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Oxygen Vacancies in reduced Rh- and Pt-ceria for Highly Selective and Reactive Reduction of NO into N_2 in excess of O_2

Yixiao Wang[a], Ramon Oord[b], Daniël van den Berg[a], Bert M. Weckhuysen[b], and Michiel Makkee[a,]*

Abstract: The issue of current commercial $DeNO_x$ abatement systems are that the NO_x emissions on road exceed its regulation limit. Commercial $DeNO_x$ catalyst exhibits poor performance in the selective conversion NO to N_2, 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_2. Small amounts of NO can completely compete with excess O_2 in a temperature window between 250 and 600°C and high GHSV of 170.000 l/l/h. N_2O is not detected during the whole NO reduction process. NO_2 is formed when the catalysts are oxidised when both NO and O_2 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^{o}C, most of injected fuel was used for combustion with O_2. Below 250^{o}C, ceria support will not be reduced and the oxidation rate of the deposited carbon will be too low.

Nitrogen Oxides (NO_x) 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_x pollution, according to World Health Organization. The NO_x concentration in the air of most European countries are above the 40 µg/m^3, which is the safety limit value according to Air Quality Standards of European Emission[1]. Above 40% of NO_x 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 $deNO_x$ systems (Urea-Selective Catalytic reduction (SCR) and Lean NO_x Traps (NSR) or a combination thereof), aiming at 0.08 g/km NO_x emission. However, the real NO_x emission during the real driving actually is on average 6 times higher than the NO_x emission regulation standard[2]. 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_x emission which is even 2.1 times of Euro 6. In future, both the NO_x emission and test condition will be more stringent. The current available technologies, including Three-Way Catalyst (TWC)[3], SCR[4], NSR[5], 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 ($Pt/Rh/Ba/K/Ce/Al_2O_3$) [6]. The Di-Air system is a promising technology to meet the future NO_x 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_2. 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 [7]. 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_2, 5% CO_2, and 5-10% H_2O. In addition, NO_2 and N_2O (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[8]. Therefore, the study on selectivity and reactivity of NO reduction processes are essential.

In order to investigate whether NO can be reduced into N_2 under real conditions, *i.e.,* trace amounts of NO in excess O_2 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% ^{15}NO (and/or ^{14}NO) co-feeding with 5% O_2 over ceria, Pt/ceria, and Rh/ceria at 450^{o}C and 600^{o}C. To mimic fuel injection in the Di-Air system, C_3H_6 was used as a model fuel to pre-treat the catalyst. ^{15}NO was used to distinguish $^{14}N_2$ and CO (both at m/e = 28) as well as CO_2 and $^{14}N_2O$ (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 ^{15}NO, O_2, and $^{15}N_2$ evolution during 0.2% ^{15}NO + 5% O_2 over at 600^{o}C C_3H_6 reduced Rh/ceria with GHSV of 125.000 l/l/h, detected by MS. $^{15}N_2$ was observed until 70s and there was no $^{15}N_2O$ and $^{15}NO_2$ detected by MS during these first 70s. ^{15}NO and O_2 started to breakthrough from 35s, followed by the formation of $^{15}NO_2$, detected by FT-IR (**Figure S1A, SI**). The absence of $^{15}NO_2$ in MS was caused by that NO_2 was

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Supporting information for this article is available unstable and easily decomposed into NO by high energy electrons in the mass spectrometer filament. The formation of CO and CO_2, shown in **Figure S1B, SI**, started to decline after 35s and vanished after 70s. The formation of CO and CO_2 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_2 declined after 35s indicated that the deposited carbon was almost oxidised and Rh/ceria started to be oxidised from the 35s onwards. N_2, as the exclusive N-containing product during the first 35s, indicated that NO was selectively reduced to N_2 in the presence of excessO_2 when Rh/ceria was largely reduced at 600°C.

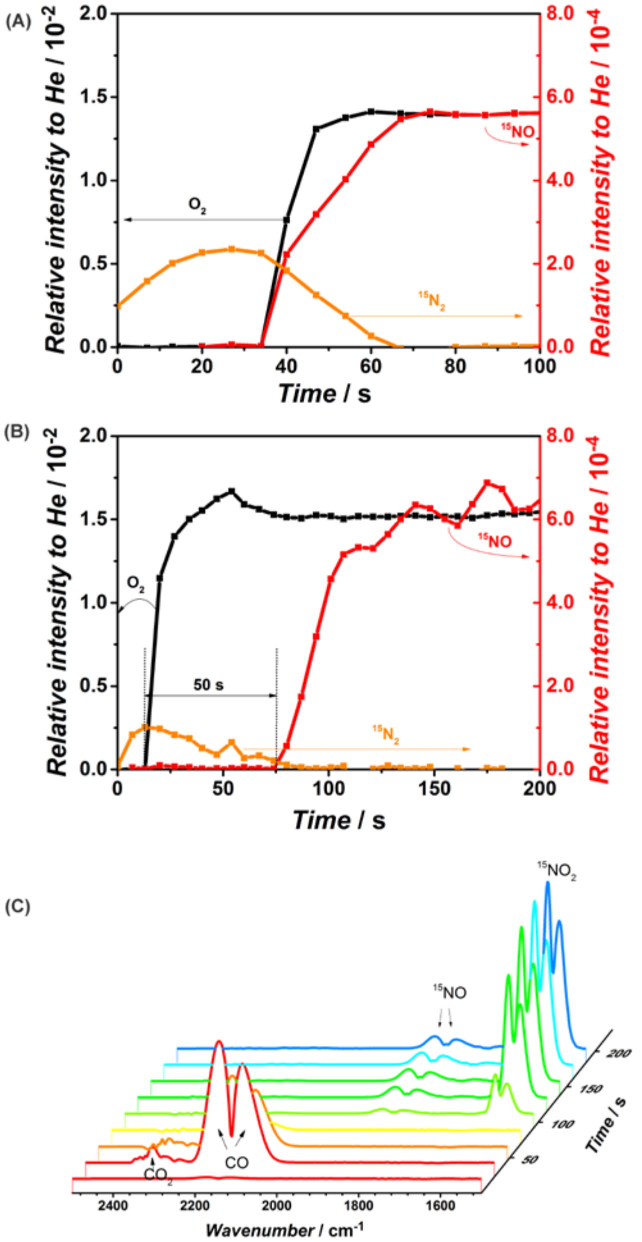


Figure 1. ^{15}NO, $^{15}N_2$, and O_2 evolution upon 0.2 % ^{15}NO + 5% O_2 exposure over reduced Rh/ceria (A) at 600°C with space velocity at 125.000 l/l/h, (B) at 450 °C with GHSV of 67.000 l/l/h; (C) FT-IR spectral responses of (B).

The same breakthrough times of ^{15}NO and O_2 indicated that ^{15}NO and O_2 had the same reactivity towards oxygen defects at 600°C. The same selectivity and reactivity of NO and O_2 was also observed over C_3H_6 reduced Pt/ceria and ceria (**Figure S2, SI**) and even at higher GHSV (up to 170.000 l/l//h), ^{15}NO was still selectively reduced into $^{15}N_2$ (**Figure S3, SI**). The selective reduction of ^{15}NO into $^{15}N_2$ was also observed at lower temperature, *e.g.* 450°C **(Figure 1B)**, where $^{15}N_2O$ was not observed (detection limit of 1 ppm) and $^{15}NO_2$ started to breakthrough after ^{15}NO breakthrough (**Figure 1C**). ^{15}NO started to breakthrough 50s later than the breakthrough of O_2. Therefore, NO was more reactive than O_2 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_2. Table 1 summarized the NO and O_2 breakthrough time during 0.05% NO + 5% O_2 over ceria based catalysts with GHSV of 67.000 l/l/h at 600°C. NO and O_2 had same breakthrough time when the reactions were performed at 600°C. However, O_2 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_2 for oxygen defect.

Table 1. The difference of NO and O_2 breakthrough time during 0.05 % NO + 5% O_2 over C_3H_6 reduced samples with GHSV of 67.000 l/l/h.

Items Catalyst	T	Breakthrough time / s t (NO)	 t (O_2)	t(NO)-t(O_2)
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 ^{14}NO were performed to further confirm the selectivity of NO, especially over noble metal loaded ceria. ^{14}NO with O_2 gas mixtures were used besides ^{15}NO with O_2 gas mixture to distinguish IR bands of CO (2174 and 2116 cm^{-1}) and $^{14}N_2O$ (2235 and 2208 cm^{-1}). The $^{15}N_2O$ bands were located at 2174 and 2116 cm^{-1} due to isotopic shifting [9], which were the same as for CO. **Figure S4** showed the FI-IR spectra during 0.05% ^{14}NO + 5% O_2 exposure over C_3H_6 reduced Rh/ceria at 400°C. The peaks at 2174 and 2116 cm^{-1}, assigned to CO, were observed from the initial flow of 0.05% ^{14}NO + 5% O_2 and vanished after 92s. In addition, a broad band at 2350 cm^{-1} was assigned to CO_2, which also initially appeared and vanished after 92s. The bands at 1908 and 1850 cm^{-1} were observed from 253s onwards. These two bands were both assigned to ^{14}NO. During the whole time interval, the FT-IR peak at 2235 cm^{-1}, assigned to $^{14}N_2O$, was not observed (detection limit of 1 ppm). The rise of 1601 and 1628 cm^{-1} bands from 285s were attributed to the formation of $^{14}NO_2$. $^{14}NO_2$ was only observed when both ^{14}NO and O_2 had broken through. NO and NO_2 were adsorbed when ceria was fully re-oxidised[10]. Ceria was then acting as NO_x storage component[11] like K[12] and BaO[13]. The result of 0.2% ^{14}NO + 5% O_2 over the ceria and Pt/ceria (**Figure S5 and S6, SI**) again showed no N_2O formation during the whole experiment and NO_2 was formed when NO and O_2 started to breakthrough and the ceria was fully re-oxidised. Therefore, it can be concluded that the NO was selectively converted into N_2 even in the presence of up to 100 times more O_2 on the reduced ceria surface at both 600 and 400°C. NO started to oxidize into NO_2 when reduced ceria based catalysts were largely re-oxidised.

Figure 2 showed the summaries of NO and O_2 breakthrough time during 0.2% NO + 5% O_2 flow over C_3H_6 reduced ceria at 600°C with the different GHSV between 33.000 l/l/h and 170.000 l/l/h. The result showed that NO and 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 CO_2. The NO and O_2 breakthrough time was largely depended on the space velocity, *i.e.,* the amount of NO and O_2 per time unit. The higher space velocities, the more NO and O_2 were flowed per the time unit, the earlier breakthrough time of NO and O_2. The same phenomenon was also observed for 0.2% NO + 5% O_2 exposure over C_3H_6 reduced Pt/ceria at 600°C with the different GHSV from 33.000 l/l/h to 170.000 l/l/h (**Figure S7, SI**), where NO and O_2 breakthrough times was again inverse proportion to GHSV. Experiments with NO_2 and N_2O over C_3H_6 reduced ceria or Pt/ceria showed that NO_2 and N_2O were all selectively reduced into 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 N_2.

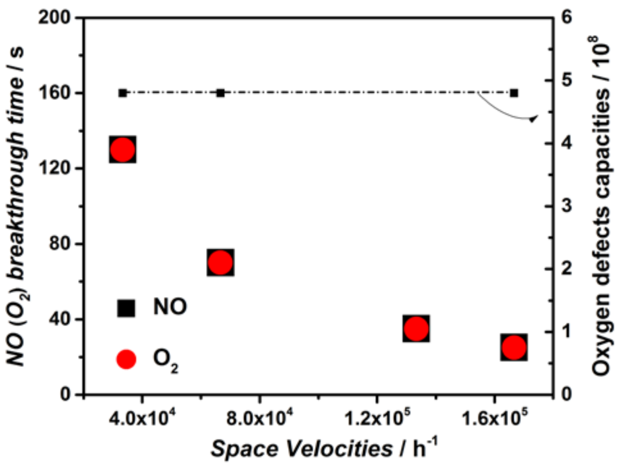
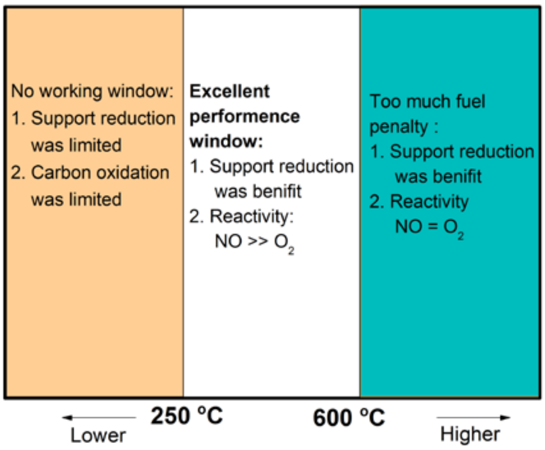


Figure 2. NO and O_2 breakthrough time during 0.2% NO + 5% O_2 exposure over ceria as a function of the GHSV. All sample were pre-treated by 1.25 % C_3H_6 at 600°C.

Evidenced by 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 O_2 reaction and not for the NO reduction.

Due to the experimental limitation, dynamic injection of fuel onto the catalyst was not aimed for. In this study, C_3H_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 NO and O_2 can possibly be tuned even wider temperature window.

The prominent advantage of the Di-Air system is retaining a high NO conversion at a higher reaction temperature, *e.g.* 600°C and even higher, and high GHSV, *e.g.* 40.000l/l/h and even higher, where NSR and SCR are not working properly anymore [6]. The NSR system relies on the NO_x storage components, which can hardly work at 600°C and causes the NSR system to fail in the high temperature regime. NO_x storage will also fail when storage demands cannot be compensated for higher GHSV (above 40.000 l/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 NO reduction into N_2 even in excess oxygen. The existence of a buffer reductant (deposited carbon during fuel injection) extends the NO reduction capacity. The carbon buffer capacity makes the Di-Air system not only to rely on the capacity and storage rate of 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 NO into N_2 in oxygen excess.

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

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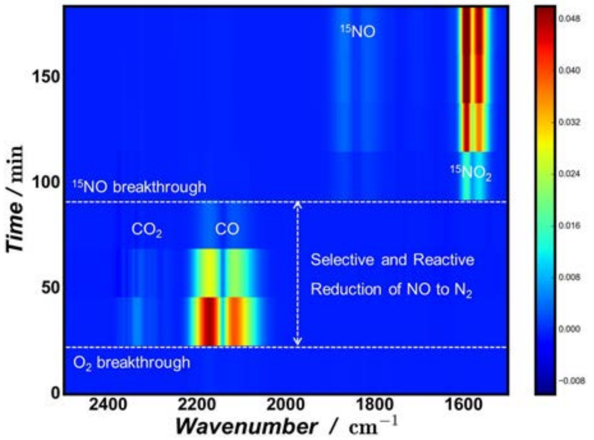

The selectivity and reactivity for the reduction of NO in the presence excessO_2 over by C_3H_6 pre-treated reduced (noble metal-loaded) ceria are reported. It was found that small (trace) amounts of NO can completely compete with excess O_2 to reduce into N_2 over both reduced ceria and noble metal loaded ceria. Oxygen defects of ceria (directly) and deposited carbon (indirectly) are responsible for these selectivity reactivity at a broad temperature window (250-600^{o}C) and high GHSV (up to 170.000 l/l/h). No N_2O was observed and NO_2 was only when NO and O_2 breakthrough and ceria is fully re-oxidised.