Fundamental understanding of the Di-Air system (an alternative NOx abatement technology). I: The difference in reductant pre-treatment of ceria

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**ABSTRACT**

Toyota’s Di-Air DeNOx system is a promising DeNOx system to meet NOx emission requirement during the real driving, yet, a fundamental understanding largely lacks, e.g. the benefit of fast frequency fuel injection. Ceria is the main ingredient in Di-Air catalyst composition. Hence, we investigated the reduction of ceria by reductants, e.g. CO, H2, and hydrocarbons (C3H8 and C3H6), with Temporal Analysis of Product (TAP) technique. The results show that the reduction by CO yielded a faster catalyst reduction rate than that of H2. However, they reached the same final degree of ceria reduction. Hydrocarbons generated almost three times deeper degree of ceria reduction than that with CO and H2. In addition, hydrocarbons resulted in carbonaceous deposits on the ceria surface. The total amount of converted NO over the C3H8 reduced sample is around ten times more than that of CO. 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 NOx abatement system.

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1. Introduction

In the European Union (EU) the regulated NOx emissions have decreased over the past two decades. Nevertheless, 9% of EU-28 urban live in areas in which NOx concentrations still exceed regulated NOx standards in 2013, according to the Air quality for EU in 2014 (source European Environmental Agency [1]). In the European Union, around 40% of the NOx emissions are from the traffic sector [2]. Due to the limited effectiveness of currently available NOx abatement technologies, as of September 2017, 2.1 times the current Euro 6 NOx 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 this future NOx emission will become even more stringent, which clearly indicates that currently available technologies: Three-way catalyst (TWC), Urea-SCR (Selective Catalytic Reduction), Lean NOx Traps (NSR – NOx Storage & Reduction), still need significant improvements. Therefore, efficient exhaust emissions after-treatment technologies are highly demanded. Recently, Bisajji et al. (Toyota company) developed the Di-Air system (Diesel DeNOx System by Adsorbed Intermediate Reductants). Short rich

and lean time intervals are created by high frequency directly injecting hydrocarbons (diesel fuel injection) into the exhaust system upstream of a typical NSR catalyst (Pt/Rh/Ba/K/Ce/Al2O3) [4,5]. The Di-Air system has shown promise to meet future NOx emission standards under realistic driving test conditions.

In the Di-Air system, hydrocarbons are the most powerful reductants in the reduction of NOx, as compared to other reductants, e.g. CO and H2 [5]. However, the 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 is 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 H2 under rich conditions [6]. In our research, a commercially available model Zr and La-doped ceria is used. The Zr–Ce solid solution, in which zirconium partially replaces cerium, provides a higher (hydro)thermal 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 (N2), even in the presence of an excess of oxygen [9].

In this study, we mainly focus on the investigation of the reduction behavior of the Zr and La-doped ceria catalyst, using H2, CO, C3H6, and C3H8 as reductants. Temporal Analysis of Products (TAP) is used to ascertain the reaction between the reductants and the
catalyst. Since high intensity of hydrocarbon reductant injections is applied in the Di-Air system, these pulses will create a locally reduced environment. Therefore, all the experiments in this study are performed in the absence of gas-phase O₂. The performed experiments will provide an illustrative model of the product evolution as a function of the catalyst-reduction degree in an attempt to obtain a fundamental understanding of the Di-Air system. To demonstrate the effect of different reductants on NO reduction, NO reduction is performed over the Zr–La doped ceria by pre-treatment of various reductants. The re-oxidation of the reduced ceria by NO is identical to the reduction of NO into N₂ over reduced ceria.

2. Experimental

The catalyst used is a commercial Zr–La doped ceria (BASF company, denoted as ceria) which serves as a core component in the Di-Air catalyst formulation. The characterisation of this Zr–La doped ceria is described in more detail elsewhere [10].

2.1. Pulses experiment in TAP

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 × 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 are 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 elsewhere [9,11].

21.2 mg ceria (100–250 μm, BET surface area 65 m²/g) was used in the TAP reactor. In all experiments a starting pulse size of approximately 1.6 × 10⁻¹⁵ molecules (excluding internal standard gas) was used, the pulse size gradually decreased as an experiment during the reagent was pulsed from the closed and calibrated volume of the pulse-valve line. Prior to the reduction, the ceria was firstly re-oxidised at the same temperature at which the reduction was performed, using pulses of 80 vol.% O₂ in Ar until a stable O₂/Ar signal ratio was obtained. The reduction was carried out by pulsing reductant of either 80 vol.% C₃H₆ in Ne or 80 vol.% C₃H₈ in Ne or 80 vol.% CO in Ar or 67 vol.% H₂ in Ar until a stable reactant and product to the internal standard signal ratio was achieved, indicating that the ceria was equilibrated. NO pulse experiments were performed using 80 vol.% NO in Ar.

The consumption of the oxygen species from the ceria during H₂, CO, C₃H₆, and C₃H₈ pulses experiments was calculated using the following mass balance:

\[ n_{O, consumed} = n_{H₂O, obs} + n_{CO, obs} + 2n_{CO₂, obs} \]  

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

The number of carbon species deposited on the doped ceria surface in the C₃H₈ pulse experiments was calculated using the following mass balance:

\[ n_{C, deposited} = 3n_{C₃H₆, in} - 3n_{C₃H₆, obs} - n_{CO, obs} - n_{CO₂, obs} \]  

Similarly, the number of carbon species deposited on the ceria surface in the C₃H₈ pulse experiments was calculated using the following mass balance:

\[ n_{C, deposited} = 3n_{C₃H₆, in} - 3n_{C₃H₆, obs} - n_{CO, obs} - n_{CO₂, obs} \]  

The number of carbon species during CO pulse experiments on the ceria surface was calculated using the following material balance:

\[ n_{C, deposited} = n_{CO, obs} - n_{CO₂, obs} \]  

The average particles size of ceria was around 5 nm, based on XRD and TEM analyses [10]. 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 (0.316 nm). Assuming a perfect cubic crystal structure of ceria (size 5.0 nm), the total number of hypothetical ceria layers were determined to be 16 (111) layers. Assuming that Zr is identical to Ce, a maximum of 25% of the number of O ions in each crystal layer can be reduced, the number of reducible oxygens in one hypothetical ceria layer with BET surface area of 65 m²/g is calculated to be 5.4 × 10⁻¹⁸/21.2 mCat. Details can be found in [9,10].

2.2. In situ Raman

In situ Raman spectra (Renishaw, 2000) were recorded using a temperature controlled in situ 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 spectra were recorded during the flow of C₃H₆ (1000 ppm in N₂, flow rate 200 mL/min).

3. Results

3.1. Reduction of ceria by CO

Fig. 1 showed the result of CO pulses experiment at 580 °C. During the initial period (pulse number 0–2000, Fig. 1A), the CO was completely converted into CO₂. Pulse number 2000 corresponded to 0.4 hypothetical reduced ceria layers (Fig. 1B). After this initial period, the CO conversion and CO₂ 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 can be consumed, as can be seen from the oxygen balance (Table 2). No carbon deposits were observed on the catalyst within experimental error.

Similar results were obtained at 400–500 °C (not shown), but CO conversion did not 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 (1.2–1.0) were relatively constant in the 400–580 °C temperature window (Table 2).

3.2. Reduction by H₂

Fig. 2 shows the result of H₂ pulses experiment at 560 °C For a very short period (pulse number 0–210, Fig. 2A), hydrogen conversion was relatively high without a clear desorption of water. In contrast to the CO experiment, the H₂ conversion did not accomplish full conversion. The H₂ conversion and H₂O production decreased progressively during the remainder of the experiment.
3.3. Reduction by \( \text{C}_3\text{H}_6 \)

Fig. 3 showed the result of \( \text{C}_3\text{H}_6 \) pulses experiment at 580 °C. Different phases were applied to define \( \text{C}_3\text{H}_6 \) reactivity profiles with pulse number, as shown in Table 1. The definition of different phases was also applied to \( \text{C}_3\text{H}_6 \) reactivity in Fig. 5.

Fig. 3A showed the product and reactants evolution versus pulse number during \( \text{C}_3\text{H}_6 \) pulses. In phase I (pulse number 0–80), a high activity was observed, where predominantly total oxidation products, 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 \( \text{CO} \) production was initially zero. Both \( \text{H}_2 \) and \( \text{CO} \) production increased during this phase I. After this short highly active phase I, \( \text{C}_3\text{H}_6 \) conversion rapidly declined in phase II (pulse number 80–500). In phase III and IV (pulse number 400–8000) predominantly partial oxidation took place and mainly \( \text{CO} \) and \( \text{H}_2 \) were observed. From pulse number 2800–8000 (phase III), \( \text{C}_3\text{H}_6 \) conversion increased to full conversion. \( \text{H}_2 \) was the major product and the formation of \( \text{CO} \) declined with time in this phase III. In phase V (pulse number 8000–end), both \( \text{C}_3\text{H}_6 \) conversion and \( \text{H}_2 \) production declined. The \( \text{H}_2 \) production and \( \text{C}_3\text{H}_6 \) conversion remained persistent although at a low level no CO was observed.

Some carbon (Fig. 3C) started to deposit on the surface from phase II (determined from the carbon mass balance). Significant

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**Table 1**

<table>
<thead>
<tr>
<th>Phases</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 drop</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>

(pulse number 210–end, Fig. 2B). The number of extracted oxygen atoms, characterised as the number of hypothetical reduced ceria layers, was at the end of the experiment around 1 reduced layer (Table 2).

**Table 2**

<table>
<thead>
<tr>
<th>Deposited carbon</th>
<th>Extracted oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atoms</td>
</tr>
<tr>
<td>580 °C ( \text{C}_3\text{H}_6 )</td>
<td>(3.1 \times 10^{19})</td>
</tr>
<tr>
<td>560 °C ( \text{C}_3\text{H}_6 )</td>
<td>(3.4 \times 10^{19})</td>
</tr>
<tr>
<td>540 °C ( \text{C}_3\text{H}_6 )</td>
<td>(3.3 \times 10^{19})</td>
</tr>
<tr>
<td>500 °C ( \text{C}_3\text{H}_6 )</td>
<td>(1.9 \times 10^{19})</td>
</tr>
<tr>
<td>580 °C ( \text{C}_3\text{H}_6 )</td>
<td>(1.5 \times 10^{19})</td>
</tr>
<tr>
<td>540 °C ( \text{C}_3\text{H}_6 )</td>
<td>(1.1 \times 10^{19})</td>
</tr>
<tr>
<td>580 °C ( \text{CO} )</td>
<td>–</td>
</tr>
<tr>
<td>500 °C ( \text{CO} )</td>
<td>–</td>
</tr>
<tr>
<td>400 °C ( \text{CO} )</td>
<td>–</td>
</tr>
<tr>
<td>560 °C ( \text{H}_2 )</td>
<td>–</td>
</tr>
</tbody>
</table>

* Hypothetical reduced ceria layers.
amounts of carbon depositions were observed when the CO formation started to decline, while \( \text{H}_2 \) formation persisted (phase IV). \( \text{C}_3\text{H}_6 \) showed full conversion during phase I and IV, corresponding to 0–0.25 and 1.5–2.7 hypothetical reduced ceria layers, respectively, as shown in Fig. 3B.

The estimated oxygen atom consumption and carbon atom deposition during the \( \text{C}_3\text{H}_6 \) pulse experiment at 580 °C were calculated to be \( 1.5 \times 10^{19} \) and \( 3.1 \times 10^{19} \) carbon atoms (2.9 wt.%), respectively, shown in Table 2. Fig. 4 showed the \( \text{C}_3\text{H}_6 \) conversion versus pulse number in a temperature window between 500 and 580 °C. Similar \( \text{C}_3\text{H}_6 \) reactivity profiles were observed, although the overall reactivity of \( \text{C}_3\text{H}_6 \) decreased, when reaction temperature declined. No significant \( \text{C}_3\text{H}_6 \) activity and reduction of ceria were observed below 500 °C. Table 2 summarised the oxygen consumption (hypothetical reduced ceria layers) and carbon deposits for the 500–580 °C temperature window.

3.4. Reduction by \( \text{C}_3\text{H}_6 \)

Fig. 5 showed the result of \( \text{C}_3\text{H}_6 \) pulses experiment at 580 °C. As compared to \( \text{C}_3\text{H}_6, \text{C}_3\text{H}_4 \) in phase I did not have a full conversion time interval. Fig. 5A shows the product and reactant evolution versus pulse number during \( \text{C}_3\text{H}_6 \) pulses. In phase II (pulse number 80–1000), a short period of a higher activity (up to 40% conversion) was observed, where predominantly total oxidation products, i.e., CO 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 phase II. The \( \text{C}_3\text{H}_6 \) conversion declined during phase II and increased during phase III (up to 60% conversion). In phase III and IV, partial oxidation took place and CO and \( \text{H}_2 \) were observed, while \( \text{C}_3\text{H}_6 \) was only observed during phase III. The level of \( \text{C}_3\text{H}_8 \) conversion was substantially lower as compared to that of \( \text{C}_3\text{H}_6 \).

During the partial oxidation time interval (phase III, IV, and V), CO and \( \text{H}_2 \) were observed as the main products. The reaction rate increased with pulse number during phase III and IV. During phase III the \( \text{C}_3\text{H}_6 \) production, resulting from the dehydrogenation of \( \text{C}_3\text{H}_8 \), increased progressively but vanished towards the end of phase III. A maximum in CO production was observed when the activity for the dehydrogenation reaction vanished. In this phase the partial oxidation period, in contrast to the \( \text{C}_3\text{H}_6 \) pulse experiment, the \( \text{C}_3\text{H}_6 \) conversion was never complete. Initially, the \( \text{C}_3\text{H}_6 \) conversion was around 10% and reached a maximum conversion of 60% at the point of maximum CO production (Fig. 6). Following the maximum in the CO production, the \( \text{C}_3\text{H}_8 \) conversion and \( \text{H}_2 \) production also reached their maximum level (phase IV, Fig. 5). In phase V, the \( \text{C}_3\text{H}_6 \) conversion and CO and \( \text{H}_2 \) production declined. CO evolution stopped after pulse number 22,000, while \( \text{C}_3\text{H}_6 \) conversion and \( \text{H}_2 \) production remained persistent at a low level. At a temperature of 500 °C and lower, the reactivity of \( \text{C}_3\text{H}_8 \) was negligible or none (not shown).

As shown in Table 2, the amounts of deposited carbon ranged from 1.4 to 0.9 wt.% for temperatures from 580 °C to 540 °C, which
were 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 double than that of C3H6.

In Fig. 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 phase 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 gray line in Fig. 6, C3H8 was less active and took around two times more pulses than that of C3H6 to reach the final state. As shown in Table 2, the amount of deposited carbon during C3H8 at 540 °C was around three times less than that for C3H6 at the same temperature.

3.5. In situ Raman experiment of C3H8 flow over ceria

In situ Raman was used to analyse the deposited carbon formed over ceria during C3H8 flow at 580 °C. D band and G bands of carbon were observed during the C3H8 flow as shown in Fig. 7. The G band corresponded to graphitic in-plane vibrations with E2g symmetry. D band generally was assigned to the presence of defects in and disorder of carbon.

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 (N2) over (pre-reduced) La–Zr doped ceria, NO was used in the re-oxidation of CO, H2 (not shown), C3H8, and C3H6 pre-reduced La–Zr doped ceria, as illustrated in Fig. 8 at 540 °C.

For the CO (and H2) pre-treated samples, a full NO conversion was obtained till pulse number 2340. The total amount of NO converted was around 6.8 × 10^{18} molecules. For the propane pre-treated ceria, complete NO conversion maintained approximately till pulse number 1200. The total amount of NO converted was around 2.9 × 10^{18} molecules. For the C3H8 pre-treated ceria sample, however, NO showed full conversion up to pulse number 5600, followed by a conversion decline to 76% at pulse number 9000. Subsequently, the NO conversion for the C3H8 increased to full conversion till pulse number 40,000. NO lost its activity after pulse number 97,300. The total amount of NO being converted was around 7.6 × 10^{19} molecules.
4. Discussion

4.1. Reduction of ceria by CO and H2

The CO pulse experiments over Zr–La doped ceria resulted in an overall catalyst reduction of around on average one hypothetical reduced ceria layer in the 400–580 °C temperature window (Table 2), indicating that a complete surface layer of Zr–La doped ceria can be reduced by CO. The extraction of one oxygen resulted in the reduction of two Ce^4+ ions into two Ce^3+ ions. The oxidation of CO to CO2 can be described as:

\[ \text{CO} + 2\text{Ce}^{4+} + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{Ce}^{3+} + \square \quad \text{(oxygenvacancy)} \quad (5) \]

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 the CO pulse experiment. The full CO2 conversion dropped at the point corresponding to 0.5 hypothetical reduced ceria layers (Fig. 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 by 0.5 and 1 hypothetical reduced ceria layers (Fig. 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 hardly any deposited carbon was observed and could be quantified for the calculated carbon mass balance (Fig. 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 low temperatures, i.e. 400 °C (i.e. 580 °C) (not shown).

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 0.5–1 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 pulse experiments (Fig. 1B).

For the H2 pulse experiments, a high H2 activity was observed from the start of the experiment (Fig. 2) in the absence of any water desorption. This indicated that water or its precursor species were initially stored on the catalyst’s surface. H2 activity dropped immediately after the initial pulses until hardly any conversion was observed when one hypothetical reduced ceria layer was reached. Similar to the CO 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 pulse experiment suggested the presence of an equilibrium between H2, H2O, Ce3+, and Ce4+, which may limit a deeper reduction of ceria by H2.

4.2. Reduction by hydrocarbons

4.2.1. Reduction by C3H6

The reduction of Zr–La doped ceria by C3H6 led to an overall 2.7 hypothetical reduced ceria layers at 580 °C (Table 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 (Fig. 3).

The initial high conversion to total oxidation products (phase 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 Eq. (6) [16–18]:

\[ \text{O}_2(\text{ad})+e^-→\text{O}_2^-+2e^-\quad \text{O}_2^-→2\text{O}^-+2\text{Ce}^{4+} \]

These active surface oxygen species reacted with C3H6 resulting mainly in the formation of H2O and CO2 as described in Scheme 1. The adsorbed C3H6 was activated by the active oxygen species from oxygen activation chain (Eq. (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 remained hydrocarbon fragment (C3H5) will react with active oxygen species, forming oxygen-containing hydrocarbon intermediate (C3H4O), and finally oxidation of some part of C3H4O to CO2, the remained C3H4O will be deposited as “coke” as illustrated in Scheme 1.

C3H6 conversion dropped (phase II), accompanied by a decline in total oxidation products and the start of C3H6 cracking/partial oxidation reaction. The fall of C3H6 conversion during phase II was likely caused by less availability of the active surface oxygen species which were largely consumed during phase I. As described in Scheme 2, 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. Another H will be further abstracted from C3H5•. However, on the reduced catalyst surface (less active surface oxygen), H surface species preferred to recombine with each other to form H2. The remained hydrocarbon fragment (C3H5) will react with active oxygen species, forming oxygen-containing hydrocarbon intermediate (C3H4O), and some part of C3H4O will be converted to CO, the remained C3H4O will be deposited as coke. The...
Scheme 2 was also applied to the C$_3$H$_6$ cracking reaction during the phase III. C$_3$H$_6$ conversion increased during phase III accompanied by an increased H$_2$ and CO formation, indicating the main cracking/partial oxidation/dehydrogenation were taking place.

The CO formation arrived at a maximum formation rate at 1.5 hypothetical reduced ceria layers, while CO$_2$ and H$_2$O were not observed around 1 hypothetical reduced ceria layer. This observation indicated that the formation of CO consumed oxygen from the bulk of ceria, resulting in a deeper degree of catalyst reduction by C$_3$H$_6$, as compared to CO and H$_2$ treatment. The CO formation declined at the point of 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 be limited when the catalyst reduced to 1.5 hypothetical reduced ceria layers. This can be explained by the scariness of surface active oxygen species either due to slow bulk oxygen diffusion or the activation of bulk oxygen to active oxygen species. The formation of CO caused the additional extraction of oxygen from ceria bulk, i.e. degree of reduction of the bulk ceria up to 2.7 hypothetical reduced ceria layers (phase V).

The increase of C$_3$H$_6$ conversion during phase III was also likely due to the regeneration of active oxygen species from activation oxygen from bulk diffusion to surface, which led to CO formation increasing and less carbon deposition as compared to phase II, based on the carbon mass balance calculations. The CO formation, however, declined from 1.5 hypothetical reduced ceria layers, where still a full C$_3$H$_6$ conversion and persistent H$_2$ formation were observed (phase IV). The full C$_3$H$_6$ conversion (C$_3$H$_6$ cracking) during phase 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 C$_3$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 × 10$^{15}$ carbon atoms. Assuming that the carbon structure will be graphene-like structure, the coverage of Zr-La doped ceria by carbon corresponded to roughly 4% of the available surface area. Carbonaceous deposited (coke) that formed on the metal oxides can be regarded as the real catalyst site for (oxidative) dehydrogenation. The formation of deposited carbon was observed from the in situ Raman (Fig. 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 in Fig. 7. The full C$_3$H$_6$ conversion with persistent H$_2$ formation will be attributed to the deposited carbon and will play a role in the deeper C$_3$H$_6$ dehydrogenation. The oxygen transport from ceria bulk will become the catalytically active site on the coke (C$_3$H$_5$OH), and CO was formed by the oxidation of coke (C$_3$H$_5$OH).

When the number of available lattice oxygen declined, the CO formation declined as well. The deeper dehydrogenation of C$_3$H$_6$ will lead to more and more deposited carbon.

Till phase V, C$_3$H$_6$ lost its reactivity completely, whereas H$_2$ formation declined as well from 2.2 hypothetical reduced ceria layers, indicating the deeper dehydrogenation reaction largely slowed down. CO was hardly observed the end, while C$_3$H$_6$ conversion and H$_2$ formation were persistent although at a lower level.

Since the coke with quinone group could be regarded as the catalytic site for the C$_3$H$_6$ dehydrogenation, the disappearance of this group might explain the final C$_3$H$_6$ deactivation. The oxygen transport from ceria bulk and spillover the deposited carbon will be terminated. The formation of C$_3$H$_4$O was largely limited when the catalyst was reduced to around 2.2 hypothetical reduced layers. The oxidation of C$_3$H$_4$O to CO was persistent although at a low level.

Carbon deposited will often be regarded as one of the leading causes for the deactivation in hydrocarbon reactions [23]. The amount of deposited carbon on the catalyst surface during the C$_3$H$_6$ pulses was around 3.1 × 10$^{15}$ carbon atoms, which accounted for about 2.9 wt% g$^{-1}$cat. Assuming that the carbon structure will be graphene-like structure and ceria surface will be flat, the coverage of Zr-La doped ceria by carbon will correspond to roughly 60% of the available surface area. There would be still about 40% of the surface area available. The surface of the ceria with or without carbon deposits will be a network of pores. The blocking of the pores in combination with a slow-down of the oxygen spillover mechanism from the bulk to the surface and over the deposited carbon will be the main reasons for the final lost in the C$_3$H$_6$ conversion activities.

Similar C$_3$H$_5$ reactivity profiles were also observed at 500–580°C temperature window. The maximum observed C$_3$H$_5$ conversion during the cracking reaction period (phase III) shifted to higher pulse numbers in the 580–500°C temperature range, as shown in Fig. 4. This observation indicated that more time was needed for the enhanced C$_3$H$_5$ reactivity in phase III when the temperature decreased. Such phenomenon also pointed out that the reactivity of C$_3$H$_6$ during phase III was likely controlled by the availability of active oxygen species on the surface regenerated by bulk oxygen diffusion, which was affected by temperature. At 400°C, only complete oxidation to CO$_2$ and H$_2$O was observed (no carbon deposition) and could be calculated from the carbon mass balance.

The total amount of reducible oxygen during C$_3$H$_6$ oxidation was significantly influenced by the temperature, as shown in Table 2. The number of oxygen atoms extracted in the C$_3$H$_6$ pulse experiments declined from 1.5 × 10$^{19}$ to 0.9 × 10$^{19}$, i.e. from 2.7 to 1.7 hypothetical reduced ceria layers when the temperature decreased from 580 to 500°C. The total amount of deposited carbon during the C$_3$H$_6$ pulse experiment at 580°C is twice that of the pulse experiment at 500°C. At 400°C, carbon was hardly deposited, and no cracking/partial oxidation/dehydrogenation activities were observed.

### 4.2.2. Reduction of ceria by C$_3$H$_6$

C$_3$H$_6$ (Fig. 5), showed the same trend as C$_3$H$_6$, although C$_3$H$_8$ conversion was lower than that of C$_3$H$_6$ during phase 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 C$_3$H$_8$ as compared to the saturated C$_3$H$_4$ due to either the interaction with the surface through hydrogen bonding or Van der Waals forces for C$_3$H$_4$ and more strong electron-rich π orbital interactions on Lewis acid sites for C$_3$H$_6$ [24]. The lower reactivity, that C$_3$H$_8$ displayed toward oxygen species, did not affect the total amount of oxygen extracted during the whole C$_3$H$_8$ pulse experiment. It, however, affected strongly on the amount of carbon deposited on the surface and the time frame to achieve the same degree of ceria reduction. Since the carbon deposition took predominantly place during phase IV, the lower C$_3$H$_8$ reactivity led to less carbon deposition. Comparing C$_3$H$_6$ and C$_3$H$_8$
pre-treatment at 580 °C, the amount of carbon deposited for the C3H8 pre-treatment was twice that for C2H8, as shown in Table 2.

The C–H bond cleavage was regarded as the first step in the activation of saturated hydrocarbons (C2H8). Due to the initial high concentration of surface active oxygen species in phase II, complete oxidation was observed with the formation of both H2O and CO2, similar as illustrated in Scheme 1. The conversion of C2H8 decreased during phase II was due to the depletion of active oxygen species on the surface. A gradual increase in the amount of the C2H8 dehydration product (Fig. 5) was observed from phase III, where the C2H8 conversion was enhanced. Similarly to C2H8 pulse experiments (Fig. 3), the C2H8 reactivity (Fig. 5) increased during phase III was due to the reformation of surface active oxygen species by the diffusion of oxygen from the bulk of the ceria. Dehydrogenation of C2H8 to C2H4 was observed from initial of phase III and declined from the end of phase III. C2H8 evolution completely vanished from phase IV. The dehydrogenation selectivity of C2H8 to C2H4 in phase III can be explained by a particular type of reformed active oxygen species, e.g. O−·C2H4 formation declined around 1.3 hypothetical reduced layers, indicating that these oxygen species, e.g. O−· [25], was less present from 1.3 hypothetical reduced layers.

Identically to the C2H8 pulse experiment, the formation of CO during C2H8 pulse experiment consumed oxygen from catalyst bulk, i.e. deeper reduction of bulk. Deposited carbon started to play a role in C2H8 dehydrogenation during phase IV, where C2H8 conversion was around 60%.

The maximum C2H8 conversion during C2H8 the cracking/partial oxidation/dehydrogenation reactions (phase III) shifted to a higher pulse number when the temperature was changed from 580 to 540 °C, as shown in Fig. 6. Similarly to the observation in the C2H8 pulse experiments, the reactivity of C2H8 during phase III was controlled by the availability of active oxygen species on the surface regenerated by bulk oxygen diffusion, which was temperature dependent. The observed C2H8 lost in activity can be explained with the same reasoning as discussed above for C2H8.

The total amount of reducible oxygen during C2H8 oxidation was significantly influenced by the temperature, as shown in Table 2. The number of oxygen atoms extracted in the C2H8 pulse experiments declined from 1.5 × 10^19 to 0.9 × 10^19, i.e. from 2.7 to 1.7 hypothetical reduced ceria layers as the temperature was lowered from 580 to 540 °C.

4.3. Re-oxidation of reduced ceria with NO

The pre-treatment of ceria by CO, H2, C2H8, and C3H8 at 540 °C led to a degree of catalyst reduction corresponding to 1, 1.7, and 1.8 hypothetical reduced ceria layers, respectively. The pre-treatment with C2H8 and C3H8 additionally resulted in the deposition of 3.3 × 10^19 and 1.7 × 10^19 carbon atoms, respectively.

The differences observed in the reduction of NO into N2 over ceria by using either CO, C2H8 or C3H8 pulses at 540 °C was shown in Fig. 6. CO and H2 pre-treatments showed only a short time interval, where NO was reduced into N2. The reduction of NO to N2 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 (N2) [9,10]. When all the oxygen defects were refilled, the NO reduction was ended. Both C3H8 and C2H8 pre-treated reduced ceria were able to convert considerably more NO into N2 (much longer time interval) as compared to CO and H2 pre-reductions. The pre-treatment of C3H8 and C2H8 resulted in a deeper catalyst reduction and more deposited carbon. These carbon deposits acted as buffered reductant: 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. C3H8 pre-treatment exhibited a longer period of NO reduction to N2 as compared to C2H8 pre-treatment: C3H8 pre-treatment led to approximately 3 times more deposited carbon as compared to C2H8.

The CO and H2 pre-treatments resulted only in the reduction of surface oxygen and hardly any or no deposited carbon. Therefore, CO and H2 pre-treatments cannot compete with a hydrocarbon pre-treatment. Deposited carbon, acting as a reductant buffer, extended the period in which NO can be reduced into N2. C3H8 will be preferred over C2H8 due to its higher reactivity and increased tendency to form carbon deposits.

5. Conclusion

1) The reduction degree of ceria obtained by C3H8 and C3H6 reduction, corresponded to up to 2.7 hypothetical reduced ceria layers. As compared to H2 and CO, the obtainable reduction degrees for these hydrocarbons were around 3 times higher at 580 °C (Table 2). Pre-treatment by C2H8 due to its higher reactivity will be preferred over that of C2H8.

2) Hydrocarbon pre-treatment led to carbon deposits on the reduced ceria surface. Not the deposited carbon, but the depletion and availability of surface active oxygen species were the main causes for the deactivation of hydrocarbon cracking/partial oxidation/dehydrogenation. 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].

3) The deeper degree of reduction of Zr-La doped 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 H2 and CO pre-treatment, the apparent existence of H2, H2O, Ce4+ and Ce3+ (or CO, CO2, Ce4+ and Ce3+) 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.

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References
