO₂ hardly affected NO reduction into N₂ (Chapter 7).

The research in this thesis demonstrates that the Di-Air system is a promis-
Summary and Outlook

Ceria is a promising base/starting material for an optimised catalyst formulation for the Di-Air system. Noble metals (especially Rh) and perhaps other metals are indispensable in order to lower fuel oxidation temperatures. NO\textsubscript{x} storage components such as potassium and barium are not contributing positively to the performance of a Di-Air catalyst.

In this thesis, C\textsubscript{3}H\textsubscript{6} or C\textsubscript{3}H\textsubscript{8} were used to mimic fuel. Instead of high-frequency fuel injection upstream of the catalyst bed, a continuous flow of C\textsubscript{3}H\textsubscript{6} or C\textsubscript{3}H\textsubscript{8} is used to simulate fuel injection. Therefore, more research is needed with regard to an optimal fuel injection strategy.

Ceria is the core component in the Di-Air catalyst composition. The redox property of ceria (Ce\textsuperscript{4+} $\leftrightarrow$ Ce\textsuperscript{3+}) is essential for NO\textsubscript{x} reduction in the Di-Air system. However, the long-term usage of the catalyst in automotive and truck applications (at least 5 years in Europe and up to 12 years in for example the USA) requires a highly stable structure. Doping of ceria by Zr in the form of a Zr-Ce solid solution is commonly reported to stabilise the ceria structure. However, the redox behaviour of ceria is related to both the composition and the structure of the solid solution. Trovarelli et al. reported that the content of doped ZrO\textsubscript{2} should not exceed 50% in the Zr-Ce solid solution [1]. The inclusion of yttrium (Y), lanthanum (La) or gadolinium (Ga) ions in the Ce\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{2} lattice can enhance oxygen anion diffusion, thereby decreasing its reduction temperature. The induced decrease in reduction temperature by these tri-valent dopants might enhance the reactivity of ceria towards hydrocarbons, especially at lower temperatures, thereby alleviating the need for noble metals. Therefore, a test series in which different dopants in various Zr-Ce solutions are screened is recommended for the final application of the Di-Air system. Other reducible rare earth oxide-based solid solutions, e.g., PrO\textsubscript{2} and TbO\textsubscript{2}, might also be considered as (research) alternatives for ceria in the Di-Air system. Although the abundance of Pr and Tb, 1.3 and 0.1 ppm, respectively, versus 8.9 ppm for Ce, does not contribute to the use of abundant elements in catalysis. The study of these materials might, however, yield a better understanding of the relation between the reducibility of the material and its catalytic properties. PrO\textsubscript{2}-based solid solutions, e.g., Zr-Pr or Y-Pr, have shown a better redox
performance as compared to CeO$_2$-based solid solutions [2], which may be beneficial for fuel activation and subsequent creation of oxygen vacancies at a lower temperature.

In this thesis, a simple incipient wetness method was used to load 0.5 wt.% noble metal (Rh) on ceria in order to demonstrate the role of Rh in the Di-Air system. The loading of noble metal onto ceria significantly decreased the hydrocarbon activation temperature (Chapter 5). The Rh loading and the dispersion and the (hydro-thermal) stability on ceria should be optimised before final application in the Di-Air system.

High temperature has an adverse effect on noble metal stability when supported on oxides. High temperature may cause sintering of the noble metal particles, resulting in loss of specific surface area and hence a loss in activity. In automotive exhaust gas abatement, the vapour-phase transport of PtO$_2$ to the downstream SCR catalyst is regarded as a leading cause of Diesel Oxidation Catalyst (DOC) catalyst degradation [3]. Surface oxygen vacancies on ceria have been proposed to act as a trap for noble metals and, therefore, protect against sintering through strong chemical bond formation [4, 5]. This work may also be a good basis/starting point to develop highly dispersed and stable Rh/ceria catalysts.

Going back to the automotive DeNO$_x$ system. In Europe, 40% of the NO$_x$ emissions find their origin in transportation. Although the application of electrical cars in cities can reduce NO$_x$ pollution in cities to some extent, the overall pollution produced by the electrical cars, e.g., the production of electricity, the pollution by making the battery and the disposal of the battery, etc., is more than that of fuel cars. More importantly, the higher cost associated with electric cars and the limited progress in battery technology and the uncertainty in live time, thereof (at least 12-15 years should be required) impedes their popularity amongst potential users. Urea (ammonia)-SCR technology has proven its potential already in numerous passenger cars, which are compliant with the current Euro 6 legislation. However, refill costs and the necessity for refills within a service interval is a drawback. More importantly, ‘NH$_3$’ slip will remain a problem, since it is a challenge to obtain the right amount of urea at the right time in the extremely dynamic transient. The NO$_x$ concentration in the exhaust gas depends on the current dynamic driving behaviour. In addition, the trend of downsizing engines will also
challenge the requirements on the SCR technology, by increasing the gas hourly space velocity and the temperature. With regard to the NSR system, the large issue is the narrow temperature window, the low allowable gas hourly space velocity, and the formation of undesired products, NO\textsubscript{2} and N\textsubscript{2}O. The use of K and Ba components as NO\textsubscript{x} adsorbents may give rise to problems when they cannot be regenerated very easily (high temperature and strong reducing environment) in the driving behaviour of the vehicle. Furthermore, K and Ba in the catalyst formulation have the tendency to form N\textsubscript{2}O (nitrous oxide) under defined driving conditions. N\textsubscript{2}O is a very strong greenhouse gas (600 times of that of CO\textsubscript{2}) and contributes to the depletion of the ozone layer.

This thesis demonstrates that the Di-Air system is a promising system to meet more stringent NO\textsubscript{x} abatement requirements under realistic test conditions (RDE test). The deposited carbon from the fuel injection acts as a reductant buffer, which makes this DeNO\textsubscript{x} system more dynamic as compared to the NSR and SCR system. However, the implementation of this system in the current market requires the installation of the fuel injection valve downstream of the engine and upstream of the catalyst/monolith, This redesign of the engine system, catalyst formulation and system optimisation (motor management system, coupled with a guaranteed performance over the life time of the car, etc.) are an enormous challenge. More work is really needed for a successful application of the Di-Air system and we are just at the beginning.
Samenvatting en Vooruitzicht
Stikstofoxide (NO\textsubscript{x}, voornamelijk alleen NO en NO\textsubscript{2}) zijn een verzameling schadelijke en toxische gassen, die een negatieve invloed hebben op zowel het milieu als de gezondheid van de mens, zoals zure regen, smog, en in het bijzonder op het ademhalingssysteem. De NO\textsubscript{x} concentratie in de meeste EU steden overschrijdt de jaarlijkse EU limiet (40 μg/m\textsuperscript{3}). Ongeveer 40% van de uitgestoten hoeveelheid NO\textsubscript{x} is aan de transportsector gerelateerd. In de praktijk zijn de NO\textsubscript{x} emissies van diesels ruim 400% hoger dan de Euro 6 norm. Alhoewel de NSR en SCR DeNO\textsubscript{x} systemen uitgebreid zijn onderzocht en commercieel worden toegepast om de NO\textsubscript{x} uitstoot te reduceren, blijven een aantal wetenschappelijke uitdagingen bestaan, zoals het beperkte temperatuurbereik van 150 tot 350 °C en een beperkte contactsnelheid (GHSV (gas hourly space velocity) tot 50,000 L/L/h) om NO\textsubscript{x} selectief in N\textsubscript{2} te kunnen omzetten. Door de in praktijk hoge NO\textsubscript{x} emissies, is vanaf september 2017 additionele wetgeving van kracht om de zeer dynamische NOx emissie te verminderen door onder andere de introductie van praktijk e rijemissie ('real driving emission' (RDE)) in de certificeringsprocedure op te nemen. In 2011-2012 is het Toyota Di-Air ('Diesel NO\textsubscript{x} aftertreatment by Adsorbed Intermediate Reductants') systeem in ontwikkeling genomen in de ontwikkeling de Dit Di-Air systeem oogt veelbelovend, daar het hoge NO\textsubscript{x} omzetting bij hoge temperatuur (tot 600 °C) en zeer korte contacttijden (GHSV tot 125,000 L/L/h). Dit systeem opteert om aan de huidige en toekomstige strenge NO\textsubscript{x} reductievereisten onder RDE test condities te voldoen (Hoofdstuk 1).

Over dit systeem is echter weinig bekend. De werking van het Di-Air is gebaseerd op frequente brandstofinjectiepulsen in de uitslaat vòòr het nabehandelingsysteem voor schonere uitaatgassen. Dit houdt in dat de katalysator in het nabehandelingsysteem onder wisselende omstandigheden opereert. Dit is een open uitnodiging voor een onderzoek met een transiënte onderzoekstechniek als de ‘Temporal Analysis of Products’ (TAP). In Hoofdstuk 2 wordt dit nano-puls reactor systeem beschreven en worden de kwaliteiten van dit in eigen huis gebouwd systeem gedemonstreerd, waarbij voor mijn onderzoek de kwantitatieve prestaties van dit apparaat essentieel zijn. Afhankelijk van de analyse complexiteit door de fragmentatie van de onderzochte moleculen in de massaspectrometer sluiten alle massabalansen in het algemeen tussen de 85% en 100%.
Fundamentele kennis van dit Di-Air systeem is de voorwaarde voor de optimalisatie en toepassing van deze technologie. De eerste stap naar het ontrafelen van het reactiemechanisme is het begrijpen van de rol die elke katalysatorcomponent in de door Toyota geclaimde complexe katalysatorcompositie (Rh, Pt, K, Ba, Ce gedragen op een alumina support) in het NO-reductie reactienetwerk. De rol van de belangrijkste Di-Air katalysatorcomponenten kan als volgt worden samengevat.

- **Al_2O_3**
  C₃H₆, C₃H₈, CO, CO₂, H₂, en NO moleculen vertoonden een zeer bescheiden interactie met het Al₂O₃ oppervlak, *i.e.*, adsorptie en desorptie. Er konden geen reacties tussen deze moleculen en het alumina worden vastgesteld in het temperatuursinterval van kamertemperatuur tot 600 °C (niet in dit proefschrift).

- **Ceriumoxide**
  Ceriumoxide is in staat om zowel brandstof (koolwaterstoffen) te oxideren tot H₂O en CO₂, als NO om te zetten naar N₂ of NO₂.

Geoxideerd ceriumoxide vertoonde een hoge activiteit in de oxidatie van CO, H₂, en koolwaterstoffen in de afwezigheid van zuurstof. De reductiegroei van ceriumoxide is ongeveer 3 maal hoger, als koolwaterstoffen (C₃H₆ en C₃H₈) werden gebruikt als reductor in plaats van H₂ en CO. Het gebruik van koolwaterstoffen leidt tevens tot de vorming van koolstofafzettingen op het gereduceerde ceriumoxide-oppervlak. De hogere reductiegroei van ceriumoxide, verkregen door het gebruik van C₃H₆ en C₃H₈ boven 500 °C, kan Toyota’s waarneming verklaren, dat (koolwaterstof) brandstoffinjections tot een hogere NOₓ conversie en efficiency leidde in vergelijking tot CO en H₂ (Hoofdstuk 3).

Geoxideerd ceriumoxide vertoonde geen enkele activiteit in de reductie van NO naar N₂. Voor H₂, CO of koolwaterstof voor-gereduceerd ceriumoxide blijkt dat deze zeer actief was in de reductie van NO naar N₂. Zuurstofanionroofstergaten in ceriumoxide zijn verantwoordelijk voor de omzetting van NO naar N₂, waarbij deze roostergaten worden opgevuld. De oxidatie van de koolstofafzettingen door het zuurstof uit het ceriumoxide rooster, zal er voor zorgen dat het ceriumoxide gereduceerd zal blijven. Deze koolstofafzettingen kunnen dan als een opgeslagen reductor
Samenvatting en Vooruitzicht

met een uitgestelde werking beschouwd worden (Hoofdstuk 4).

- **Edelmetaal (Rh, Pt en Pd)**

Edelmetalen op het ceriumoxide-oppervlak verhogen de snelheid van de reductie en de reductiegraad van het ceriumoxide als koolwaterstof voor de reductie wordt gebruikt. Rh is het meest actief in de groep van de onderzochte edelmetalen. Wat betreft de NO-reductie, versnellen de edelmetalen de selectieve reductie van NO naar N$_2$ en vindt er aanzienlijk minder N ophoping op de katalysator plaats in vergelijking met de NO reductie over puur ceriumoxide. De vorming van zowel N$_2$O als NO worden over gereduceerd edelmetaal/ceriumoxide uitgesloten (Hoofdstuk 5).

- **Alkali- en aardalkali-metalen (K en Ba):**

De toevoeging van kalium aan Rh/ceriumoxide resulteerde in een verlaging van de NO omzetting in de tijd. Kalium kan NO$_x$ adsorberen, maar een hoge temperatuur van boven de 700 °C is noodzakelijk voor de desorptie ervan. Dit heeft tot gevolg dat de reductie van het op het kalium geadsorbeerde NO$_x$ beperkt wordt. Daardoor heeft de toevoeging van kalium en/of barium alleen in de eerste cyclus effect. De toevoeging van kalium en barium aan de rhodium-ceriumoxide katalysator resulteert in een gedeeltelijke omzetting van NO naar N$_2$O (lachgas) over de gereduceerde katalysator. Lachgas heeft een zeer sterk broeikaseffect (300 x sterker dan CO$_2$ (niet beschreven in dit proefschrift)).

Andere oxidatiemiddelen, zoals O$_2$, CO$_2$, en H$_2$O, zullen eveneens met gereduceerd ceriumoxide reageren. De competitie om zuurstofroostergaten tussen NO en andere oxidatiemiddelen kan cruciaal zijn. Om deze reden werd de activiteit en selectiviteit van NO-reductie onderzocht in een overmaat O$_2$ en CO$_2$. Hieruit bleek dat zeer kleine (spoor) hoeveelheden NO in een overmaat zuurstof en CO$_2$ de competitie om deze zuurstofroostergaten aan kan onder vorming van N$_2$ Dit geldt zowel voor gereduceerd ceriumoxide als voor met edelmetaal beladen gereduceerd ceriumoxide. Zuurstofroostergaten in ceriumoxide (direct) en de koolstofafzetting (indirect) zijn verantwoordelijk voor de hoge activiteit en selectiviteit over een zeer breed temperatuurinterval (250 - 600 °C) en tot hoge gasdebieten (GHSV tot 170.000 L/L/h). N$_2$O werd niet waargenomen en NO$_2$ werd alleen waargenomen wanneer NO en O$_2$ doorbraken en het ceriumoxide volledig was geoxideerd. (Hoofdstuk 6).
CO₂ bleek een mildere oxidatiemiddel te zijn. Het was in staat zuurstofroostergaten te oxideren, maar was niet in staat om de koolstofafzettingen te oxideren. De aanwezigheid van een overmaat CO₂ had nauwelijks invloed op de reductie van NO naar N₂ (Hoofdstuk 7).

Het onderzoek in dit proefschrift laat duidelijk zien dat het Di-Air systeem een zeer veelbelovend is voor de zeer efficiënte katalytische omzetting van NO naar N₂ in oxiderend milieu. Zuurstofroostergaten in het ceriumoxide spelen een sleutelrol in de selectieve omzetting van NO naar N₂. Ceriumoxide vormt een veelbelovende basis voor een geoptimaliseerde katalysator voor het Di-Air systeem. Edelmetalen (met name Rh), en wellicht andere metalen, zijn onmisbaar om een lager en dus breder temperatuurinterval te realiseren voor de NO reductie. Toevoeging van NOₓ opslagcomponenten, zoals kalium en barium, leveren een negatieve bijdrage aan de prestatie van de Di-Air katalysator.

In dit proefschrift worden C₃H₆ of C₃H₈ gebruikt om de dieselbrandstof na te bootsen. In plaats van hoog frequente brandstofinjectie stroomopwaarts van de katalysator, wordt er een continue C₃H₆ of C₃H₈ stroom toegepast om de brandstofinjectie te simuleren. Door deze aanpak is verder onderzoek nodig om een optimale brandstofinjectiestrategie te kunnen vaststellen.

Ceriumoxide is het hoofdbestanddeel van de Di-Air katalysator. De redox eigenschap van ceriumoxide (Ce⁴⁺ ↔ Ce⁴⁺) is essentieel voor de NOₓ reductie in het Di-Air systeem. De lange wettelijke levensduur van de katalysator in transporttoepassingen (ten minste 5 jaar in Europa en tot 12 jaar in bijvoorbeeld de VS) vereist een zeer stabiele structuur. Het doteren van ceriumoxide met Zr in de vorm van een Zr-Ce mengkristal ter stabilisatie van de ceriumoxidestructuur wordt algemeen gerapporteerd. Echter, het redoxgedrag van ceriumoxide is gerelateerd aan zowel de samenstelling als de structuur van het mengkristal. Trovarelli et al., rapporteerde dat de ZrO₂ hoeveelheid niet de 50% mag overstijgen in het Zr-Ce mengkristal [1]. De inclusie van yttrium (Y), lanthaan (La) of gadolinium (Ga) ionen in het Ce₁₋ₓZrₓO₂ kristalrooster kan de zuurstofaniondiffusie verhogen, waardoor de reductietemperatuur van het mengkristal afneemt. De geïnduceerde afname van de reductietemperatuur door deze trivale doteringselementen kan de reactiviteit van ceriumoxide naar koolwaterstoffen verhogen met name bij lagere temperatuur, waardoor mogelijk de noodzaak voor het ge-
bruik van edelmetalen verdwijnt. Om deze reden wordt een vervolgonderzoek, waarin verschillende doteringselementen in verscheidene Zr-Ce mengkristallen worden onderzocht, aanbevolen voorafgaand aan de daadwerkelijke toepassing van het Di-Air systeem. Andere op reduceerbare zeldzame aardmetalen gebaseerde mengkristallen, e.g., PrO₂ and TbO₂, kunnen als (onderzoeks)alternatieven voor ceriumoxide in het Di-Air systeem worden overwogen, alhoewel de beschikbaarheid van Pr en Tb, 1.3 en 0.1 ppm, respectievelijk tegen de 8.9 ppm voor Ce, niet bijdraagt aan de doelstelling om alleen goed beschikbare elementen voor katalyse te gebruiken. Een studie naar deze materialen zou echter wel tot een beter inzicht in de relatie tussen de reduceerbaarheid van het materiaal en de katalytische eigenschappen kunnen leiden. Op PrO₂ gebaseerde mengkristallen, e.g., Zr-Pr of Y-Pr, laten betere redoxprestaties in vergelijking met op CeO₂ gebaseerde mengkristallen zien [2], wat een positieve uitwerking kan hebben op de brandstofreactiviteit en de daarop volgende vorming van zuurstofroostergaten bij een lagere temperatuur.

In dit proefschrift wordt een simpele porievolume impregnatie methode gebruikt om 0.5 wt.% edelmetaal (Rh) op ceriumoxide aan te brengen om het effect van Rh in het Di-Air systeem te demonstreren. Het aanbrengen van het edelmetaal op ceriumoxide resulteerde in een significante afname van de koolwaterstofactivatietemperatuur (Hoofdstuk 5). De hoeveelheid Rh, de dispersie en (hydro-thermische) stabiliteit op ceriumoxide zouden moeten worden geoptimaliseerd voor de daadwerkelijke applicatie van het Di-Air systeem.

Extreem hoge temperaturen hebben een negatieve impact op de stabiliteit van edelmetalen gedragen op oxiden. Het kan het sinteren (samenklotseren) van de edelmetaaldeeltjes veroorzaken, wat resulteert in een verlies van specifiek oppervlak en daardoor een verlies aan activiteit. In het reinigen van dieseluitletgas wordt het transport door de gasfase van het vluchtige PtO₂ naar de stroomafwaarts gelegen SCR katalysator beschouwd als een hoofdoorzaak voor de degradatie van de oxidatiekatalysator (‘Diesel Oxidation Catalyst’ (DOC)) [3]. Zuurstofroostergaten aan het oppervlak van ceriumoxide zijn voorgesteld als zijnde gaten voor edelmetalen en zouden om deze reden bescherming bieden tegen het sinteren van edelmetalen door de vorming van een sterke chemische binding [4, 5]. Voor een vervolgstudie
kan dit uitgangspunt een goed startpunt zijn voor het ontwikkelen van zeer disperse en stabiele Rh/ceriumoxide katalysatoren.

Terugkerend naar het DeNO$_x$ systeem voor de transportsector. In Europa is deze verantwoordelijk voor 40% van de NO$_x$ uitstoot. Alhoewel de toepassing van elektrische auto’s in steden deNO$_x$ vervuiling in die steden tot op zekere hoogte kan reduceren, dan kan de algehele vervuiling veroorzaakt door deze elektrische auto’s, e.g., de productie van elektriciteit, de vervuiling veroorzaakt tijdens de productie van de batterijen en de verwerking van afgedankte baterijen, etc., groter zijn dan de vervuiling veroorzaakt door auto’s rijdend op fossiele brandstoffen. Nog belangrijker zijn de hogere kosten ge-relateerd aan elektrische auto’s, de bescheiden vooruitgang die is geboekt op het gebied van de batterijtechnologie en de onzekerheid omtrent de levensduur daarvan (ten minste 12-15 jaar is vereist) welke de populariteit onder potentiële gebruikers dempen. Ureum (ammonia-) SCR technologie heeft haar potentieel inmiddels bewezen in talloze auto’s en vrachtwagen l, die voldoen aan de huidige Euro 6 norm. Echter, de bijvulkosten van ureum en de noodzaak van het bijvullen tussen de onderhoudsbeurten zijn een nadeel. Tevens is het van belang dat het doorslippen van ‘NH$_3$’ een serieus emissieprobleem blijft en het is een uitdaging om precies de juiste hoeveelheid ureum op precies het juiste moment tijdens het extreem dynamische rijgedrag te doseren. De NO$_x$ concentratie in de uitlaat is sterk afhankelijk van het dynamische rijgedrag van de autonome bestuurder. Bovendien zal de huidige motor-verkleiningstrend (meer vermogen uit een kleiner motorvolume) het nodige vergen van de SCR technologie door de toename van een veel hogere gasdoorvoersnelheid en temperatuur van het uitlaatsysteem. Ten aanzien van het NSR (NO$_x$ Storage and Reduction) systeem zijn de problemen het krappe temperatuurwerkingsinterval, de relatief lage gasdoorvoersnelheid en de vorming van ongewenste bijproducten zoals NO$_2$ en N$_2$O. Het gebruik van K en Ba componenten als NO$_x$ adsorbentia kan tot problemen in het rijgedrag op de weg leiden, indien deze niet makkelijk zijn te regenereren (hoge temperatuur en een sterk reducerende atmosfeer). Daar komt nog bij dat deze K en Ba katalysatorcomponenten onder bepaalde rijcondities de neiging hebben om N$_2$O (lachgas) te vormen. N$_2$O is een sterk broeikasgas (300 keer sterker dan CO$_2$) en draagt bij aan de aantasting van de ozonlaag.
Dit proefschrift laat zien dat het Di-Air systeem een veelbelovende kandidaat is om aan de verscherpte NO\textsubscript{x} emissievereisten onder realistische testcondities (RDE test) te voldoen. Het door de brandstofinjecties op de katalysator afgezette koolstof functioneert als een reductorbuffer, waardoor dit DeNO\textsubscript{x} systeem veel dynamischer is in vergelijking met de NSR en SCR systemen. Echter, de implementatie van dit systeem in de huidige markt vereist de installatie van een brandstofinjectieklep na de motor en vòòr de (Di-Air) katalysator. Het vereiste herontwerp van het motor en uitlaatsysteem, de optimalisatie van de katalysatorsamenstelling en de gehele systeemoptimalisatie (motor management systeem gekoppeld aan de gegarandeerde prestatie over de levensduur van de auto, etc.) zijn enorme uitdagingen. Meer onderzoek is vereist voordat een succesvolle toepassing van het Di-Air systeem kan worden gerealiseerd.

We staan nog maar aan het begin.

Bibliografie


Fundamental understanding of the Di-Air system I: The difference in reductant pre-treatment of ceria
Figuur A.1: An atomic-scale hexagonal lattice of graphene structure.

<table>
<thead>
<tr>
<th>Items</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C length</td>
<td>0.142 nm</td>
</tr>
<tr>
<td>Hexagonal unit area</td>
<td>0.524 nm²</td>
</tr>
<tr>
<td>Carbon atoms in one hexagonal unit</td>
<td>2</td>
</tr>
<tr>
<td>BET area of ceria</td>
<td>65 m²/g</td>
</tr>
<tr>
<td>Sample weight</td>
<td>21.2 mg</td>
</tr>
<tr>
<td>Sample BET area</td>
<td>1.378 m²</td>
</tr>
</tbody>
</table>

The deposited carbon during the C₃H₆ or C₃H₈ pre-treatment is assumed as graphene structure, as showed as in Figure A1. The parameters of hexagonal lattice of graphene and the ceria catalyst is shown in Table A.1.

In case of 2·10¹⁸ carbon atoms deposited, the number of hexagonal unit (N) is calculated to be 1·10¹⁸ using Equation A.1:

\[ N = \frac{\text{Thenumberofdepositedcarbonatoms}}{\text{Thenumberofcarbonatomsinonehexagonalunit}} \]  

(A.1)

The total area of deposited carbon S is calculated to be 0.0524 m² using the Equation A.2:
Figuur A.2: CO multi-pulse experiment over a pre-oxidised ceria at 580°C.

\[ S = N \times \text{Hexagonal unit area} \]  \hspace{1cm} (A.2)

The surface coverage of deposited carbon (θ) is calculated to be 4% using Equation A.3:

\[ \theta = \frac{S}{\text{Sample BET area}} \]  \hspace{1cm} (A.3)
Figuur A.3: CO multi-pulse experiment over a pre-oxidised ceria at 500 °C.
List of Presentations

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- Posthuma de Boer, J., **Wang, Y.**, Kapteijn, F., and Makkee, M. Novel concepts in TAP design. 1\textsuperscript{st} Temporal Analysis of Products (TAP) workshop, Denver, CO, USA, 2017.

- Makkee, M., and **Wang, Y.** NO\textsubscript{x} abatement via the Toyota Di-Air Technology, Global Automotive Management Council, Frankfurt, Germany, 2017. *Invited speaker*

**Poster Presentations at International Conferences:**

- **Wang, Y.**, Kapteijn, F., and Makkee, M. Oxygen Vacancies of ceria for Highly Selective and Reactive Reduction of NO into N\textsubscript{2}. 18\textsuperscript{th} Netherlands’ Catalysis and Chemistry Conference (NCCC), Noordwijkerhout, The Netherlands, 2017.

- **Wang, Y.**, Kapteijn, F., and Makkee, M. Oxygen Vacancies of ceria for Highly Selective and Reactive Reduction of NO into N\textsubscript{2}. 25\textsuperscript{th} North American Catalysis Society Meeting (NAM), Denver, CO, USA, 2017.
List of Publications

Publications related to this thesis:


- **Wang, Y.,** and Makkee, M. (2018). The influence of CO\(_2\) on NO reduction to N\(_2\) over reduced ceria - based catalyst, Applied Catalysis B: Environmental. (221),196-205


- **Wang, Y.,** Kapteijn, F., and Makkee, M., Evaluation the role of noble metals in NO reduction in the Di-Air DeNO\(_x\) system (submitted)

- **Wang, Y.,** and Makkee, M., The role of potassium in NO reduction in the Di-Air DeNO\(_x\) system (in preparation)
• **Wang, Y.,** and Makkee, M., The investigation of N₂O and NO₂ reduction over ceria (in preparation)

• **Wang, Y.,** and Makkee, M., Mechanism study of N₂O decomposition over ceria catalyst by the TAP (in preparation)

**Other publications:**


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**About the Author**

**Yixiao Wang**, was born on the 8<sup>th</sup> of January 1987 in Fuzhou, China. From 2005 to 2009, she studied at the department of Environmental Engineering in Beijing University of Chemistry and Technology (China), where she did her BSc project under the supervision of Prof. Xiujin Chen with the research topic of gas anaerobic digestion performance of the straw. She obtained the Bachelor degree in 2009. After graduation, she moved to Xiamen University (China) in 2010 to start her MSc education in Materials under the supervision of Prof. Zhang Qiqing and Hou Zhenqing. Her MSc thesis research was entitled: “controllable synthesis of metal oxides microcrystals”. She obtained her MSc degree in 2013. In September of the same year, she started her PhD, on the topic of NO<sub>x</sub> abatement for lean burn Engine of automotive, under the supervision of Prof.dr.ir. Michiel Makkee and Prof.dr. Freek Kapteijn, in the section of Catalysis Engineering, TU Delft. During her PhD, she joined a cooperation project with Fudan university for the topic of NO<sub>x</sub> reduction using ceria catalyst in 2015. From 2016.6 to 2016.12, she was a guest researcher in Utrecht University (The Netherlands), in the group of prof. dr. ir. B.M. (Bert) Weckhuysen, department of Inorganic Chemistry and Catalysis.

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