

Reaction Mechanism Study of the Di-Air System and Selectivity and Reactivity of NO Reduction in Excess O₂

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ABSTRACT

We studied the mechanism of NO reduction as well as its selectivity and reactivity in the presence of excess O₂. Results show that fuel injection and/or pretreatment are important for ceria catalyst reduction and carbon deposition on the catalyst surface. Oxygen defects of reduced ceria are the key sites for the reduction of NO into N₂. The deposited carbon acts as a buffer reductant, *i.e.*, the oxidation of carbon by lattice oxygen recreates oxygen defects to extend the NO reduction time interval. A small amount of NO showed a full conversion into only N₂ both on the reduced Zr-La doped ceria and reduced Pt-Zr-La doped ceria. Only when the catalyst is oxidised NO is converted into NO₂.

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1. INTRODUCTION

A mandatory introduction of a CO₂ emission target of 95 g/km by the year 2020 in the EU for automotive manufactures drives the development of increasingly fuel efficient cars. The requirement of the current Euro 6 emission standard has led to the development of highly efficient lean burn turbo-charged engines and catalytic deNO_x systems (Lean NO_x Traps (NSR) for gasoline engines and Urea-Selective Catalytic reduction (SCR) and or a combination of SCR and NSR for diesel engines). Euro 7 (or EURO 6B and 6C) requires a further reduction of the NO_x emissions from 0.18 g/km (Euro 5) via 0.08 g/km (Euro 6) to 0.04 g/km, while particulate matter emissions remain at 0.0045 g/km. Currently, the amount of NO emission, tested in the laboratory, does not reflect the amount emitted during the real driving conditions [1, 2, 3]. As of September 2017, the European Commission will proclaim that the real driving emission (RDE) will partially replace the current laboratory test in order to introduce new car models into the market [4]. These new regulation means that the tested cars will be driven outside on a real road under conditions of acceleration and deceleration that are beyond the current laboratory testing procedures. The pollutant emissions will be measured by portable emission measuring systems (PEMS). The RDE testing is expected to reduce the current difference of the pollutant emissions between laboratory and road.

Up to 2.1 times NO_x emission (0.168 g/km), relatively to the current Euro 6 NO_x emission standard (0.08 g/km), is allowed under the RDE testing by September 2017 [4]. This highly indicated that current available technologies: Three-way catalyst (TWC) [5, 6, 7], Urea-SCR (Selective Catalytic Reduction) [8, 9, 10], Lean NO_x Traps (NSR) [11, 12, 13] and combination thereof still need to be significantly improved since almost all Euro 6 certified diesel cars in the RDE testing emitted on average 8 times higher than the current

NO_x emission standard [1, 2, 3]. In future, the NO_x emission will become more and more stringent. Therefore, effective exhaust emissions after-treatment technologies will be needed.

Recently, Bisaiji *et al.* (Toyota Motor Company) developed the Di-Air system in which short fuel rich and long fuel lean periods are created by the directly injecting hydrocarbons (HC's) at a high frequency downstream of the engine in the exhaust system upstream of a NSR catalyst (Pt/Rh/Ba/K/Ce/Al₂O₃) [14]. The Di-Air system is promising to meet the future NO_x emission standards under real driving test conditions. Compared to the current NSR system's narrow operating temperature window, caused by the requirement to store the NO_x as nitrite/nitrate on the Ba component, the Di-Air system retains a high NO_x conversion (above 80%) up to 800 °C at a high space velocity up to 1.2 · 10⁵ l/h. They found that HC's injection was more effective in the NO_x reduction in comparison to that of CO and H₂ [14, 15]. The unique performance of the Di-Air system was attributed to the formation of stable isocyanate (CNO) and isocyanide (CN) intermediates on the catalyst surface as being evidenced by FTIR observations [16]. However, CN and CNO species were observed at a low temperature (200 °C) and their intensities decreased as the temperature increased. The CN and CNO species were hardly detected at 600 °C. The high NO reduction efficiency at high temperatures in Di-Air system as reported can be difficult to relate to these CN and CNO species.

A different explanation can be conceived to explain the performance of the Di-Air system. In the 1990's Illán-Gómez *et al.* [17, 18] reported that activated carbon is active in NO_x reduction in a temperature window between 400 and 500 °C. A large fuel injection upstream of a catalyst bed might promote the carbon formation and this in turn might enhance the NO_x reduction. Another explanation

can be that the reduced catalyst sites reduce NO_x directly, while the formed adsorbed hydrocarbon fragments and carbon deposits act as an oxygen scavenger under lean conditions.

The working principle of the Di-Air system has not been clearly illustrated by the inventor (Toyota), academia, or industry, making it difficult to further optimise the system for real application due to the lack of fundamental understanding and reasoning. In order to test the aforementioned alternative explanations, we initiated a detailed investigation into the operating principle of the Di-Air. The TAP (Temporal Analysis of Products) technique (a vacuum pulse-response technique) was mainly utilised to investigate the mechanism of NO reduction and the role of each Di-Air catalyst component (Pt/Rh/Ba/K/Ce/ Al_2O_3) [19]. In addition, a flow reactor (under an atmosphere pressure) was used to mimic the NO reduction in the real operation system, *i.e.*, a small amount of NO in O_2 . This study aims to unveil the mechanism of the NO reduction and the competition and the selectivity of the NO reduction in the presence of excess O_2 .

2. EXPERIMENTAL

A commercially available Zr-La doped ceria (hereafter denoted as ceria) was obtained from Engelhard (now BASF). The BET surface area of ceria is $65 \text{ m}^2/\text{g}$, detailed characterisation was previously reported [19]. Pt/ceria was prepared via incipient wetness impregnation. Tetra-ammine platinum (II) nitrate was used as the precursor. Subsequently, the sample was dried at 110°C overnight and calcined at 550°C for 24 h. The loading of Pt is 0.5 wt%, measured by inductively coupled plasma-atomic emission spectroscopy (ICP).

Temporal Analysis of Products (TAP) was used for the mechanism study. TAP is a vacuum pulse-response technique. Reactant gas pulses are introduced to a small finite volume upstream of a packed catalyst bed. The introduced reactant and formed product(s) upon interaction with the catalyst diffuse through the packed catalyst bed until they leave the packed bed. The reactant and product(s) are recorded *versus* time (response) by a mass spectrometer, details of this set-up can be found elsewhere [19]. In the TAP experiments with ^{15}NO and $^{18}\text{O}_2$ pulses: 1) the catalyst was firstly oxidised using an O_2 pulse train; 2) secondly, a pre-reduction step with C_3H_6 pulses was performed until the effluent of the reactor remained constant.

In-situ Raman spectra (Renishaw, 2000) were recorded using a temperature controlled *in-situ* Raman cell (Linkam, THMS 600). Ten scans were collected for each spectrum in the $100\text{--}4000 \text{ cm}^{-1}$ range using a continuous grating mode with a resolution of 4 cm^{-1} and scan time of 10 s. The spectrometer was calibrated daily using a silicon standard with a strong band at 520 cm^{-1} . The ceria was firstly pre-treated by C_3H_6 (1000 ppm in N_2 , flow rate 200 mL/min) for 2 h. N_2 was used to flush the cell for 20 min. Subsequently, NO (1000 ppm NO in N_2 , flow rate of 200 mL/min) was admitted to the cell.

A flow reactor was used to explore the reactivity and selectivity of NO in O_2 . 200 mg catalyst was placed in a 6 mm inner-diameter quartz reactor tube. A feed composition of 0.2 % or 0.05% of NO and 5% of O_2 (with He for balance) was used with a space velocity of $6.7 \cdot 10^4 \text{ l/h}$. The reactor effluent was online analysed by mass spectrometry

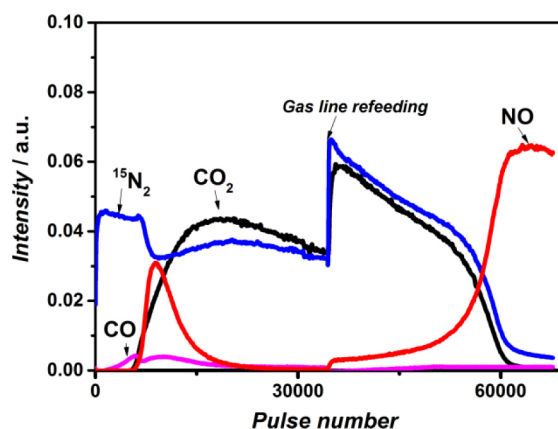
(MS, Hiden Analytical, HPR-20 QIC) and infrared (IR) spectroscopy (Perkin-Elmer, Spectrum One). For IR analysis a gas cell with KBr windows with a path length of $\sim 5 \text{ cm}$ was used. The spectra were measured in a continuous mode using the Perkin-Elmer 'Time-Base' software between $4000\text{--}700 \text{ cm}^{-1}$ wavenumbers with a spectral resolution of 8 cm^{-1} and an acquisition of 8 scans per spectrum, resulting in a time interval of 23 s between each displayed spectrum.

3. RESULTS

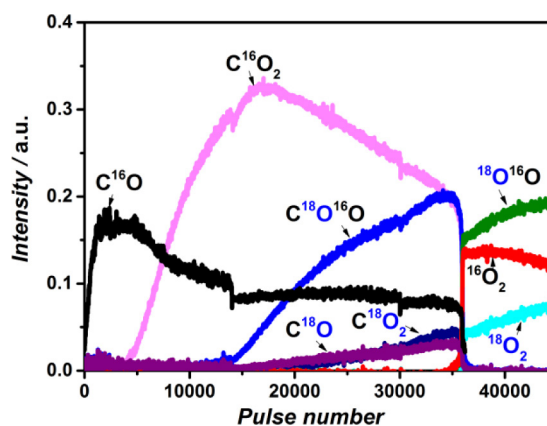
3.1 Mechanism Study

3.1.1 ^{15}NO and $^{18}\text{O}_2$ Pulses Over C_3H_6 Reduced Ceria in TAP

In order to mimic fuel injection in the Di-Air system, C_3H_6 is used as a model fuel to pre-treat the catalyst. Ceria was pre-treated (reduced) by C_3H_6 at 560°C before ^{15}NO pulse experiment.



A.



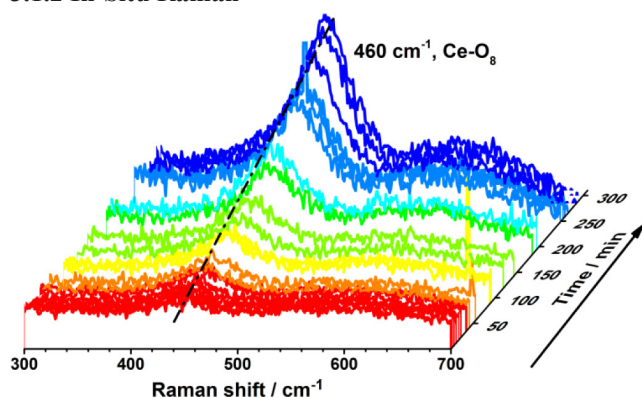
B.

Figure 1. Reactant and product evolution upon pulsing (A) ^{15}NO at 560°C and (B) $^{18}\text{O}_2$ at 530°C over by C_3H_6 reduced ceria (21.2 mg) in TAP.

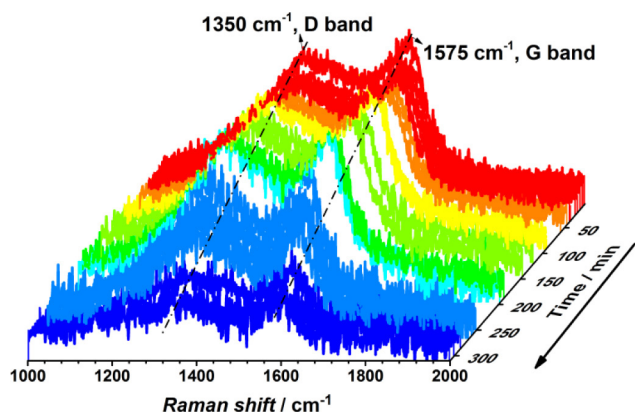
The pre-treatment of C_3H_6 resulted in $5.2 \cdot 10^{17}$ oxygen atoms / mg_{Cat} extraction from the ceria lattice and $1.6 \cdot 10^{18}$ carbon atoms / mg_{Cat} deposition on the ceria surface. Figure 1A showed the result of ^{15}NO pulses over C_3H_6 reduced ceria at 560°C . The discontinuities in Figure 1A was attributed to the refilling of the ^{15}NO buffer vessel in the TAP. From 0 to 5340 pulses (Figure 1A) a full NO conversion was observed with $^{15}\text{N}_2$ as the main product (hardly any CO was

formed). The evolution of CO_2 was observed from pulse number 5340 onwards. The evolution of CO_2 was closely followed by a temporary decrease in NO conversion. The NO conversion increased again from pulse number 8900. From pulse number 20000 to 35000, a full NO conversion was once again observed, while $^{15}\text{N}_2$ and CO_2 were the exclusive products. From pulse number 35000 till the end of the experiment, a progressive decrease to zero in NO conversion was observed. The N_2 and CO_2 production showed the same trend as the NO conversion. No or hardly any $^{15}\text{N}_2\text{O}$ or $^{15}\text{NO}_2$ were formed and no traces of -CN or -CNO were detected. In order to identify the oxygen species participating in the oxidation of deposited carbon after C_3H_6 pre-treatment, an $^{18}\text{O}_2$ pulse experiment over at 530°C C_3H_6 reduced ceria was carried out. The pre-treatment of C_3H_6 led to approximately 2 hypothetical reduced ceria layers and 2-3 wt.% carbon deposition. Figure 1B showed the product evolution during the $^{18}\text{O}_2$ pulse experiment. The discontinuities in Figure 1B were at points where the $^{18}\text{O}_2/\text{He}$ buffer vessel in the TAP was refilled. All introduced $^{18}\text{O}_2$ were completely converted until a steep oxygen breakthrough profile was observed from pulse number 35000. Exclusive C^{16}O was evolved until pulse number 4000, where C^{16}O_2 started to form, and gradually became the dominant product. After 14000 pulses $\text{C}^{18}\text{O}^{16}\text{O}$ and C^{18}O_2 were observed. After 35000 pulses C^{16}O , C^{16}O_2 , $\text{C}^{18}\text{O}^{16}\text{O}$, C^{18}O , and C^{18}O_2 decreased to zero, where $^{18}\text{O}_2$, $^{16}\text{O}_2$, and $^{18}\text{O}^{16}\text{O}$ started to breakthrough in a kind of exchange equilibrium. The observed C^{18}O ($m/e=30$) was due to the fragmentation from C^{18}O_2 and $\text{C}^{18}\text{O}^{16}\text{O}$ and showed the same trend as the C^{18}O_2 and $\text{C}^{18}\text{O}^{16}\text{O}$ products. $^{18}\text{O}^{16}\text{O}$ was the main product after oxygen breakthrough.

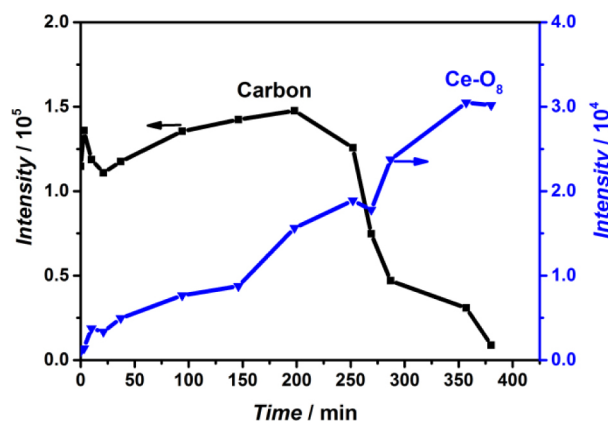
3.1.2 In-Situ Raman



A.



B.



C.

Figure 2. In-situ Raman response for NO over at 560°C C_3H_6 reduced ceria, Raman spectra of band at (A) 460 cm^{-1} and (B) 1575 and 1350 cm^{-1} ; (C) Raman bands intensity of 460 , 1575 , and 1350 cm^{-1} responses versus time.

Figure 2 showed *in-situ* Raman spectra for the NO reduction over at 560°C C_3H_6 reduced ceria. The band at 460 cm^{-1} was attributed to the symmetric stretch mode of Ce-O_8 crystal unit, which was characteristic for the fluorite ceria structure [20]. The bands at 1575 and 1350 cm^{-1} were assigned to G band and D band of carbon in the form of graphene or graphite, respectively [21]. The G band was usually assigned to zone centre phonons of E_{2g} symmetry of the perfect graphite structure, and the D peak was a breathing mode of A_{1g} symmetry which was forbidden in a perfect graphite structure and only became active in the presence of structural defects and disorders. The band at 460 cm^{-1} was initially hardly visible and its intensity increased during the NO flow (Figure 2A and C). In contrast to the band at 460 cm^{-1} (Figure 2A and C), the band at 1575 and 1350 cm^{-1} had the same intensities during the NO flow and started to decrease after 200 min (Figure 2B and C).

3.1.3 ^{15}NO Over C_3H_6 Reduced Pt/Ceria in TAP

Similarly to ceria, Pt/ceria was also pre-treated by C_3H_6 . Instead of 560°C , Pt/ceria pre-treatment with C_3H_6 was carried out at 450°C , which was 110°C lower than those of the experiments performed over bare ceria (Figure 1 and 2). The pre-treatment of C_3H_6 resulted in $6.3 \cdot 10^{17}$ oxygen atoms / mg_{Cat} extraction from the ceria lattice and $2.8 \cdot 10^{17}$ carbon atoms / mg_{Cat} deposition on the catalyst surface. Figure 3 showed the result of ^{15}NO pulse over at 450°C C_3H_6 reduced Pt/ceria. From pulse number 0 to 1000 (Figure 3), full NO conversion was observed with $^{15}\text{N}_2$ as the main product (small amount of CO formed). The evolution of CO_2 was observed from pulse number 1000. Instead of a temporary decrease in NO conversion, NO showed full conversion until pulse number 4000, where $^{15}\text{N}_2$ and CO_2 were the only products. From pulse number 4000 onwards, a progressive decrease to zero for the NO conversion was observed. The N_2 and CO_2 production followed the same trend as the NO conversion. No or hardly any $^{15}\text{N}_2\text{O}$ or $^{15}\text{NO}_2$ were formed and no traces of -CN or -CNO were detected.