A new dynamic N₂O reduction system based on Rh/ceria–zirconia: from mechanistic insight towards a practical application†

Yixiao Wang,*ab Jorrit Postuma de Boera and Michiel Makkee EID*ab

Simultaneous reduction of N₂O in the presence of co-existing oxidants, especially NO, from industrial plants, is a challenging task. This study explores the applications of a hydrocarbon reduced Rh/Zr stabilized La doped ceria (Rh/CLZ) catalyst in N₂O abatement from oxidant rich industrial exhaust streams e.g. NO, CO₂, and O₂. The reaction mechanism was studied by the temporal analysis of products. The obtained results revealed that hydrocarbon pretreatment led to the creation of ceria oxygen vacancies and the formation of carbon deposits on the Rh/CLZ catalyst surface. These ceria oxygen vacancies are the active sites for the selective reduction of N₂O into N₂, while the dissociated O atoms from N₂O fill the ceria oxygen vacancies. The oxidation of the deposited carbon via the lattice ceria oxygen generates new ceria oxygen vacancies, thereby extending the catalytic cycle. The reduction of N₂O over C₃H₆ reduced Rh/CLZ is a process combining oxygen vacancy healing and deposited carbon oxidation. The results obtained from fixed-bed reactor experiments demonstrated that the hydrocarbon reduced Rh/CLZ catalyst provided a unique and extraordinary N₂O abatement performance in the presence of co-existing competing oxidants (reactivity order: N₂O ~ NO > O₂ > CO₂ ~ H₂O).

A lot of research efforts have been directed towards the development of low temperature deN₂O catalysts, which target N₂O abatement arising from medical operating rooms, nitric acid plants, and automotive transport.7,8 In all these cases, apart from the activity at low temperatures, the tolerance to various substances present in the exhaust gases (e.g., NOₓ, O₂, H₂O, etc.) should be additionally addressed and subsequently enhanced. Few studies have addressed the simultaneous abatement of NOₓ and N₂O. The current N₂O abatement in industry is usually via a dual-bed catalytic system, in which NOₓ is firstly converted into N₂ by either NH₃-SCR or HC-SCR, while subsequently N₂O is catalytically decomposed into N₂ and O₂.9–11 Sufficient performance has rarely been achieved in a single catalyst bed.12–14 In particular, the N₂O abatement activity is strongly inhibited by the presence of NO.12

The Di-Air system, developed by Toyota Company, showed great promise in NOₓ abatement with regard to the current and future NOₓ emission standards under real driving automotive conditions (dynamic operations, high exhaust temperature, and high gas hourly space velocities (GHSV > 120 000 L L⁻¹ h⁻¹)).15 The comprehensive work by Wang and Makkee has addressed the working principle and application of this Di-Air system in NO reduction.16–21 Oxygen vacancies within the ceria lattice of a reduced ceria, Pt/ceria or Rh/ceria were found to be the selective catalytic sites for the NO reduction into only N₂ (100% selectivity).16 Even at low NO

1. Introduction

N₂O is a harmful gas to our environment, as it contributes to global warming and the depletion of the protective ozone layer. Human activities, e.g., agriculture, fossil fuel combustion, and industrial processes, contribute 4.7–7 million tons of N₂O annually, which is about 30–40% of the total N₂O emission including natural sources.1

The catalytic reduction of N₂O into N₂ has been studied over a wide variety of catalysts, including noble-metal-supported catalysts, metal oxides, and zeolite-based catalysts.2 Several CeO₂-based transition-metal catalysts (M/CeO₂, M = Co, Cu, Fe, Zr, and Ni) have been applied in N₂O reduction studies. Their T₅₀ temperature for the N₂O reduction varied between 300–660 °C.3–5 The impact of H₂O, CO, CO₂, O₂, NO, and NO₂ on N₂O reduction is particularly important, since these substances are usually present in excess in N₂O-containing gas streams. In particular, the simultaneous conversion of N₂O and NO in the presence of O₂ is a challenging task during N₂O abatement in nitric acid plants.

† Catalysis Engineering, Chemical Engineering Department, Faculty of Applied Sciences Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands. E-mail: m.makkee@tudelft.nl
‡ Idaho National Laboratory, Idaho Falls, Idaho 83415, USA.
E-mail: Yixiao.wang@inl.gov
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concentrations (ppm levels), NO could compete for oxygen vacancies with (100×) excess of O$_2$ and CO$_2$. These oxygen vacancies acted as a kind of “oxygen black hole” by catching all oxygen containing species until the holes (vacancies) were completely refilled (re-oxidized), while the captured N species would associate (recombine) into N$_2$. In the Di-Air system, the creation of reduced (metal) ceria was accomplished by pulsing diesel fuel at a high frequency upstream of the catalyst bed. The amount of diesel fuel pulsed was such that the front of the catalyst bed was in a reduced state while the back of the catalyst bed was in an oxidized state. In other words, although diesel fuel is injected, the overall catalytic bed would be in a lean (oxidized) state. During these diesel pulses carbon deposits were formed, which were oxidized in time by the lattice oxygen from the ceria catalyst and not by gaseous oxidants present in the exhaust stream such as O$_2$ and NO (mainly NO$_2$).

To the best of our knowledge, no work has been published on the application of this “oxygen black hole” concept of the Di-Air system in a den$_2$O$_i$ application. In this study, we investigated the mechanism of the N$_2$O reduction over a reduced Rh/CLZ catalyst with a clean surface and with carbon deposits on that surface.

The temporal analysis of products (TAP, an ultra-high vacuum pulse and response technique) was applied to study the reaction mechanism of the N$_2$O reduction over a Rh/CLZ catalyst pre-treated with either H$_2$ or C$_3$H$_6$ as a stand-in for a diesel fuel. Moreover, the reactivity of N$_2$O versus other oxidants (O$_2$ and NO) towards oxygen vacancies of ceria-based catalysts would be crucial for the extension of the Di-Air technology to the den$_2$O area, i.e., the simultaneous NO$_x$ and N$_2$O abatement in the presence of an excess of O$_2$. The competition between N$_2$O and NO in an excess of O$_2$ was further investigated under more industrially relevant conditions in a fixed-bed flow reactor.

2. Materials and methods

2.1. Materials preparation and characterization

Rh/CLZ, with a target loading of 0.5 wt%, was prepared via an incipient wetness impregnation method using a Zr stabilized La doped ceria (denoted as CLZ, a gift from Engelhard, now BASF). Rhodium nitrate hydrate (Sigma Aldrich) was used and dissolved as the precursor in purified demi water. Subsequently, the samples were dried at 110 °C overnight and calcined at 550 °C for 5 h. CLZ and Rh/CLZ were characterized by ICP, XRD, TEM, XPS, Raman, and H$_2$-TPR. Details on the characterization and instruments can be found in our previous publications.

2.2. Catalytic testing

2.2.1. Temporal analysis of products (TAP). The pulse experiments (step-response) were performed in an in-house developed and constructed TAP reactor. The mode of the gas transport within the TAP catalyst is purely Knudsen diffusion. Upon interaction with the catalyst, the reactant and product molecules can be converted into different products. The evolution of the reactant and product molecules was tracked (one mass at a time) in time with a high time resolution of 10 kHz using a Pfeiffer QMG 422 quadrupole mass spectrometer. The pulse size gradually decreased during an experiment since the reactant was pulsed from a closed and calibrated volume of the pulse-valve line. The pulse size of the reactant gas was determined for each pulse by fitting the pulse valve pressure using an exponential equation and compensation for the environmental temperature. All relevant MS signals were calibrated and quantified at room temperature by using an inert bed of 200 mg quartz beads (particle size 150–212 μm) fully filled in a stainless-steel SS 316 reactor. Detailed TAP quantification methods can be found elsewhere.

In the TAP experiments at 450 °C 10 mg of as-prepared CLZ and Rh/CLZ (150–212 μm) were sandwiched between inert quartz bead beds. Prior to the catalyst reduction, the catalyst was firstly oxidized by pulsing 80 vol% O$_2$ in Ar overnight at 450 °C. The catalyst reduction was carried out by pulsing the reductant of either 80 vol% C$_3$H$_6$ (propene) in Ne or 66.7 vol% H$_2$ in Ar. The re-oxidation experiment was conducted at 450 °C by pulsing either 80 vol% CO$_2$ or 80 vol% O$_2$ in Ar, or 80 vol% $^{15}$N$_2$O in Kr, or co-pulsing 80 vol% $^{14}$NO in He and 80 vol% $^{15}$N$_2$O in Kr.

The number of consumed oxygen species from the catalyst during the C$_3$H$_6$ and H$_2$ multi-pulse experiments was calculated using eqn (1):

\[ n_{O,\text{consumed}} = n_{H_2O,\text{out}} + n_{CO_2,\text{out}} + 2n_{CO,\text{out}} \]

and the number of carbon species deposited on the catalyst in the C$_3$H$_6$ multi-pulse experiments was calculated using eqn (2):

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

The number of oxygen atoms consumed during the C$_3$H$_6$ and H$_2$ multi-pulse experiments was equal to the number of oxygen vacancies created in the ceria lattice.

Similarly, the amount of oxygen accumulation, the carbon consumption, and the nitrogen balance during the $^{15}$N$_2$O, CO$_2$, and O$_2$ multi-pulse experiments were calculated using the following atomic balances:

\[ n_{O,\text{accumulated}} = n_{N_2O,\text{in}} - n_{CO_2,\text{out}} - 2n_{CO,\text{out}} - n_{NO_2,\text{out}} - n_{NO_2,\text{out}} \]

\[ n_{C,\text{accumulated}} = n_{C_3H_6,\text{in}} - n_{CO_2,\text{out}} - n_{CO,\text{out}} \]

\[ n_{N,\text{accumulated}} = 2n_{N_2O,\text{in}} - 2n_{N_2O,\text{out}} - 2n_{N_2O,\text{out}} - n_{NO_2,\text{out}} \]

The hypothetical ceria layer concept was used to obtain insight into the reactivity of the actual surface as a function of the degree of reduction (surface oxidation state). Each O–Ce–O tri-layer on the (BET) surface was regarded as one hypothetical ceria layer. The total number of O atoms in each
hypothesised ceria layer can be calculated to be \(1.04 \times 10^{18}\) atoms per mg\(_{\text{cat}}\). Assuming that Zr and La were Ce, a maximum of 25% of the total number of O ions in each crystal layer can be reduced, according to eqn (6)

\[
\text{CeO}_2 \rightarrow \text{CeO}_{1.5} + \frac{1}{2} \text{O} \tag{6}
\]

The number of oxygen defects on one hypothetically reduced ceria layer was calculated to be 2.6 \(\times 10^{17}\) oxygen atoms per mg\(_{\text{cat}}\). More details about these calculations with regard to the hypothetically ceria layer can be found elsewhere.\(^{16}\)

### 2.2.2. Reactivity measurement in a flow reactor

A flow reactor was used to study the N\(_2\O\) reduction reactivity with and without O\(_2\) and NO. The as-prepared catalyst (200 mg) with particle sizes between 150 and 215 \(\mu\)m was placed in a 6 mm inner-diameter quartz reactor tube. The reactor effluent was online analyzed by mass spectrometry (MS, Hiden Analytical, HPR-20 QIC) and infrared (IR) spectroscopy (Perkin-Elmer, Spectrum One). For the IR analysis a gas cell with KBr windows with a path length of \(\sim 5\) cm was used. The spectra were measured in continuous mode using the Perkin-Elmer ‘Time-Base’ software between wavenumbers of 4000–700 cm\(^{-1}\) with a spectral resolution of 8 cm\(^{-1}\) and an acquisition rate of 8 scans per spectrum, resulting in a time interval of 23 s between each acquired spectrum. In all experiments, the catalyst was initially oxidized by O\(_2\)/He until the O\(_2\) signal reached a stable level in MS. The reduction of the catalyst was performed by flowing 1.25% Cl\(_2\)H\(_4\) in He for 2 h with a flow rate of 200 mL min\(^{-1}\) and subsequently flushing with He (200 mL min\(^{-1}\)) for 30 min at 450 °C. For the N\(_2\O\) reduction experiments, feed composition of either 2000 ppm N\(_2\O\)/He or (2000 ppm N\(_2\O\) + 5% O\(_2\))/He or (2000 ppm N\(_2\O\) + 2000 ppm NO)/He was used at a space velocity of 67 000 L L\(^{-1}\) h\(^{-1}\) at 450 °C.

### 3. Results and discussion

#### 3.1. Structure, composition, and texture properties

Characterization details of the CLZ support and Rh/CLZ catalyst were reported in detail elsewhere.\(^{16–21}\) In brief, a 0.5 wt% Rh loading was confirmed by ICP-OES (0.0486 mmol g\(_{\text{cat}}\)^{-1} Rh loading). A typical fluorite structure of CLZ was observed for both CLZ and Rh/CLZ samples by Raman as well as XRD. Rh metals or any rhodium oxides could not be observed by XRD, confirming a high Rh dispersion. Room temperature Raman results indicated that the Rh/CLZ samples had more oxygen vacancies as compared to CLZ.\(^{18}\) A 5 nm ceria crystal size was determined by the Scherrer equation (XRD) and was further confirmed by the analysis of the TEM micrographs. The particle size of Rh was around 2 nm as indicated in the TEM micrographs. The bulk composition of CLZ, with an atomic ratio of Ce, Zr, and La of 0.64 : 0.15 : 0.21, was determined by ICP. The BET surface area of bare (fresh and up to >2000 h time on stream) CLZ was 65 m\(^2\) g\(^{-1}\). The BET surface areas of Rh/CLZ (fresh and spent) were similar to that of the bare CLZ support (66 ± 2 m\(^2\) g\(^{-1}\)).

#### 3.2. Transient N\(_2\O\) reduction

##### 3.2.1. The role of oxygen vacancies and deposited carbon

H\(_2\) and Cl\(_2\)H\(_4\) were applied as reductants to pretreat the Rh/CLZ catalyst samples at 450 °C in order to obtain a reduced Rh/CLZ sample and a reduced Rh/CLZ sample with deposited carbon on its surface, respectively. The H\(_2\) pulses led only to H\(_2\O\) formation (Fig. S4)\(^{16}\) and the Cl\(_2\)H\(_4\) pulses led to the formation of H\(_2\O\), CO\(_2\), CO, H\(_2\), and carbon deposits (Fig. S5).\(^{18}\) By means of eqn (1) and (2), the total amount of oxygen vacancies and carbon deposits formed during the H\(_2\) and Cl\(_2\)H\(_4\) pulses could be obtained. A total amount of 2.0 \(\times 10^{17}\) oxygen vacancies per mg\(_{\text{cat}}\) formed during the 1.3 \(\times 10^{4}\) pulses of H\(_2\), which corresponded to a reduction of 0.8 hypothetical ceria layers. During the 1.0 \(\times 10^{4}\) pulses of Cl\(_2\)H\(_4\), 5.3 \(\times 10^{17}\) oxygen vacancies per mg\(_{\text{cat}}\) were formed and 2.6 \(\times 10^{17}\) carbon atoms per mg\(_{\text{cat}}\) were deposited, which corresponded to a reduction of 2.2 hypothetical ceria layers. The pure CLZ support was barely active towards H\(_2\) and Cl\(_2\)H\(_4\). The reduction of CLZ by H\(_2\) at 450 °C led to 6 \(\times 10^{16}\) oxygen vacancies per mg\(_{\text{cat}}\), which corresponded to a reduction of 0.2–0.3 hypothetical ceria layers (see Fig. S2 in the ESI†). The presence of Rh promoted the reduction of CLZ at a lower temperature with a deeper degree of reduction.

Fig. 1A shows the reactant and product evolution during a \(^{15}\)N\(_2\O\) pulse experiment over H\(_2\) reduced Rh/CLZ at 450 °C. A \(^{15}\)N\(_2\O\) conversion of 100% was observed, while \(^{15}\)N\(_2\) was observed as the only N containing product from pulse numbers of 0 to 3400 (Fig. 1A, reduced state of Rh/CLZ). \(^{15}\)NO was not observed during the whole experiment. There was no indication of any \(^{15}\)N species accumulation on the catalyst (Fig. 1B), which suggested that N\(_2\O\) was instantaneously reduced into N\(_2\) with 100% selectivity. Oxygen atoms were observed to accumulate incrementally within the catalyst and 99% of the oxygen vacancies were refilled during the first 3400 \(^{15}\)N\(_2\O\) pulses. The results shown in Fig. 1 suggested that the N\(_2\O\) reduction over the reduced Rh/CLZ catalyst was an oxygen vacancy refilling process, which was also evidenced by \textit{in situ} Raman and XPS results from the study by Bueno-López et al.\(^{22}\) Gradually a \(^{15}\)N\(_2\O\) breakthrough was observed after pulse number 3400 (Fig. 1A), corresponding to a \(^{15}\)N\(_2\O\) conversion of roughly 95%. From pulse number 3400 onwards, the Rh/CLZ catalyst became completely oxidized and O\(_2\) evolution was observed. From this point on the N\(_2\O\) reduction proceeded \textit{via} adsorbed O species recombination forming gas phase O\(_2\) thereby regenerating two active sites, \(\text{e.g.}\), reduced Rh metal sites and ceria oxygen vacancy sites. A slightly lower \(^{14}\)N\(_2\O\) conversion was observed when the catalyst was in a fully oxidized state (Fig. 1A), as compared to the reduced state. This was likely caused by a slower ‘O’ association into O\(_2\) over the oxidized Rh/CLZ surface. The O\(_2\) formation process consisted of a surface ‘O’ association step and an O\(_2\) desorption step. In order to elucidate the slow O\(_2\) formation step, O\(_2\) was pulsed over an oxidized Rh/CLZ surface at the same temperature as the N\(_2\O\) pulse experiment. As shown in Fig. S1,† a clear O\(_2\) response was observed during the O\(_2\) pulses, while no clear O\(_2\) desorption curve was observed during
the N₂O pulses over an oxidized Rh/CLZ surface. Therefore, a slow 'O' association step was likely the cause of the slow O₂ desorption over the oxidized Rh/CLZ surface during N₂O reduction. A similar dynamic trend was observed with the H₂ pre-reduced CLZ bare support under the same reaction conditions (Fig. S2, ESI†) although the time until 100% ¹⁵N₂O conversion was shorter due to the significantly lower reduction degree for the H₂ reduction of CLZ. In this case, a full conversion of ¹⁵N₂O into ¹⁵N₂ was observed when the CLZ was in a reduced state. After that, the N₂ production decreased with a lower N₂O reduction activity (only 12% conversion of N₂O). The results obtained for the reduced CLZ (Fig. S2, ESI†) indicated that the N₂O reduction was an oxygen vacancy refilling process as well. From Fig. 1 and S2† it follows that the total amount of N₂O converted over the reduced catalysts was equal to the total amount of oxygen vacancies created during the H₂ reduction. Therefore, the role of Rh is to increase the CLZ support reduction degree by the H₂ reduction process. The presence of Rh did not noticeably alter the N₂O reduction rate, since 100% N₂O conversion was observed over reduced Rh/CLZ and CLZ. However, over oxidized CLZ the presence of Rh led to a significant improvement in the N₂O reduction activity, as the conversion of N₂O over oxidized Rh/CLZ was approximately 8 times that over oxidized CLZ. From in situ XPS results obtained for a Rh/CeO₂ system by Parres-Esclapez et al.,22 it was known that the reduced rhodium sites could be re-oxidized afterwards by either N₂O or ceria lattice oxygen. These vacant oxygen positions in ceria were subsequently oxidized by N₂O. The active sites for the N₂O chemisorption and reduction were not only located on rhodium, but were also present on the ceria. Additionally, Rh was a powerful promoter in enhancing the surface oxygen diffusion and lowering the oxygen activation barrier,23,24 and therefore, Rh could promote a faster surface oxygen association and desorption of gas-phase O₂ on the oxidized catalyst surfaces during the N₂O reduction. Rh could be a distinctive mechanistic feature for the promotion of the N₂O reduction process.25

Transient N₂ formation during the ¹⁵N₂O pulses was compared between the H₂ reduced Rh/CLZ and CLZ samples as shown in Fig. 2. In these experiments exclusively ¹⁵N₂ was observed as a reaction product. No observable N₂ flux difference was observed, which suggested that N₂O most likely reacted on the same reaction sites. These active sites were most likely the surface oxygen vacancies on the reduced CLZ support. The reduction of N₂O led to the oxidation of Ce³⁺ to Ce⁴⁺, while N₂ was released. If two active sites should exist, i.e., oxygen vacancies on the reduced CLZ support and Rh, then two distinguishable responses would have been expected26–28 rather than a single peak response that was observed in the current experiment. The hypothesis that only oxygen vacancy active sites were used on the reduced CLZ even in the presence of Rh explained the observed 100% ¹⁵N₂O conversion over both reduced CLZ and Rh/CLZ. The results presented in Fig. 1, S2† and 2 all indicated that the oxygen vacancies on CLZ were the only active sites for the N₂O reduction. During the N₂O reduction, the O species refilled the CLZ lattice oxygen vacancies and N₂ desorbed to the gas phase. The role of Rh was the promotion of the deep CLZ reduction at lower temperatures, however this deep reduction had an insignificant impact on the N₂O reduction, when the catalyst was in a reduced state, i.e., the presence of ceria oxygen vacancies. The presence of Rh started to promote the N₂O reduction only when the catalyst was in an oxidized state, i.e., the absence of ceria oxygen vacancies.

![Fig. 1](https://example.com/fig1.png)

**Fig. 1** A) Product and reactant evolution and B) O and N balance versus pulse number during the ¹⁵N₂O multi-pulse experiment over H₂ reduced Rh/CLZ at 450 °C.

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** Comparison of the height normalized intensity of ¹⁵N₂ between the H₂ reduced Rh/CLZ sample and reduced CLZ sample during the ¹⁵N₂O pulses.
The investigation of the impact of deposited carbon on N₂O reduction is presented in Fig. 3. Fig. 3A shows the reactant and product evolution achieved over C₃H₆ reduced Rh/CLZ at 450 °C versus the incremental pulse number. Full ¹⁵N₂O conversion was observed until pulse number 4500, while ¹⁵N₂ evolved as the dominant product. From pulse number 45 000 onward, a progressive, but small decline in the ¹⁵N₂O conversion to 95% was observed. This decline was accompanied by the formation of O₂, while hardly any CO and/or CO₂ was formed at this stage. No ¹⁵NO was observed during the whole experiment.

A small amount of CO evolution was observed during the first 15 000 ¹⁵N₂O pulses, during this time frame 80% of the ceria oxygen vacancies were refilled, while only 10% of the deposited carbon was consumed (Fig. 3B). This indicated that the carbonaceous residues, left on the surface after the C₃H₆ pre-reduction, did not directly participate in the reduction of ¹⁵N₂O into ¹⁵N₂. The formation of ¹⁵N₂ indicated that ¹⁵N₂O was dissociated on reduced CLZ sites, the O atom of ¹⁵N₂O refilled the ceria oxygen vacancies and at the same time the remaining adsorbed ¹⁵N₂ species desorbed as ¹⁵N₂. A significant role of the direct reaction between ¹⁵N₂O and deposited carbon could be ruled out since the formation of a ¹⁵N₂ molecule would yield one CO molecule, according to eqn (7).

\[\text{N}_2O + C \rightarrow \text{N}_2 + \text{CO}\]

(7)

The majority of deposited carbon consumption was found from pulse number 15 000 onward in the form of CO₂. Oxygen accumulation dropped to zero starting from pulse number 20 000, at that point almost 100% of the oxygen vacancies were refilled. The direct interaction of N₂O with deposited carbon, leading to the formation of CO₂ and N₂, could be ruled out, since an identical N₂ response with a single characteristic peak was observed for both the C₆H₆ reduced and the H₂ reduced Rh/CLZ samples (Fig. S3, ESI†). The deposited carbon consumption decreased after pulse number 450 000. The ¹⁵N species accumulation on the catalyst surface was insignificant. The ratio between N₂ and CO₂ was around 2 in the time interval between pulse numbers 10 000 and 450 000, which clearly demonstrated that for the formation of one CO₂ molecule two ¹⁵N₂O molecules had to be reduced forming two ¹⁵N₂ molecules. Such a phenomenon suggested that the oxidation of one deposited carbon atom to CO₂ created two oxygen vacancies, which allowed for the reduction of two ¹⁵N₂O molecules into two ¹⁵N₂ molecules. The formation of CO₂ started when the catalyst was largely oxidized, which suggested that CO₂ formed via a CO intermediate, which was subsequently oxidized into CO₂ by a ceria lattice oxygen. In previous studies,¹⁸,¹⁹ we have demonstrated that CO could reduce oxidized ceria up to almost one hypothetical ceria layer under identical reaction conditions.

Over H₂ reduced Rh/CLZ ¹⁵N₂O reduction proceeded for approximately 3400 pulses (Fig. 1), while over C₆H₆ reduced Rh/CLZ this proceeded for approximately 45 000 pulses (Fig. 3); this remarkable difference indicated that the deposited carbon acted as a reductant buffer. N₂O was reduced over ceria oxygen vacancies, which led to the re-oxidation of these oxygen vacancies while N₂ was released at the same time. When most ceria oxygen vacancies were filled, ceria lattice oxygen became capable of oxidizing the carbon deposits into CO and CO₂, thereby regenerating the ceria oxygen vacancies. The total amount of deposited carbon determined the additional ceria oxygen vacancies the Rh/CLZ system could provide, besides the ceria oxygen vacancies present after the reduction. The benefit of using hydrocarbons as reductants arose from the extended time interval in which 100% N₂O conversion was observed. In a previous publication we have demonstrated by means of an ¹⁸O₂ pulse experiment over C₆H₆ reduced Rh/CLZ at 450 °C that only lattice oxygen was responsible for the oxidation of deposited carbon, since only C¹⁸O and C¹⁶O₂ oxidation products containing exclusively ¹⁶O from the CLZ lattice were observed.¹⁸

![Fig. 3](image-url)

**Fig. 3** A) Reactant and product evolution and B) ¹⁵N, O, and C balance versus pulse number during the ¹⁵N₂O multi-pulse experiment over C₃H₆ reduced Rh/CLZ at 450 °C; (a)-(c) represent the catalyst stage of the reduced catalyst with carbon deposits, oxidized catalyst with carbon deposits, and oxidized catalyst, respectively.

3.2.2. N₂O bond cleavage on a reduced catalyst. Fig. 4A shows the gas evolution during ¹⁵N₂O and ¹⁴NO co-pulses over a H₂ pre-reduced Rh/CLZ. The observed ¹⁵N₂ and ¹⁴N₂ products arose from the reduction of ¹⁵N₂O and ¹⁴NO, respectively. There was no evidence of any ¹⁴N₁⁵N and ¹⁵NO formation. These experiments confirmed that ¹⁵N₂O reduction proceeds via the dissociation of a ¹⁵N-O bond of ¹⁵N₂O, of which O refilled a ceria oxygen vacancy and a desorbed ¹⁵N₂O molecule was formed. Apparently, ¹⁵N=¹⁵N bond cleavage was absent, since ¹⁴N¹⁵N products were not observed. The transient kinetic data of ¹⁵N₂ and ¹⁴N₂ showed that ¹⁴N₂ formation was faster than ¹⁴N₂ formation, as ¹⁴N₂ was observed prior to ¹⁵N₂ (Fig. 4B). The formation of ¹⁴N₂ required the cleavage of the ¹⁴NO bond and the subsequent association of two ¹⁴N species, which was expected to proceed more slowly than ¹⁵N₂ formation via the direct cleavage of the ¹⁵NO bond of ¹⁵N₂O.

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3.2.3. Effect of other oxidants on oxygen vacancy competition and deposited carbon consumption. In the Di-Air system, oxygen vacancies and buffer reductants (carbon deposits) were effectively re-created by periodical high frequency fuel injections. These vacancies were re-oxidized by the abstraction of oxygen atoms from oxidants present in the exhaust stream (H₂O, CO₂, NO, N₂O, and O₂). The reactivity of these oxidants towards the ceria oxygen vacancies could depend on the reactivity of the O atoms in these oxidants. The reactivity of the O atoms in NO, CO₂, and O₂ was investigated by pulsing each oxidant over C₃H₆ reduced Rh/CLZ. As shown in Fig. 5A, all pulsed ¹⁵NO converted to ¹⁵N₂ until the catalyst became oxidized. ¹⁵NO is a powerful oxidant and is capable of filling all ceria oxygen vacancies (those on reduced CLZ and those created by the oxidation of carbon deposits by the CLZ lattice oxygen). The results presented in Fig. 4A suggested that the ¹⁵N₂O reduction activity was not affected by the presence of ¹⁴NO when the catalyst was in a reduced state. However, the ¹⁵N₂O reduction activity was dramatically inhibited by NO when the catalyst switched to an oxidized state.

CO₂ fully converted into CO when the catalyst was in a significantly reduced state (Fig. 5B). However, when the catalyst was almost completely (re-)oxidized, the CO₂ reactivity suddenly dropped down while most of the deposited carbon was still on the Rh/CLZ surface (Fig. 5B). CO₂ hardly consumed any deposited carbon. A quasi-equilibrium between CO, CO₂, Ce³⁺, and Ce⁴⁺ appeared to limit the achievable oxidation degree of reduced ceria. Therefore, it can be concluded that CO₂ was a mild oxidant as compared to NO and N₂O, as it could hardly oxidize the deposited carbon. In the field of the dry CO₂ reforming of methane (DRM) reaction, the oxygen vacancies of a ceria support provided the catalytic sites for the CO₂ reduction to CO. The oxygen transport from the ceria lattice to the metal (Rh) largely reduced the carbon deposition during the DRM reaction. Fig. 5C shows the results obtained in an O₂ pulse experiment over C₃H₆ pre-reduced Rh/CLZ. O₂ was fully converted while CO and CO₂ formed which originated from the oxidation of deposited carbon (Fig. 5C). O₂ broke through when the catalyst became oxidized. Therefore, O₂ was a strong oxidant, which can compete with NO and N₂O for oxygen vacancies. However, NO was a more reactive and competitive reactant towards the oxygen vacancies as compared to O₂ as evidenced in previously published experiments in which 500–2000 ppm NO and 5% O₂
were co-fed over C,H, reduced Rh/CLZ at 450 °C. The current study presented in Fig. 4A suggested that N,O was comparably reactive towards ceria oxygen vacancies as NO did, and therefore, N,O was a more reactive and competitive reactant towards the oxygen vacancies as compared to O₂.

In our previous publication, H₂ pulses over an oxidized ceria (CLZ) led to the formation of H₂O, yielding less than one monolayer of reduced ceria. This indicated the presence of a quasi-equilibrium established between H₂, H₂O, Ce³⁺, and Ce⁴⁺, which limited the deeper reduction of ceria by H₂ or complete re-oxidation of reduced ceria by H₂O. Therefore, H₂O was a weaker oxidant towards oxygen vacancies. As a consequence, the presence of H₂O would not affect the NO and N,O reduction over a reduced ceria. Ceria-based catalysts are among others the best candidates for the water gas shift reaction. Oxygen vacancies on the ceria surface played an essential role in the water dissociation, yielding H₂ while the oxygen atoms filled the ceria oxygen vacancies during the WGS reaction. The reaction of CO with ceria lattice oxygen led to the formation of CO₂ thereby recreating a ceria oxygen vacancy. The WGS reaction was an equilibrium-limited reaction. The water dissociation would produce H₂ and oxidize the reduced ceria while the formed CO₂ from CO would create the ceria oxygen vacancy. Therefore, the O reactivity of CO₂ and H₂O was expected to be relatively small and CO₂ and H₂O would not inhibit NO and N,O reduction into N₂ to a large extent.

3.3. Catalytic fixed-bed reactor evaluation with regard to a potential industrial application

To confirm the results obtained in the TAP experiments, similar experiments were performed over Rh/CLZ in a flow reactor at atmospheric pressure and industrial exhaust concentrations. Similar to the TAP experiment, the flow of 1.25% C,H, /He in a fixed-bed reactor at 450 °C for 2 h led to the formation of H₂O, CO₂, CO, H₂ and carbon on the catalyst surface. The quantification of the oxygen and carbon balance was performed, according to eqn (1) and (2), respectively, and showed a reduction of around 3 CLZ layers and deposition of 8.2 × 10⁻¹⁷ carbon atoms per mgcat. N,O reduction over the C,H, pre-reduced Rh/CLZ was investigated under a gas mixture of 2000 ppm N₂O/He, (2000 ppm N₂O + 5% O₂)/He, and (2000 N₂O ppm + 2000 ppm NO)/He. Both MS and FTIR were used to detect the gas evolution. m/z = 28 can be attributed to either CO or N₂, and m/z = 44 to either CO₂ or N₂O. Gas species which contributed to the vibration peaks in the FT-IR spectrum can be seen in Table 1.

Fig. 6 shows the results of the exposure of a C,H, reduced Rh/CLZ catalyst to 2000 ppm N₂O at 450 °C with a GHSV of 67 000 L L⁻¹ h⁻¹. In Fig. 6A, m/z = 28 was observed, which could be attributed to the formation of N₂ and CO. The formation of CO was confirmed by FT-IR (Fig. 6B). The CO yield increased up to a maximum of 2500 ppm, after which it declined to zero (Fig. 6B and C). After CO had vanished (t = 1000 s), m/z = 28 was still observed in the MS (Fig. 6A). Therefore, in addition to CO, N₂ also contributed to m/z = 28. m/z = 44 was observed between 400 s and 1500 s, which could be attributed to the formation of CO₂ and the slip of N₂O. The formation of the latter could be excluded, during this time interval, FT-IR results indicated the absence of peaks at 2235 and 2208 cm⁻¹ and the presence of a peak at 2350 cm⁻¹, which confirmed the formation of CO₂ and excluded the presence (slip) of N₂O in the reactor effluent. The formation of CO and CO₂ indicated the oxidation of deposited carbon by the reduction of N₂O. No NO or N,O formation was observed during the whole experiment. N₂O was completely converted into N₂ as evidenced by FTIR where no N₂O and/or NO₂ peaks were observed within the detection limit of 1 ppm. The observation of N₂ in the MS indicated an extremely selective reduction of N₂O into N₂. O₂ arising from N₂O started to break through roughly from 1400 s onward, while the CO₂ yield started to decrease. The breakthrough of O₂ implied that the catalyst was largely oxidized and coincided with the disappearance of CO and CO₂ from the FTIR spectrum, indicating that all deposited carbon was oxidized. These observations indicated that the N₂O reduction over C,H, pre-reduced Rh/CLZ consisted of the refilling of the oxygen vacancies and the oxidation of the carbon deposits. Overall, the results presented in Fig. 6 clearly demonstrate that the HC pre-reduced Rh/CLZ catalyst exhibited excellent N₂O reduction performance, which was in line with the conclusion from the TAP study (Fig. 3).

In order to explore the performance of Rh/CLZ in real industrial applications, a good catalytic activity for only N₂O is not sufficient. The N₂O reduction activity has to be studied in the presence of potential inhibitors in the exhaust stream under atmospheric pressure. NO and O₂ are the most challenging inhibitors as they both can compete with N₂O for the oxygen vacancies. Fig. 7 and 8 summarize the results obtained in the presence of O₂ and NO.

The influence of O₂ addition to the N₂O (2000 ppm) gas feed on N₂O reduction is shown in Fig. 7. O₂ (m/z = 32) started to break through after approximately 20 s, while N₂O was not observed (detection limit of 1 ppm) until 160 s. From that point on around 25 ppm N₂O was detected by FT-IR. The N₂O breakthrough time was 8× later than that of O₂ (50 000 ppm), which indicated that a small concentration of N₂O (2000 ppm) was able to compete with an excess of O₂, NO and NO₂ were not detected anytime in the reactor effluent. This clearly suggested that N₂O could be selectively reduced into N₂ in the presence of O₂. The observation of 25 ppm of N₂O after O₂ breakthrough (Fig. 7C), i.e., 98.8% N₂O...
conversion, suggested that the presence of O2 inhibited the catalytic reduction of N2O to a very small extent when the catalyst became oxidized. These results indicated that the reduction of N2O into N2 over reduced Rh/CLZ was not affected by the addition of O2. N2O was much more competitive towards the oxygen vacancies as compared to O2.

Fig. 8 evaluates the effect of adding NO to the N2O gas feed. N2O and NO roughly broke through at the same time while CO formation decreased, which indicated that N2O and NO compete equally for the active sites. The presence of NO did not affect the reduction of N2O into N2, while the deposited carbon was oxidized. Only 100 ppm of NO2 was observed when NO appeared in the reactor effluent as noticed in the FT-IR spectrum (Fig. 8C). This NO2 likely formed due to the reaction of NO with surface oxygen species in the N2O reduction through steps (8)–(10):

\[
N_2O + \cdot \rightarrow N_2 + \cdot - O
\] (8)
When there was no deposited carbon on the surface, NO affected the N₂O reduction dramatically, while this was less significant when co-feeding only O₂. The detection of NO₂ over the oxidized sample implied that surface nitrite and nitrate species formed on the catalyst surface catalyzed by the rhodium surface sites. The formation of NO₂ could proceed via the reaction of NO with surface O species, which originated either from N₂O reduction or catalyst surface lattice oxygen. These surface nitrite and nitrate species would affect the surface oxygen species mobility, and the O₂ association and desorption from the Rh sites. Another NO₂ formation pathway could proceed via the disproportionation of NO into N₂ and NO₂. The discrimination between and/or the extent of contribution of the two pathways was beyond the scope of this study.

Fig. 9 summarizes the observed N₂O conversion for the different gas feeds over O₂ pre-oxidized and C₃H₆ pre-reduced Rh/CLZ. For N₂O, the catalyst displayed 100% N₂O conversion over both O₂ pre-oxidized and C₃H₆ pre-reduced samples. For N₂O + O₂ (excess), the N₂O conversion dropped from 100% to 98.8% when the catalyst switched from a reduced to an oxidized state. For N₂O + NO, the conversion of N₂O dropped from 100% to 37% when the catalyst switched from a reduced into an oxidized state. The inhibition of the N₂O reduction by NO was a common issue in the N₂O abatement, since the majority of explored catalysts had a very low tolerance towards NO. In summary, the above experiment clearly demonstrated that a C₃H₆ pre-reduced Rh/CLZ catalyst exhibited a unique and extraordinary N₂O reduction performance, when the Rh/CLZ was in a reduced state. Again, carbon deposits extended the time frame during which the Rh/CLZ catalyst remained reduced.

Besides our previous publication, the experiment of (5% CO₂ + 2000 ppm NO)/He over C₃H₆ pre-reduced Rh/CLZ in a fixed bed flow reactor indicated that NO by far was a more powerful reductant in the competition for the oxygen vacancies as compared to CO₂. Around 90% of the deposited carbon was consumed by NO via the lattice oxygen of the ceria. NO was selectively reduced into N₂ regardless of the CO₂ presence. The presence of CO₂ did not affect the NO reactivity and selectivity over the reduced CLZ and Rh/CLZ catalysts. The presence of CO₂ would, therefore, not affect both the N₂O and NO reduction into N₂ over reduced Rh/CLZ.
4. Conclusion

This work shows that a C₃H₆ pre-reduced Rh/CLZ catalyst exhibits a unique and extraordinary performance in the reduction of N₂O in the presence of other oxidants, e.g., most importantly O₂ and NO. The reductive pretreatment with C₃H₆ created oxygen vacancies and carbon deposits on the Rh/CLZ surface. These oxygen vacancies were the catalytic sites for an extremely selective reduction of N₂O into N₂, in which the oxygen vacancies were replenished. The deposited carbon acted as a buffer reductant and was responsible for the generation of new oxygen vacancies. This new N₂O reduction system could be cycled by short pulses of hydrocarbons upstream of the catalyst bed, which allowed regeneration of the oxygen vacancies and deposited carbon. Our work clearly indicated that the DiAir DeNOₓ system could be applied in simultaneous NOₓ and N₂O reduction under oxygen rich conditions, using a single Rh/CLZ catalyst bed, under industrial relevant conditions.

Conflicts of interest

There are no conflicts to be declared.

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