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# Oxygen Vacancies in reduced Rh- and Pt-ceria for Highly Selective and Reactive Reduction of NO into N<sub>2</sub> in excess of O<sub>2</sub>

Yixiao Wang<sup>a</sup>, Ramon Oord<sup>b</sup>, Daniël van den Berg<sup>a</sup>, Bert M. Weckhuysen<sup>b</sup>, and Michiel Makkee<sup>a,\*</sup>

**Abstract:** The issue of current commercial DeNO<sub>x</sub> abatement systems are that the NO<sub>x</sub> emissions on road exceed its regulation limit. Commercial DeNO<sub>x</sub> catalyst exhibits poor performance in the selective conversion NO to N<sub>2</sub>, especially in high temperature and high gas hourly space velocity. In this study, oxygen vacancies of reduced ceria and Pt- or Rh-ceria are found the efficient and selective catalytic sites for NO reduction into N<sub>2</sub>. Small amounts of NO can completely compete with excess O<sub>2</sub> in a temperature window between 250 and 600°C and high GHSV of 170.000 l/h. N<sub>2</sub>O is not detected during the whole NO reduction process. NO<sub>2</sub> is formed when the catalysts are oxidised when both NO and O<sub>2</sub> start to breakthrough. Oxygen defects act as 'oxygen black hole' that will catch all oxygen containing species. Oxygen vacancies can be created by injecting fuel on the catalyst. Considering the fuel economy, the working temperature should be between 250 and 600°C. Above 600°C, most of injected fuel was used for combustion with O<sub>2</sub>. Below 250°C, ceria support will not be reduced and the oxidation rate of the deposited carbon will be too low.

Nitrogen Oxides (NO<sub>x</sub>) are a family of poisonous, highly reactive gases, which have adverse effect on our environment and human health. Each year around 2.6 million people' deaths are related to NO<sub>x</sub> pollution, according to World Health Organization. The NO<sub>x</sub> concentration in the air of most European countries are above the 40 µg/m<sup>3</sup>, which is the safety limit value according to Air Quality Standards of European Emission<sup>[1]</sup>. Above 40% of NO<sub>x</sub> emission are contributed from the on-road transportation. The current Euro 6 emission standard has led to the development of highly efficient lean-burn turbo-charged diesel engines and catalytic deNO<sub>x</sub> systems (Urea-Selective Catalytic reduction (SCR) and Lean NO<sub>x</sub> Traps (NSR) or a combination thereof), aiming at 0.08 g/km NO<sub>x</sub> emission. However, the real NO<sub>x</sub> emission during the real driving actually is on average 6 times higher than the NO<sub>x</sub> emission regulation standard<sup>[2]</sup>. These huge variation among others is caused by the difference between mild test condition in the laboratory and very dynamic acceleration and deceleration during the real driving. Therefore, from September 2017 the European Committee will partly replace the current laboratory test by the real driving emission (RDE), aiming at 0.168 g/km NO<sub>x</sub> emission which is

even 2.1 times of Euro 6. In future, both the NO<sub>x</sub> emission and test condition will be more stringent. The current available technologies, including Three-Way Catalyst (TWC)<sup>[3]</sup>, SCR<sup>[4]</sup>, NSR<sup>[5]</sup>, and combination 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 NSR catalyst (Pt/Rh/Ba/K/Ce/Al<sub>2</sub>O<sub>3</sub>)<sup>[6]</sup>. The Di-Air system is a promising technology to meet the future NO<sub>x</sub> emission standards under real driving test conditions (dynamic operations, high exhaust temperature, and high gas hourly space velocities (GHSV)).

However, detailed research is required to further develop and optimise this catalytic system before it can be commercialised at a large scale. Oxygen defects in reduced ceria have found to act as the vital catalytic sites for NO reduction into N<sub>2</sub>. Both oxygen defects and deposited carbon created during the direct fuel injection in the exhaust can explain the high effectiveness of the Di-Air system<sup>[7]</sup>. However, the reactivity of NO towards oxygen defects could be an issue in a typical diesel gas exhaust stream, where approximately 200 ppm NO has to compete with 5% O<sub>2</sub>, 5% CO<sub>2</sub>, and 5-10% H<sub>2</sub>O. In addition, NO<sub>2</sub> and N<sub>2</sub>O (even a worse effect on our environment and human health) are common side products in the NO reduction technologies especially using noble metal as an active ingredient in the catalyst composition<sup>[8]</sup>. Therefore, the study on selectivity and reactivity of NO reduction processes are essential.

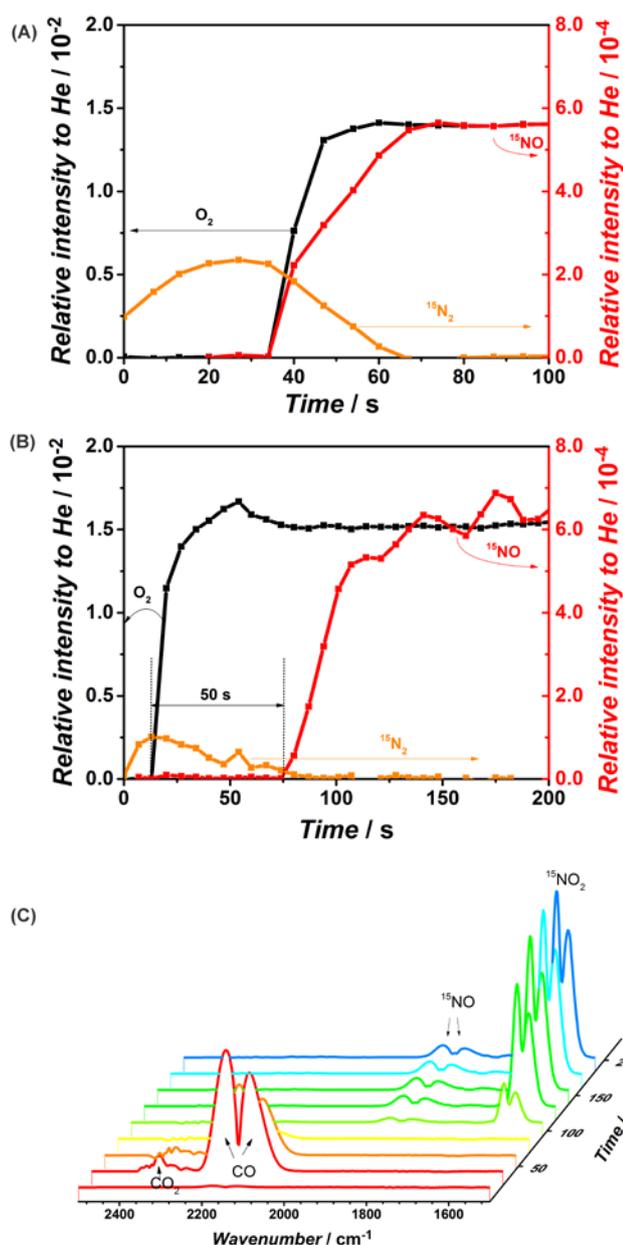
In order to investigate whether NO can be reduced into N<sub>2</sub> under real conditions, *i.e.*, trace amounts of NO in excess O<sub>2</sub> with high GHSV and high temperature, we have studied the selectivity and reactivity of NO over ceria and noble metal impregnated ceria in a fixed bed flow reactor. A series of experiments were performed by using 0.2% <sup>15</sup>NO (and/or <sup>14</sup>NO) co-feeding with 5% O<sub>2</sub> over ceria, Pt/ceria, and Rh/ceria at 450°C and 600°C. To mimic fuel injection in the Di-Air system, C<sub>3</sub>H<sub>6</sub> was used as a model fuel to pre-treat the catalyst. <sup>15</sup>NO was used to distinguish <sup>14</sup>N<sub>2</sub> and CO (both at m/e = 28) as well as CO<sub>2</sub> and <sup>14</sup>N<sub>2</sub>O (both at m/e = 44). The effluents were analysed with Mass Spectrometer (MS) and Fourier Transform Infrared Spectroscopy (FT-IR). Zr-La doped ceria (hereafter denoted as Ceria) is selected as a model of a ceria catalyst due to its (hydro) thermal stability. Pt and Rh were explored as noble metals ingredients. Details on these experiments as well as on characterisation of the applied catalysts can be found in Supporting information (SI).

**Figure 1A** showed <sup>15</sup>NO, O<sub>2</sub>, and <sup>15</sup>N<sub>2</sub> evolution during 0.2% <sup>15</sup>NO + 5% O<sub>2</sub> over at 600°C C<sub>3</sub>H<sub>6</sub> reduced Rh/ceria with GHSV of 125.000 l/h, detected by MS. <sup>15</sup>N<sub>2</sub> was observed until 70s and there was no <sup>15</sup>N<sub>2</sub>O and <sup>15</sup>NO<sub>2</sub> detected by MS during these first 70s. <sup>15</sup>NO and O<sub>2</sub> started to breakthrough from 35s, followed by the formation of <sup>15</sup>NO<sub>2</sub>, detected by FT-IR (**Figure S1A, SI**). The absence of <sup>15</sup>NO<sub>2</sub> in MS was caused by that NO<sub>2</sub> was

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unstable and easily decomposed into NO by high energy electrons in the mass spectrometer filament. The formation of CO and CO<sub>2</sub>, shown in **Figure S1B, SI**, started to decline after 35s and vanished after 70s. The formation of CO and CO<sub>2</sub> were due to the oxidation of deposited carbon by oxygen from ceria lattice [7a], which re-created the oxygen defects and kept the ceria surface reduced. Therefore, the deposited carbon acted as buffer reductant. The formation of CO and CO<sub>2</sub> declined after 35s indicated that the deposited carbon was almost oxidised and Rh/ceria started to be oxidised from the 35s onwards. N<sub>2</sub>, as the exclusive N-containing product during the first 35s, indicated that NO was selectively reduced to N<sub>2</sub> in the presence of excess O<sub>2</sub> when Rh/ceria was largely reduced at 600°C.



**Figure 1.** <sup>15</sup>NO, <sup>15</sup>N<sub>2</sub>, and O<sub>2</sub> evolution upon 0.2 % <sup>15</sup>NO + 5% O<sub>2</sub> exposure over reduced Rh/ceria (A) at 600°C with space velocity at 125.000 l/h, (B) at 450 °C with GHSV of 67.000 l/h; (C) FT-IR spectral responses of (B).

The same breakthrough times of <sup>15</sup>NO and O<sub>2</sub> indicated that <sup>15</sup>NO and O<sub>2</sub> had the same reactivity towards oxygen defects at 600°C. The same selectivity and reactivity of NO and O<sub>2</sub> was also observed over C<sub>3</sub>H<sub>6</sub> reduced Pt/ceria and ceria (**Figure S2, SI**) and even at higher GHSV (up to 170.000 l/h), <sup>15</sup>NO was still selectively reduced into <sup>15</sup>N<sub>2</sub> (**Figure S3, SI**). The selective reduction of <sup>15</sup>NO into <sup>15</sup>N<sub>2</sub> was also observed at lower temperature, e.g. 450°C (**Figure 1B**), where <sup>15</sup>N<sub>2</sub>O was not observed (detection limit of 1 ppm) and <sup>15</sup>NO<sub>2</sub> started to breakthrough after <sup>15</sup>NO breakthrough (**Figure 1C**). <sup>15</sup>NO started to breakthrough after 50s later than the breakthrough of O<sub>2</sub>. Therefore, NO was more reactive than O<sub>2</sub> in refilling the oxygen defects and the oxidation of the deposited carbon at 450°C.

NO reactivity studies were further investigated over reduced ceria, Pt/ceria, and Rh/ceria using even smaller amount of NO in excess O<sub>2</sub>. Table 1 summarized the NO and O<sub>2</sub> breakthrough time during 0.05% NO + 5% O<sub>2</sub> over ceria based catalysts with GHSV of 67.000 l/h at 600°C. NO and O<sub>2</sub> had same breakthrough time when the reactions were performed at 600°C. However, O<sub>2</sub> breakthrough time at 400°C was 210 and 245s earlier than that of NO over Pt/ceria and Rh/ceria, respectively. These observations indicated that small amount NO can compete with excess of O<sub>2</sub> for oxygen defect.

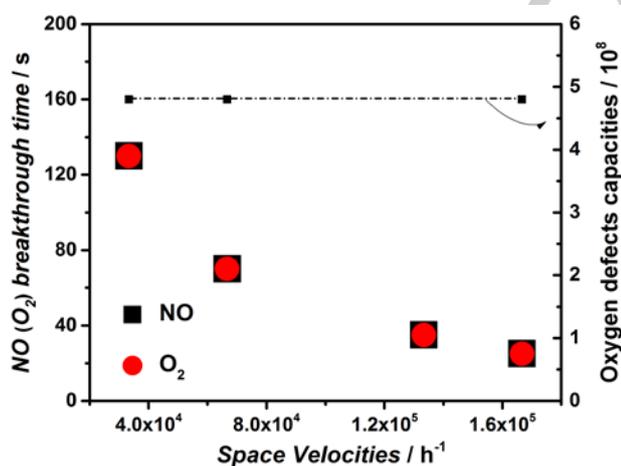
Table 1. The difference of NO and O<sub>2</sub> breakthrough time during 0.05 % NO + 5% O<sub>2</sub> over C<sub>3</sub>H<sub>6</sub> reduced samples with GHSV of 67.000 l/h.

Items	T	Breakthrough time / s		t(NO)-t(O <sub>2</sub> )
Catalyst		t (NO)	t (O <sub>2</sub> )	
Pt / ceria	600	60	60	0
Pt / ceria	400	215	5	210
Rh / ceria	600	65	65	0
Rh / ceria	400	253	10	245
Ceria	600	70	70	0

Experiments using <sup>14</sup>NO were performed to further confirm the selectivity of NO, especially over noble metal loaded ceria. <sup>14</sup>NO with O<sub>2</sub> gas mixtures were used besides <sup>15</sup>NO with O<sub>2</sub> gas mixture to distinguish IR bands of CO (2174 and 2116 cm<sup>-1</sup>) and <sup>14</sup>N<sub>2</sub>O (2235 and 2208 cm<sup>-1</sup>). The <sup>15</sup>N<sub>2</sub>O bands were located at 2174 and 2116 cm<sup>-1</sup> due to isotopic shifting [9], which were the same as for CO. **Figure S4** showed the FI-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 peaks at 2174 and 2116 cm<sup>-1</sup>, assigned to CO, were observed from the initial flow of 0.05% <sup>14</sup>NO + 5% O<sub>2</sub> and vanished after 92s. In addition, a broad band at 2350 cm<sup>-1</sup> was assigned to CO<sub>2</sub>, which also initially appeared and vanished after 92s. The bands at 1908 and 1850 cm<sup>-1</sup> were observed from 253s onwards. These two bands were both assigned to <sup>14</sup>NO. During the whole time interval, the FT-IR peak at 2235 cm<sup>-1</sup>, assigned to <sup>14</sup>N<sub>2</sub>O, was not observed (detection limit of 1 ppm). The rise of 1601 and 1628 cm<sup>-1</sup> bands from 285s were 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. NO and NO<sub>2</sub> were adsorbed when ceria was fully re-oxidised [10]. Ceria was then acting as NO<sub>x</sub> storage component [11] like K [12] and BaO [13]. The result of 0.2% <sup>14</sup>NO + 5% O<sub>2</sub> over the ceria and Pt/ceria (**Figure S5 and S6, SI**)

again showed no  $\text{N}_2\text{O}$  formation during the whole experiment and  $\text{NO}_2$  was formed when  $\text{NO}$  and  $\text{O}_2$  started to breakthrough and the ceria was fully re-oxidised. Therefore, it can be concluded that the  $\text{NO}$  was selectively converted into  $\text{N}_2$  even in the presence of up to 100 times more  $\text{O}_2$  on the reduced ceria surface at both 600 and 400°C.  $\text{NO}$  started to oxidize into  $\text{NO}_2$  when reduced ceria based catalysts were largely re-oxidised.

**Figure 2** showed the summaries of  $\text{NO}$  and  $\text{O}_2$  breakthrough time during 0.2%  $\text{NO}$  + 5%  $\text{O}_2$  flow over  $\text{C}_3\text{H}_6$  reduced ceria at 600°C with the different GHSV between 33.000 l/h and 170.000 l/h. The result showed that  $\text{NO}$  and  $\text{O}_2$  breakthrough time was inverse proportion to GHSV. Since the reduction of ceria support were performed at the same conditions, the amount of oxygen defects and deposited carbon were identical, *i.e.*, same oxygen defects capacities based on assuming that all deposited carbon will be oxidised to  $\text{CO}_2$ . The  $\text{NO}$  and  $\text{O}_2$  breakthrough time was largely depended on the space velocity, *i.e.*, the amount of  $\text{NO}$  and  $\text{O}_2$  per time unit. The higher space velocities, the more  $\text{NO}$  and  $\text{O}_2$  were flowed per the time unit, the earlier breakthrough time of  $\text{NO}$  and  $\text{O}_2$ . The same phenomenon was also observed for 0.2%  $\text{NO}$  + 5%  $\text{O}_2$  exposure over  $\text{C}_3\text{H}_6$  reduced Pt/ceria at 600°C with the different GHSV from 33.000 l/h to 170.000 l/h (**Figure S7, SI**), where  $\text{NO}$  and  $\text{O}_2$  breakthrough times was again inverse proportion to GHSV. Experiments with  $\text{NO}_2$  and  $\text{N}_2\text{O}$  over  $\text{C}_3\text{H}_6$  reduced ceria or Pt/ceria showed that  $\text{NO}_2$  and  $\text{N}_2\text{O}$  were all selectively reduced into  $\text{N}_2$  until there was no oxygen defects left on the catalyst surface (not shown). Therefore, the oxygen defects acted as a kind of 'oxygen black hole' for catching all the oxygen containing species until the hole was refilled (completely re-oxidised) and the caught N will recombine to  $\text{N}_2$ .



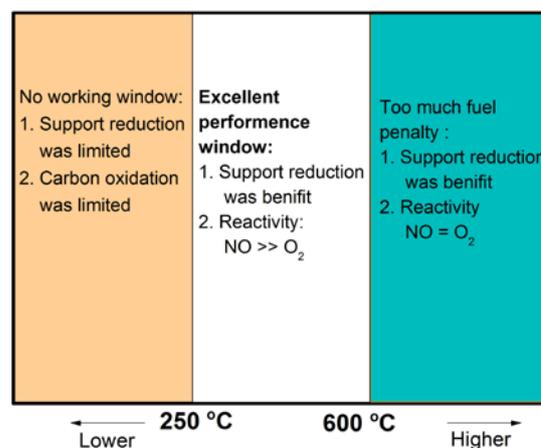
**Figure 2.**  $\text{NO}$  and  $\text{O}_2$  breakthrough time during 0.2%  $\text{NO}$  + 5%  $\text{O}_2$  exposure over ceria as a function of the GHSV. All sample were pre-treated by 1.25 %  $\text{C}_3\text{H}_6$  at 600°C.

Evidenced by  $\text{H}_2$ -TPR (**Figure S9, SI**), the bulk oxygen reduction for noble metal loaded ceria was around 300°C. TGA of deposited carbon ceria showed that the carbon oxidation effectively started from around 250°C onwards (**Figure S8, SI**). Therefore, as displayed in **Scheme 1**, the working temperature window for the Di-Air system will be around 250 - 600°C. Below

250°C, the reduction of ceria and oxidation of deposited carbon will become the rate limiting steps. Above 600°C, most of the deposited carbon will be primarily used for the  $\text{O}_2$  reaction and not for the  $\text{NO}$  reduction.

Due to the experimental limitation, dynamic injection of fuel onto the catalyst was not aimed for. In this study,  $\text{C}_3\text{H}_6$  pre-treatment in 2h 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. Therefore, the reactivity of  $\text{NO}$  and  $\text{O}_2$  can possibly be tuned even wider temperature window.

The prominent advantage of the Di-Air system is retaining a high  $\text{NO}$  conversion at a higher reaction temperature, *e.g.* 600°C and even higher, and high GHSV, *e.g.* 40.000 l/h and even higher, where NSR and SCR are not working properly anymore<sup>[6]</sup>. The NSR system relies on the  $\text{NO}_x$  storage components, which can hardly work at 600°C and causes the NSR system to fail in the high temperature regime.  $\text{NO}_x$  storage will also fail when storage demands cannot be compensated for higher GHSV (above 40.000 l/h). The same GSVH limitations are applicable for SCR. The excellent performance of the Di-Air system in the high reaction temperature and GHSV can be explained by the presence of oxygen defect sites and carbon deposits. The reduced ceria is extremely active and selective for  $\text{NO}$  reduction into  $\text{N}_2$  even in excess oxygen. The existence of a buffer reductant (deposited carbon during fuel injection) extends the  $\text{NO}$  reduction capacity. The carbon buffer capacity makes the Di-Air system not only to rely on the capacity and storage rate of  $\text{NO}_x$  storage materials.



**Scheme 1.** Demonstration of Di-Air working temperature window.

Noble metal supported ceria's are promising starting materials for the development of Di-Air system. The fuel injection direct onto the catalyst led to a reduced ceria and carbon deposition. Oxygen defects (directly and indirectly by the lattice oxygen oxidation of deposited carbon) are the active sites for the selective and reactive reduction of  $\text{NO}$  into  $\text{N}_2$  in oxygen excess.

## Acknowledgements

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**Keywords:** Noble metal • Ceria • NO reduction • Selectivity • Reactivity

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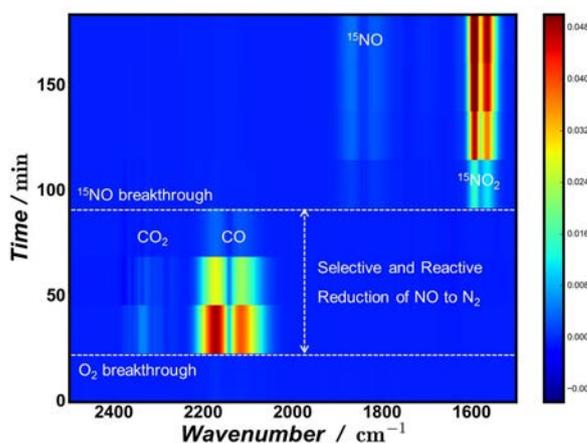
## COMMUNICATION

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The selectivity and reactivity for the reduction of NO in the presence excess O<sub>2</sub> over by C<sub>3</sub>H<sub>6</sub> pre-treated reduced (noble metal-loaded) ceria are reported. It was found that small (trace) amounts of NO can completely compete with excess O<sub>2</sub> to reduce into N<sub>2</sub> over both reduced ceria and noble metal loaded ceria. Oxygen defects of ceria (directly) and deposited carbon (indirectly) are responsible for these selectivity reactivity at a broad temperature window (250-600°C) and high GHSV (up to 170.000 l/h). No N<sub>2</sub>O was observed and NO<sub>2</sub> was only when NO and O<sub>2</sub> breakthrough and ceria is fully re-oxidised.