

Oxygen Vacancies in Reduced Rh/ and Pt/Ceria for Highly Selective and Reactive Reduction of NO into N₂ in excess of O₂

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

Currently commercial NO_x removal (DeNO_x) abatement systems for lean-burn engines exceed regulation limits on the road for NO_x emissions. Commercial DeNO_x catalysts exhibit poor performance in the selective conversion of NO to N₂, especially at high temperature and high gas hourly space velocities (GHSV). In this study, oxygen vacancies of reduced ceria and Pt/ or Rh/ ceria are found to be the efficient and selective catalytic sites for NO reduction to N₂. Even at low concentrations, NO can compete with an excess of O₂ at 600 °C and a high GHSV of 170 000 L L⁻¹ h⁻¹, conditions in which SCR and NSR DeNO_x system are not able to function well. N₂O is not detected over the whole range of conditions, whereas NO₂ is only formed upon oxidation of the catalyst, after both NO and O₂ start to appear. For consideration of the fuel economy, the working temperature should be between 250 and 600 °C. Above 600 °C, most of the injected fuel was combusted with O₂. Below 250 °C, ceria support will not be reduced by fuel and the oxidation rate of the deposited carbon through oxygen from ceria lattice will be too low.

Nitrogen oxides (NO_x) are a family of poisonous, highly reactive gasses that have an adverse effect on our environment and human health. Each year the deaths of around 2.6 million people are related to NO_x pollution according to the World Health Organization.^[1] The NO_x concentration in the air of most European countries is above the safety limit of 40 µg m⁻³, according to the Air Quality Standards of European Emission.^[2] Above 40% of the NO_x emissions originate from 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 combinations thereof), aiming at ≤ 0.08 g km⁻¹ NO_x emissions. However, the NO_x emissions under real driving conditions is on average 6

times higher than the NO_x emission regulation standard.^[3] One cause of this huge variation is the difference between the mild test conditions in the laboratory and the very dynamic acceleration and deceleration under real driving conditions. Therefore, from September 2017 the European Commission will partially replace the current laboratory test by the real driving emission (RDE) standard, aiming at 0.168 g km⁻¹ NO_x emissions, which is 2.1 times of Euro 6. In the future, test conditions will become more stringent and require lower NO_x levels. The current available technologies, including the three-way catalyst (TWC),^[4] SCR,^[5] NSR,^[6] and combinations thereof, need to significant improvement, both 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 and frequent injection of hydrocarbons (HCs) downstream of the engine in the exhaust system and upstream of a complex NSR catalyst (Pt/Rh/Ba/K/Ce/Al₂O₃).^[7] 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 still required to develop the catalytic system further and optimise it before it can be commercialised on a large scale. Oxygen defects in reduced ceria have been found to act as the vital catalytic sites for NO reduction into N₂. Both these oxygen defects and deposited carbon created during the direct fuel injection in the exhaust can explain the high effectiveness of the Di-Air system.^[8] However, the reactivity of NO towards oxygen defects could be an issue in a typical diesel gas exhaust stream, where approximately 200 ppm of NO has to compete with 5% O₂, 5% CO₂, and 5–10% H₂O. In addition, NO₂ and N₂O, both to be avoided for environmental and human health reasons, are common side products in the NO reduction technologies especially if using noble metal as an active ingredient in the catalyst composition.^[9] Therefore, the studies on reactivity and selectivity in NO reduction processes are essential.

To investigate whether NO can be reduced into N₂ under real conditions, i.e., trace amounts of NO in excess O₂ at high GHSV and high temperatures, we have studied the selectivity and reactivity of NO reduction over ceria and noble metal loaded ceria in a fixed bed flow reactor. A series of experiments were performed using 0.2% ¹⁵NO (and/or ¹⁴NO) co-fed with 5% O₂ over ceria, Pt/ceria, and Rh/ceria catalysts at 450 °C and 600 °C. To mimic fuel injection in the Di-Air system, C₃H₆ was used as a model fuel to pretreat the catalyst. ¹⁵NO was

[a] Y. Wang, D. van den Berg, Prof. Dr. Ir. M. Makkee
Catalysis Engineering, Chemical Engineering Department,
Delft University of Technology
Van der Maasweg 9, 2629 HZ Delft (The Netherlands)
E-mail: m.makkee@tudelft.nl

[b] Dr. R. Oord, Prof. Dr. Ir. B. M. Weckhuysen
Inorganic Chemistry and Catalysis group
Debye Institute for Nanomaterials Science
Utrecht University
Universiteitsweg 99, 3584 CG Utrecht (The Netherlands)

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used to distinguish $^{14}\text{N}_2$ and CO (both at $m/e=28$) as well as CO_2 and $^{14}\text{N}_2\text{O}$ (both at $m/e=44$). The effluents were analysed by mass spectrometer (MS) and Fourier transform infrared spectroscopy (FTIR). Zr-La doped ceria (hereafter denoted as ceria) was selected as a model for a ceria catalyst owing to its hydrothermal 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.

Figure 1 A shows the ^{15}NO , O_2 , and $^{15}\text{N}_2$ evolution at 600°C under $0.2\% ^{15}\text{NO} + 5\% \text{O}_2$ over C_3H_6 reduced Rh/ceria at GHSV of $125\,000 \text{ LL}^{-1} \text{ h}^{-1}$. $^{15}\text{N}_2$ was observed until 70 s whereas no $^{15}\text{N}_2\text{O}$ or $^{15}\text{NO}_2$ were detected by MS during this time interval.

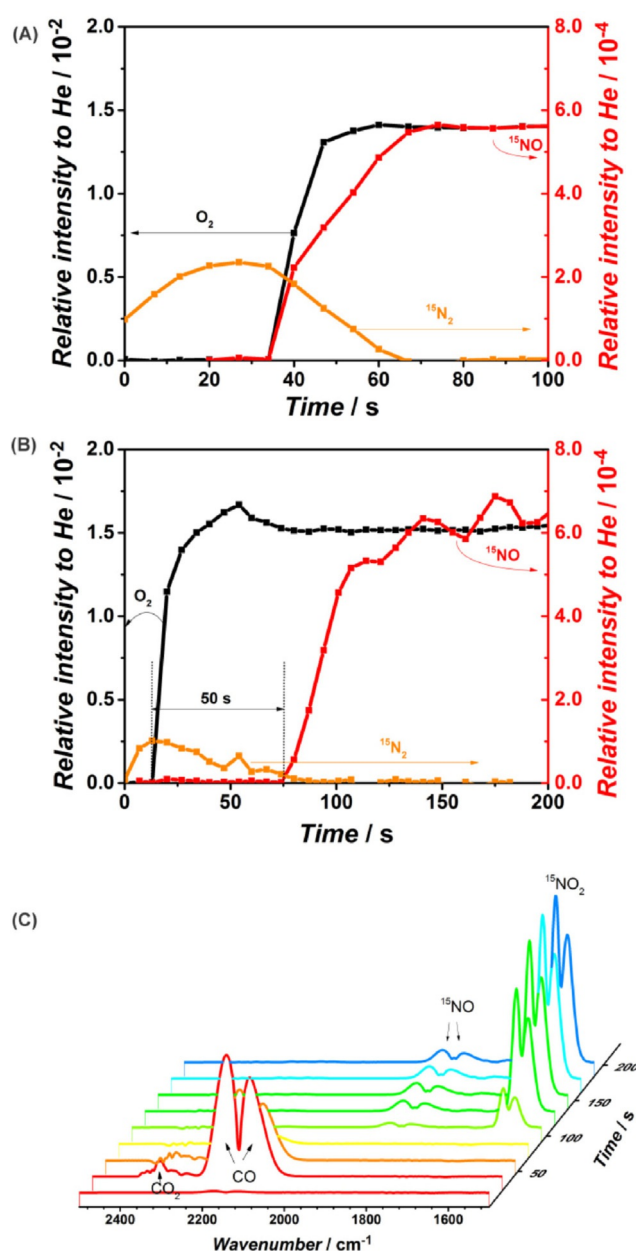


Figure 1. ^{15}NO , $^{15}\text{N}_2$, and O_2 evolution upon $0.2\% ^{15}\text{NO} + 5\% \text{O}_2$ exposure over reduced Rh/ceria (A) at 600°C with GHSV of $125\,000 \text{ LL}^{-1} \text{ h}^{-1}$, (B) at 450°C with GHSV of $67\,000 \text{ LL}^{-1} \text{ h}^{-1}$; (C) FTIR spectral responses of (B).

^{15}NO and O_2 started to appear from 35 s, followed by the formation of $^{15}\text{NO}_2$, detected by FTIR (Figure S1 A, SI). The absence of $^{15}\text{NO}_2$ in MS analysis was caused by the instability of NO_2 and its easy decomposition into NO by high energy electrons in the mass spectrometer filament. The formation of CO and CO_2 , shown in Figure S1 B (SI) started to decline after 35 s and vanished after 70 s. The formation of CO and CO_2 was owing to the reaction of deposited carbon with oxygen from the ceria lattice,^[8a] which re-created the oxygen defects and kept the ceria surface reduced. Therefore, the deposited carbon acts as buffer reductant. The decline in CO and CO_2 formation after 35 s indicates that the deposited carbon was almost entirely consumed and Rh/ceria started to be oxidised from 35 s onwards. $^{15}\text{N}_2$, as the exclusive N-containing product during the first 35 s, shows the selective reduction of NO in the presence of excess O_2 in which Rh/ceria is in a largely reduced state at 600°C .

The simultaneous appearance of ^{15}NO and O_2 indicates that ^{15}NO and O_2 have the same reactivity towards oxygen defects at 600°C . Only 2% of the oxygen vacancies were filled by NO. The same selectivity and reactivity of NO and O_2 were also observed over C_3H_6 reduced Pt/ceria and ceria (Figure S2, SI). Even up to higher GHSV of $170\,000 \text{ LL}^{-1} \text{ h}^{-1}$, ^{15}NO was still selectively reduced into $^{15}\text{N}_2$ (Figure S3, SI). The selective reduction of ^{15}NO into $^{15}\text{N}_2$ was also observed at a lower temperature, for example, 450°C (Figure 1 B), in which $^{15}\text{N}_2\text{O}$ was not observed (detection limit of 1 ppm) and $^{15}\text{NO}_2$ started to appear after ^{15}NO breakthrough (Figure 1 C). ^{15}NO started to appear 50 s later than O_2 . Thus, NO is more effective than O_2 in refilling the oxygen defects and the oxidation of the deposited carbon at 450°C . 30% of oxygen vacancies had been filled by NO, although the concentration of oxygen is 100 times that of NO.

NO reactivity studies were further investigated over reduced ceria, Pt/ceria, and Rh/ceria using NO concentrations 100 times lower than that of O_2 . Table 1 summarises the NO and O_2 appearance times under $0.05\% \text{NO} + 5\% \text{O}_2$ over C_3H_6 reduced samples with GHSV of $67\,000 \text{ LL}^{-1} \text{ h}^{-1}$. At 600°C NO and O_2 have appear at the same breakthrough time, whereas O_2 appears much earlier than NO over Pt/ceria and Rh/ceria at 400°C . Clearly, NO can compete even at low concentration under an excess of O_2 for the oxygen defect sites.

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 along with ^{15}NO with O_2 gas mixture to distinguish IR bands of CO (2174 and

Table 1. The NO and O_2 breakthrough times using $0.05\% \text{NO} + 5\% \text{O}_2$ over C_3H_6 reduced samples with GHSV of $67\,000 \text{ LL}^{-1} \text{ h}^{-1}$.

Catalyst	$T [^\circ\text{C}]$	Breakthrough time [s]		$t(\text{NO}) - t(\text{O}_2)$
		$t(\text{NO})$	$t(\text{O}_2)$	
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

2116 cm^{-1}) from those of $^{14}\text{N}_2\text{O}$ (2235 and 2208 cm^{-1}). The $^{15}\text{N}_2\text{O}$ bands were isotopically shifted to 2174 and 2116 cm^{-1} ,^[10] the same as for CO. Figure S4 shows the FTIR spectra under 0.05% $^{14}\text{NO} + 5\%$ O_2 exposure over C_3H_6 reduced Rh/ceria at 400 °C. The CO absorbance at 2174 and 2116 cm^{-1} was observed from the start and disappeared after 90 s. In addition, a broad band at 2350 cm^{-1} , assigned to CO_2 , appeared initially and disappeared after 90 s. Absorbances at 1908 and 1850 cm^{-1} were observed from 255 s onwards, both assigned to ^{14}NO . During the whole time interval, no absorbance of $^{14}\text{N}_2\text{O}$ at 2235 cm^{-1} (detection limit of 1 ppm) could be observed. The increase of 1601 and 1628 cm^{-1} bands after 285 s was attributed to the formation of $^{14}\text{NO}_2$. $^{14}\text{NO}_2$ was only observed after both ^{14}NO and O_2 had appeared. It is well-known that oxidised ceria can promote NO oxidation into NO_2 .^[11] The result of 0.2% $^{14}\text{NO} + 5\%$ 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 only formed after the appearance of NO and O_2 after ceria was fully re-oxidised. Therefore, it can be concluded that even in the presence of 100 times more O_2 , NO is selectively converted into N_2 on the reduced ceria surface at both 600 and 400 °C. NO will then be oxidised to NO_2 after the reduced ceria-based catalysts are largely re-oxidised.

Figure 2 shows the summaries of NO and O_2 breakthrough time during 0.2% NO + 5% O_2 flow over a C_3H_6 reduced ceria at 600 °C for a GHSV between 33 000 $\text{LL}^{-1}\text{h}^{-1}$ and 170 000 $\text{LL}^{-1}\text{h}^{-1}$. The results show that the NO and O_2 breakthrough times are inversely proportional with GHSV. Since the reduction of the ceria support was performed under the same conditions, the number of oxygen defects and deposited carbon were identical, i.e., the same oxygen defects capacities based on the assumption 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. With higher space velocities, the more NO and O_2 flows per unit of time, and the earlier the breakthrough times of NO and O_2 . The same phenomenon was also observed

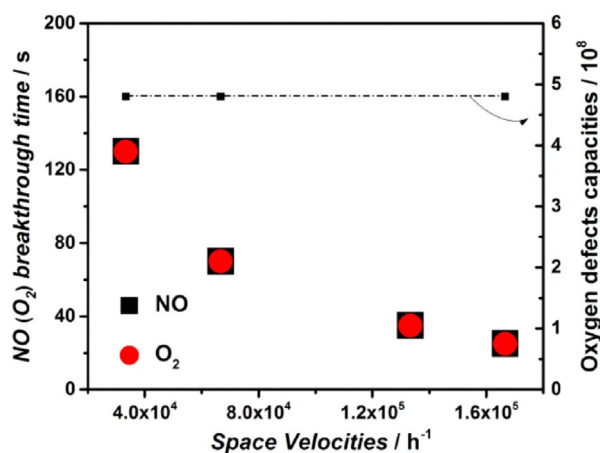
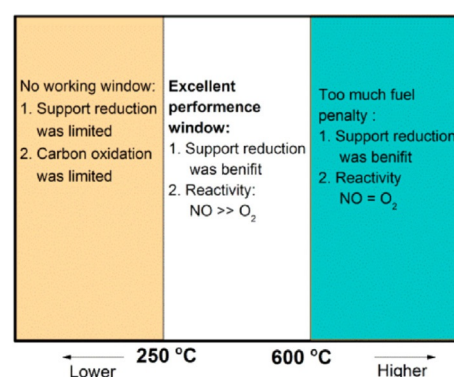


Figure 2. NO and O_2 breakthrough time during exposure of C_3H_6 reduced ceria under a gas flow with 0.2% NO + 5% O_2 at 600 °C as a function of the GHSV. All samples were pre-treated by 1.25% C_3H_6 at 600 °C.

for 0.2% NO + 5% O_2 exposure over C_3H_6 reduced Pt/ceria at 600 °C with different GHSV from 33 000 $\text{LL}^{-1}\text{h}^{-1}$ to 170 000 $\text{LL}^{-1}\text{h}^{-1}$ (Figure S7, SI), in which NO and O_2 breakthrough times are again inversely proportional 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 were no oxygen defects left on the catalyst surface (not shown). Therefore, the oxygen defects act as a kind of “oxygen black hole” for catching all the oxygen containing species until the holes are refilled (completely re-oxidised) and the captured N will recombine to N_2 .

Evidenced by temperature programmed reduction (TPR(H_2)) (Figure S9, SI), the bulk oxygen reduction for noble metal loaded ceria was around 300 °C. Thermogravimetric analysis in air of the carbon deposited ceria showed that the carbon oxidation effectively started from around 250 °C onwards (Figure S8, SI). Therefore, as displayed in Scheme 1, the operational



Scheme 1. Demonstration of Di-Air operational temperature window.

temperature window for the Di-Air system is from 250 to 600 °C. Below 250 °C, the reduction of ceria by fuel and oxidation of deposited carbon by oxygen from ceria will become the rate limiting step. Above 600 °C, most of the deposited carbon will be primarily used for the reaction with O_2 and not for NO reduction.

Owing to the experimental limitations, dynamic injection of fuel onto the catalyst was not conducted. In this study, a C_3H_6 pretreatment for 2 h was used to mimic the consequences of fuel injection, for example, 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 for an even wider temperature window.

The prominent advantage of the Di-Air system is maintaining a high NO conversion at higher reaction temperatures (≥ 600 °C) and high GHSV (≥ 40 000 $\text{LL}^{-1}\text{h}^{-1}$), at which NSR and SCR no longer function anymore.^[7] The NSR system relies on the NO_x storage components, which hardly function at 600 °C and causes the NSR system to fail in the high-temperature regime. NO_x storage will also fail if storage demands cannot be compensated at higher GHSV (above 40 000 $\text{LL}^{-1}\text{h}^{-1}$). The same GHSV limitations are applicable for SCR. The excellent performance of the Di-Air system at high reaction tempera-

tures and high 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 N₂ even in excess oxygen. The existence of a buffer reductant (deposited carbon during fuel injection) extends the NO reduction capacity. Unlike the NSR system that relies on the capacity of and storage rate of NO_x storage materials, oxygen vacancies and the buffer reductant (carbon deposits) can be effectively re-created by periodical fuel injection.

Noble metal supported ceria is a promising starting materials for the development of the Di-Air system. Fuel injection directly onto the catalyst leads to a reduced ceria and carbon deposition. Oxygen defects (directly and indirectly from the lattice oxygen reduction by deposited carbon) are the active sites for the selective and reactive reduction of NO into N₂ in oxygen excess.

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Conflict of interest

The authors declare no conflict of interest.

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