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Adverse effects of potassium on NO\textsubscript{x} reduction over Di-Air catalyst (Rh/La-Ce-Zr)

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A B S T R A C T

The influence of potassium in Rh on a lanthium promoted zirconia stabilised ceria (CZ) catalysts was studied toward NO\textsubscript{x}reduction reactivity and selectivity. The results are compared with a Rh/CZ catalyst. The samples were characterised by N\textsubscript{2} adsorption, XRD, SEM, ICP, and H\textsubscript{2}-TPR. The study highlighted the importance of stored NO\textsubscript{x} regeneration over potassium in determining the overall performance of the Rh/K/CZ catalyst. The NO\textsubscript{x} stored over Rh/K/CZ in the previous NO gas stream cannot be regenerated sufficiently during the C\textsubscript{3}H\textsubscript{6} gas stream, and stored NO\textsubscript{x} gradually decreased from one cycle to the next, resulting in deteriorating performance of Rh/K/CZ. Besides, problem of NO\textsubscript{x} slip, the formation of both NH\textsubscript{3} and N\textsubscript{2}O (selectivities up to 30\% for each side product) were observed by the addition of potassium into the Rh/CZ catalyst system, depending on the reaction conditions applied and the severity of the catalyst deactivation.

1. Introduction

Recently, the car manufactures and catalyst company are struggling to lower the NO\textsubscript{x} emission. Unfortunately, the on-road real NO\textsubscript{x} emissions are much higher than those are allowed under the Europe 6 emission regulation driving legislation [1–3]. Ammonia/ Urea-SCR is a mature technology to reduce NO\textsubscript{x} emission from stationary sources and heavy-duty vehicles [4–6]. Although NH\textsubscript{3} (or urea) is an efficient reducing agent, the requirement for an injection system and NH\textsubscript{3} slip problem affect the economics and practicability of this application to passenger car, especially under the dynamic driving conditions. NO\textsubscript{x} Storage and Reduction (NSR) system [7–9], developed by Toyota researchers, is regarded as the leading technology to control NO\textsubscript{x} emission under lean-burn conditions. The engine is operating in the order of 60 s under the excess of oxygen (lean) condition. Subsequently, small hydrocarbon pulses are (in the order of 3 to 5 s) injected into the engine to create short periods with a reducing (rich) condition. Many challenges have still to be resolved. Firstly, the NO\textsubscript{x} conversion decreases at high gas-flow conditions and at high temperatures. Secondly, during the lean and rich cycle switching step, the NO\textsubscript{x} slip problem (up to 30\% slip of the stored NO\textsubscript{x}) is highly unwanted. Thirdly, the formation of side products N\textsubscript{2}O (very strong greenhouse gas) and NH\textsubscript{3} (toxicity) are of a major environmental concern. Most importantly, in the studies on the NSR catalyst using even most active reductant (H\textsubscript{2}), the results showed that although at a relatively low temperature, the NO\textsubscript{x} storage capacity was sufficient, but that the rates of NO\textsubscript{x} release and reduction (NO\textsubscript{x} conversion into nitrogen) were slow and insufficient, respectively [10,11]. These drawbacks of the NSR technology will limit its application in the real driving, especially as of September 2017 in Europe. The European Commission had proclaimed that the real driving emission (RDE) test protocol will partially replace the current certification laboratory test [12].

The application of the RDE requires that the catalyst has to work in wide temperature window and with a high space velocity (short contact time). Alternatives to the NO\textsubscript{x} Storage Reduction and Ammonia (urea)-SCR systems, Di-Air system, Diesel NO\textsubscript{x} after treatment by Adsorbed Intermediate Reductants, is under development, which is promising technology to efficiently abate NO\textsubscript{x} especially at high temperatures and high flows all of the time in a lean burn exhaust gas stream. In this Di-Air system, continuously short fuel injections with a high frequency are applied downstream of the engine in the exhaust system upstream of a NSR catalyst (Pt/Rh/8a/K/Ce/Al\textsubscript{2}O\textsubscript{3}) [13]. Limited information and experience are reported in both the open literature and patents archives on this newly developed technology. Mechanistic studies, especially on the Individual role of each catalyst component in the Di-Air system, are required to develop to reduce more deeply NO\textsubscript{x} emissions from lean-burn gasoline and diesel vehicles and can come in compliance with the current and future more stringent NO\textsubscript{x} emission standards.

In our previous work, the catalyst containing noble metal, especially Rh, and ceria are the promising starting materials for the Di-Air system.
Ceria was found to be an critical catalyst ingredient in the Di-Air system. During the fuel injection, the oxygen from the ceria lattice can react with the fuel, resulting in several layers of ceria support reduction and a carbon deposition on the ceria surface [14]. The oxygen defects of ceria were found to be the key sites for the NO reduction into N₂ [15]. The deposited carbon formed during the fuel injection, acted as a buffer reductant. The oxidation of the deposited carbon will occur via the oxygen from the ceria lattice, which created additional oxygen vacancies for additional NO reduction. The loading of noble metals over the ceria, e.g. Rh and Pt, can efficiently lower the ceria support reduction temperature by the fuel [16]. Additionally, the presence of noble metal will accelerate the N₂ formation rate. More importantly, the reduction of NO over a reduced Rh or Pt loaded ceria showed that NO was still selectively reduced into N₂ in an excess of oxygen (a factor of 100 in respect to NO, which is a typical value for a diesel engine exhaust stream) [17].

In the Di-Air system by Toyota, potassium (K) is one of the ingredients of the catalyst composition. Potassium (and/or barium) is a common ingredient in NSR catalyst, acting as the NOx storage component during the fuel lean stage of the engine operation. The stored NOx will be released and react with reductants from and during the fuel rich stage [18]. However, the reduction of the stored NOx over potassium or barium is somewhat restricted or a kind of bottleneck for the entire NOx storage and reduction process. NOx storage sites are not completely regenerated during the fuel rich stage if the temperature was below 400 °C [19,20]. Furthermore, the amount of NOx released relatively to the amount stored decreased with decreasing temperatures, which can be determined by the relative rate of reductant production (from the fuel injection), nitrate decomposition, OSC (oxygen storage capacity) consumption, and actual NOx reduction over the noble metal site of the NSR catalyst [20].

For a further optimisation the overall catalyst formulation and improving the performance of the Di-Air catalysts, it is meaningful to clarify whether potassium is required to add in the catalyst composition. Can the addition of potassium into Di-Air catalyst influence on the NOx reduction performance, especially in NOx slip, N₂O and NH₃ formation, and the deactivation on catalyst performance, which were so far not observed in the simplified Di-Air system of only a Rh and ceria based catalyst composition. To answer these questions, the NO reduction experiments on a ceria and Rh ceria based catalyst with the addition of potassium with simulated exhaust gasses were performed. Controlled experiment without potassium loading was included into the experiment approach.

2. Experimental

2.1. Materials preparation

Rh/CZ was prepared via an incipient wetness impregnation method of a rhodium precursor on Zr-La doped ceria (denoted as CZ, a gift from Engelhard, now BASF). Rhodium (III) nitrate hydrate (Aldrich, ~36% rhodium (Rh) basis) was used as the precursor. Subsequently, the sample was dried at 110 °C overnight and calcined at 550 °C for 5 h. For Rh/K/CZ, potassium was loaded on Rh/CZ by using incipient wetness impregnation method with KHCO₃ (Aldrich) as precursor. Subsequently, the sample was dried at 110 °C overnight and calcined at 550 °C for 5 h in a static air furnace.

2.2. Characterisation

2.2.1. Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Approximately 50 mg of sample was destructed in 4.5 ml 30% HCl + 1.5 ml 65% HNO₃ using the microwave. The destruction time in the microwave was 120 min at max power of 900 W. After destruction, the samples were diluted to 50 ml with MQ water. The samples were analysed with ICP-OES (PerkinElmer Optima 5300).

2.2.2. N₂ adsorption

Tristar II 3020 Micromeritics was used to determine the textural properties like specific BET surface area and pore volume. The catalyst samples were degassed at 200 °C for 16 h in a vacuum (0.05 mbar) before the nitrogen adsorption. The adsorption measurement was carried at −196 °C.

2.2.3. Scanning Electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis

SEM images and EDX mapping of Rh/K/CZ was performed by using scanning electron microscope (JEOL JSM-6010 LA) equipped with an integrated EDX (Standard LA Version) with Silicon Drift Detector (SDD). The samples were analysed at accelerating voltage of 20 kV.

2.2.4. X-ray diffraction (XRD)

The Powder X-Ray diffraction (XRD) was recorded on a Bruker-AXS D5005 with a Cu Kα source. The data were times collected by varying the 20 angle from 30° to 90° with a step size of 0.02.

2.2.5. Temperature programming reaction (TPR)

TPR for all the samples were carried out in a fixed bed reactor system connected to a thermal conductivity detector (TCD) to monitor the consumption of hydrogen by the catalyst. 200 mg of samples were packed between SiC layers (300–425 μm). The samples were then reduced in the H₂ (10%)/Ar flow at a flow rate of 30 ml/min, with temperature from room temperature to 1000 °C with a heating rate of 5 °C/min. TCD was calibrated using CuO as a reference. A perma-pure tubular drier was used to remove the water produced during the reduction upstream of the TCD detector.

2.3. Catalytic testing

2.3.1. Reactivity and selectivity study in flow reactor

A flow reactor was explored for the study of the NO reduction reactivity and selectivity with and without gas-phase oxygen. 200 mg catalyst was placed in a 6 mm inner-diameter quartz reactor tube. The reactor effluent was online analysed by a mass spectrometry (MS, Hiden Analytikal, 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 ~5 cm was used. The spectra were measured in a continuous mode using the Perkin-Elmer ‘Time-Base’ software between 4000 - 700 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. For the NO reduction in the presence of O₂, a feed composition of 0.2% NO and 5% O₂ (with He as balance) was used with a space velocity of 67,000 L/L/h. Prior to the feeding in 0.2% NO and 5% O₂ in He, the catalyst was firstly pre-treated by 1.25% C₃H₆ in He for 2 h. Scheme 1 described the experiment procedural.

2.3.2. He-Temperature programmed desorption (TPD) after NO and O₂ co-adsorption

200 mg catalyst was placed inside a quartz tube. The reactor effluent was online analysed by infrared (IR) spectroscopy (Perkin-Elmer, Spectrum One). Prior to Temperature Programmed Desorption experiments, the sample was firstly oxidised at 600 °C with 5% O₂ in He in order to remove carbon residues, e.g. adsorbed CO₂. Subsequently, the samples were exposed to the reactive gas (2000 ppm NO + 5% O₂/He balance) at 200 °C for 10 h. Afterward, the samples were outgassed in He in order to remove the weakly bound physical adsorbed NOₓ. After cooling down to 40 °C, the samples were heated up from 40 to 700 °C with a heating rate of 5 °C / min using He as the carrier gas (200 ml / min). Concentration profiles of NO, N₂O, and NO₂ in parts per million (ppm) were obtained. The IR spectrometer was calibrated with 1% NO, 1% N₂O, and (1% N₂ + 2% O₂) in He, respectively.
3.2. Catalytic testing

3.2.1. NO reduction in the absence of O2 in fixed bed reactor

Fig. 3 shows the results of exposure 0.2% NO/He over the C3H6 reduced Rh/CZ at 450 °C with a GHSV of 67,000 L/L/h. Fig. 3A shows the MS response of gasses from the exit of the reactor. m/e = 28 was observed, attributed to the formation of N2 and CO. NO was not observed during the first 460 s. A low intensity of m/e = 44 was observed, attributed to the formation of CO2. Fig. 3B shows the FT-IR spectra of the gasses from the exit of the reactor. Peaks at 2174 and 2116 cm⁻¹, attributed to CO, were observed instantly when switching to the NO gas stream. The CO peak intensity increased to the maximum at the time of 250 s and then declining. Hardly any CO formation was observed after 1500 s. A low intensity of peak at 2350 cm⁻¹, assigned to NO2, was only observed during the first 460 s. A low intensity of m/e = 28 was observed after 460 s, which was from the impurity in the NO gas bottle at the level of 1 ppm. The NO reduction experiments were recycled 4 times over the same Rh/CZ sample, as described in Scheme 1. The results could be repeated. The NO conversion showed the same reactivity.
regardless to the number of NO cycles experiment.

The same experiments were performed over the sample containing potassium. Fig. 4 shows the results of the exposure of 0.2% NO/He over the fresh Rh/K/CZ pre-treated by C₃H₆ at 450 °C with GHSV of 67,000 L/L/h. Fig. 4A shows the MS response of the gasses from the exit of the reactor. Similar to the result over Rh/CZ, m/e = 28 was observed, attributed to the formation of N₂ and CO. The CO formation was confirmed by FT-IR peaks at 2174 and 2116 cm⁻¹ (Fig. 4B). From Fig. 4C, the highest CO concentration was less than 500 ppm. Small amount of CO₂ formation was observed from the FT-IR spectra. No NO was observed during the first 750 s, followed by NO signal intensity gradually increased. The N₂O band, centred at 2235 and 2208 cm⁻¹, started to appear from the time of 500 s, arriving at a maximum level of 25 ppm (Fig. 4C).

The NO reduction experiments were additionally performed over the used Rh/K/CZ, in which the Rh/K/CZ was firstly pre-adsorbed NO during the 1st NO reduction experiment and then pre-treated by C₃H₆ during the 2nd cycle experiment, as described in Scheme 1. During the 2nd run of the NO experiment, NO started to form from t = 500 s. The NO signal increasing rate during the 2nd run of NO experiment was much steeper than that during the 1st run (Figs. 4C and 5 B). N₂O formation was observed instantly when switching over to the NO gas stream. The highest CO concentration was around 50 ppm, which was less than that during the 1st run, as shown in Fig. 4C. During the 4th NO reduction experiment, NO started to be observed from the time of 475 s onwards. The NO signal increasing rate during the 4th run of NO experiment is similar to that during the 2nd run (Figs. 4C and 5 B). N₂O was observed instantly upon NO exposure.

### 3.2.2. NO reduction in the presence of O₂ in fixed bed reactor

Fig. 6A shows the MS response during (0.2% NO + 5% O₂)/He over the C₃H₆ reduced Rh/CZ at 400 °C. Full NO conversion was observed during the first 69 s, followed by a gradual decreasing in the NO conversion. Both m/e = 28 and m/e = 44 were observed from the t = 0 s and their intensities dropped down from t = 23 s. The observation of m/e = 28 was attributed to the formation of N₂ and CO. Both CO₂ and N₂O could contribute to the MS response at m/e = 44. O₂ started to breakthrough after 5 s and became stable after 10 s.

From the FT-IR (Fig. 6B), CO and CO₂ were formed from the start of the NO flow and reached maximum production at the time of 23 s.
afterwards the CO formation dropped down. N2O was not observed during the first 69 s. 1 ppm N2O was observed after 69 s, which came from the impurity of the NO gas bottle. Therefore, the MS response of m/e = 44 was assigned to the formation of CO2. The concentrations of NO, NO2, N2O, CO, and CO2 during the (0.2% NO + 5% O2)/He gas stream were plotted and shown in Fig. 6C. NO an NO2 started to breakthrough almost at the same time (t = 69 s) and they became stable after 250 s, and hardly any CO2 was observed.

The results of NO reduction experiments over C6H6 reduced Rh/CZ were repeated during at least 4 cycles of NO experiment. The complete NO conversion time interval remained the same during the 4 cycles of NO reduction experiment, as shown in Fig. 6D.

The NO reductions in the presence of O2 were additionally performed over the fresh propene pre-reduced Rh/K/CZ and used propene reduced and followed by a NO/O2 pre-treated Rh/K/CZ. Fig. 7 shows the MS response during (0.2% NO + 5% O2)/He as stream over the C6H6 reduced Rh/K/CZ at 400 °C for the 1st run of NO experiment over fresh Rh/K/CZ. As illustrated in Fig. 7A, O2 was broken through instantly (t = 0 s) and it became stable at time of 15 s. NO showed a period of full conversion (around 340 s). From 340 s onwards, a progressive increasing of NO was observed. m/e = 28 was observed with high intensity up to 20 s, followed by a low intensity till t = 70 s. The observed m/e = 28 was assigned to CO and N2. Similarly, a high intensity of m/e = 44 was observed between 20–340 s. A constant intensity of m/e = 44 was observed between t = 20–340 s, followed by gradual decline till the end of the experiment. The observed m/e = 44 was assigned to CO2 and N2O.

Fig. 7B shows the results of the 4th cycle of NO experiment. Low intensities of m/e = 28 and m/e = 44 were observed. NO showed a shorter time interval for full conversion (around 70 s) as compared to the 1st cycle of NO experiment (340 s). From 70 s onwards, a breakthrough of NO signal was observed in MS. O2 broke through instantly (time of 0 s) and became stable at 5 s.

Fig. 8 shows the FT-IR spectra during (0.2% NO + 5% O2)/He gas stream. For the 1st cycle of NO reduction experiment (Fig. 8A), Peak at 2350 cm⁻¹, assigned to CO2, was observed from the beginning of (0.2% NO + 5% O2)/He gas stream. Similarly, peaks at 2174 and 2116 cm⁻¹, attributed to CO, were observed instantly during the (0.2% NO + 5% O2)/He gas stream. Both CO and CO2 intensity declined from the time of t = 23 s onwards. Peaks at 1908 and 1850 cm⁻¹ were observed from 340 s onwards and was assigned to NO. The rise of two bands at 1601 and 1628 cm⁻¹ from 600 s was attributed to the formation of NO2. N2O, centring at 2235 and 2208 cm⁻¹, was observed during whole (0.2% NO + 5% O2)/He gas stream exposure. Fig. 8B shows the FT-IR results of the 4th cycle of NO reduction experiment. As compared to Fig. 8A, less CO2 and CO were formed during the (0.2% NO + 5% O2)/He gas stream. In addition, NO and NO2 started to rise from the time of 77 s and 200 s, respectively, in the 4th cycles.

Fig. 9 shows the NO (Fig. 9A) and NO2 (Fig. 9B) breakthrough time during (0.2% NO + 5% O2)/He gas stream. The full NO conversion time interval dropped from 340 s at 1st NO run to 45 s at 6th NO experiment cycle. The formation of NO2 started from 600 s at 1st NO run experiment cycle. The formation of NO2 appeared earlier when increasing the cycles.

### 3.2.3. NOx-TPD and in-situ DRIFTS

The NOx-TPD experiments were carried out over the Rh/CZ and Rh/K/CZ. Fig. 10A shows the result of NOx-TPD in He. For Rh/CZ, two NOx desorption regions were observed, centred at 250 and 400 °C, respectively. No NOx desorption were observed after 450 °C. For Rh/K/CZ, a wide NOx desorption temperature range was observed, especially, significant amount of NOx desorption was observed above 600 °C.
Fig. 4. Gases evolution from the exit of the reactor: (A) MS signal; (B) FT-IR spectra; (C) the quantitative data from (B). The experiments were performed at the condition of 0.2% NO/He gas stream over fresh Rh/K/CZ pre-treated by C₃H₆ at 450 °C, GHSV of 67,000 L/L/h.

Fig. 5. Gases evolution from the exit of the reactor: (A) and (C) FT-IR spectra; (B) and (D) are the quantitative data from (A) and (C), respectively. (A) and (C) were obtained during the 2nd and 4th NO experiment, respectively. Both experiments were performed at the conditions of 0.2% NO/He gas stream over an used Rh/K/CZ pre-treated by C₃H₆ at 450 °C, GHSV of 67,000 L/L/h.
The chemical structure and stability of adsorbed NOx species were studied by in-situ DRIFTS. A DRIFT spectrum was firstly recorded in Ar after 30 min of reaction in the 15NO/Ar gas mixture. The reaction feed stream was then switched to a C3H6/Ar gas mixture and DRIFT spectra were continuously recorded. Fig. 10B shows the recorded spectra. The pre-nitrated Rh/K/CZ sample showed peaks at 1341, 1212, and 1542 cm$^{-1}$. The IR bands centred at 1542 cm$^{-1}$ corresponded to the $\nu$NO$_2$(as), $\nu$NO$_2$(sym), and $\nu$ N–O vibrational modes of bidentate nitrate formed on the Rh/K/CZ. The band at 1212 cm$^{-1}$ could be assigned to asymmetric ($\nu_{as}$) and symmetric ($\nu_{sym}$) NO stretching mode of the chelating nitrite (NO$_2^-$). The band at 1434 cm$^{-1}$ was assigned to adsorbed nitrosyl (NO$_2^+$). The assignments of the various adsorbed NOx species were based on well-documented literature data [24]. When switching to the C3H6/Ar gas stream, the band at 1212 cm$^{-1}$ vanished after 9 min, accomplishing with three new peaks at the position of 2143, 1971 cm$^{-1}$, and 1420. The peak at 1420 cm$^{-1}$ was assigned to the carbonate [25]. The peak at 1542 cm$^{-1}$ remained constant while the peak at 1341 cm$^{-1}$ slightly decreased. The peaks at 2143 and 1971 cm$^{-1}$ did not show up over the Rh/CZ sample, as shown in Fig. 10D. In order to identify the species of the peaks at 2143 and 1971 cm$^{-1}$, an isotope switching experiment were performed. The experimental protocol was shown in the Fig. 10C. Over the fresh Rh/K/CZ sample in air, only carbonate species were observed in the region of 1420 cm$^{-1}$. When switching to 14NO/Ar gas, peaks at the position of 1542, 1341, and 1222 cm$^{-1}$ were observed, which were assigned to bidentate nitrate, nitrosyl, and chelating nitrite. The peaks at 2160 and 2036 cm$^{-1}$ were observed during C3H6/Ar gas stream while they disappeared when switching to 15NO/Ar gas stream. Chelating nitrite (15NO$_2^-$), peak at 1212 cm$^{-1}$, was observed during 15NO/Ar gas stream, which disappeared when switching to C3H6/Ar. Peaks at 2143 and

Fig. 6. (A) MS signal, (B) FT-IR spectra; and (C) the concentration of gasses during 0.2% NO + 5% O$_2$ in He flow over C$_3$H$_6$ reduced Rh/CZ at 400 °C; (D) total NO conversion time interval versus the number of NO cycles experiment.

Fig. 7. Gasses evolution during exposure of Rh/K/CZ C$_3$H$_6$ reduced at 400 °C to a 0.2% NO + 5% O$_2$ containing He flow at a GHSV of 67.000 l/l/h at 400 °C. (A) 1st cycle of NO and (B) 4th cycle of NO experiments.
1971 cm$^{-1}$ were appeared, which were the same species as peaks at 2160 and 2036 cm$^{-1}$ due to the isotope shift. Neither the peaks at 2160 and 2036 cm$^{-1}$ nor at 2143 and 1971 cm$^{-1}$ were observed during the H$_2$ gas stream over pre-nitrated Rh/K/CZ. Therefore, the peaks of 2143 and 1971 cm$^{-1}$ (2160 and 2036 cm$^{-1}$) were confirmed containing N and C, which could be assigned to the surface CNO or NC species [26,27].

### 3.2.4. H$_2$ and C$_3$H$_6$ pulses over pre-oxidised and $^{15}$NO pre-nitrated Rh/K/CZ samples in TAP

Fig. 11A shows the results of the H$_2$ pulse over the pre-oxidised fresh Rh/K/CZ sample at 400 °C. The pulse of H$_2$ led to the H$_2$O formation. H$_2$ experienced full conversion and started to breakthrough after pulse number 300. For the pre-nitrated Rh/K/CZ, as shown in Fig. 11B, the pulse of H$_2$ firstly led to the formation of NO, H$_2$O, and $^{15}$NH$_3$. The N$_2$ formation started from pulse number 100 and disappeared at pulse number 400. H$_2$ did not show a full conversion from the beginning of H$_2$ pulse. The H$_2$ conversion increased from pulse number 100 till full conversion at the pulse number of 300, subsequently, its conversion gradually declined.

The reduction of $^{15}$NO pre-nitrated Rh/K/CZ was also performed by pulsing C$_3$H$_6$. As shown in Fig. 12, C$_3$H$_6$ showed 50% conversion at the beginning of the C$_3$H$_6$ pulse, followed by a C$_3$H$_6$ conversion increase to 100% conversion at pulse number 40. C$_3$H$_6$ showed full conversion between pulse number 40 and 200, followed by a C$_3$H$_6$ conversion decay. $^{15}$N$_2$, H$_2$O, and $^{15}$NH$_3$ were formed during the first 100 C$_3$H$_6$ pulses. $^{15}$NO and $^{15}$N$_2$ formation diminished at the end of 100 C$_3$H$_6$ pulses and subsequently the C$_3$H$_6$ oxidation reaction led to the formation of CO$_2$, CO, and H$_2$.

### 3.2.5. $^{15}$N$_2$ response comparison during $^{15}$NO pulse over H$_2$ reduced Rh/CZ and Rh/K/CZ

Fig. 13A shows the $^{15}$N$_2$ response during the first 90 $^{15}$NO pulses over H$_2$ pre-reduced fresh Rh/K/CZ, where all the NO was converted, i.e., NO signal did not have a response. The $^{15}$N$_2$ showed a sharp response at the first $^{15}$NO pulse; then, the response became broader with the intensity decreasing during the subsequent $^{15}$NO pulses. Additionally, the N$_2$ peak was at $t = 0.056$ s during the 1st $^{15}$NO injection, and the peak shifted to $t = 0.126$ s at the 90th $^{15}$NO injection. $^{15}$N$_2$ peak shifted to a later time during NO pulse sequence, indicating the slower and slower $^{15}$N$_2$ formation rate with $^{15}$NO pulses. The pulses of $^{15}$NO would lead to the Rh/K/CZ was nitrated. After the $^{15}$NO pulses, C$_3$H$_6$ was used as a reductant to reduce the nitrated Rh/K/CZ. Both Fig. 13B and C show the $^{15}$N$_2$ responses during the $^{15}$NO pulses over a C$_3$H$_6$ pre-reduced nitrated Rh/K/CZ sample at the 2nd and 3rd $^{15}$NO pulsing cycles, respectively. Both Fig. 13B and C show that the N$_2$ response became broader with pulse number, indicating that $^{15}$N$_2$ formation rate became slower and slower. In contrast, over the Rh/CZ sample, $^{15}$N$_2$ responses hardly changed during the $^{15}$NO pulses as the indicated $^{15}$NO pulses number.

### 4. Discussion

Potassium (or barium) is a common ingredient in NSR catalyst, acting as the NOx storage component during the fuel-lean stage of the engine operation. The general problems of NSR technology are narrow operating temperature window, low space velocity, N$_2$O formation, NH$_3$ formation, and NOx slip. The problems are mainly caused by the NOx storage and release materials. The Di-Air system showed a broader
operating temperature window (up to 800 °C) and higher space velocity (up to 120,000 L/L/h), where the storage component hardly can have a role in the NOx reduction. From our previous work, we have found that the oxygen anion vacancies in ceria are responsible for the decomposition of NO into N2, thereby, re-oxidising these defect centres. The delayed oxidation of the carbon deposits by the oxygen species originating from the lattice oxygen will in practice maintain a reduced surface state of the ceria during the fuel-lean conditions. These carbon deposits (created from the fuel injection), therefore, can be seen as a stored reductant with a delayed (buffer) function. The loading of Rh (noble metal) is mainly to lower the fuel activation temperature, to lower the ceria support reduction temperature, and to accelerate N2 formation rate. Although potassium and barium are ingredients in the Di-Air catalyst composition, it is necessary to investigate the role of these NOx storage materials. What will be the exact role of these components and what will be the consequence by the addition. The discussion will be focused on the comparison between catalysts with and without potassium loading from the perspectives of catalyst performance stability, NO slip, NH3- and N2O- formation and in the end the effectiveness of the NO conversion into the selectivity of the N2 formation.

Fig. 10. (A) NOx-TPD in He recorded after exposure to (0.5% NO + 5%O2)/He at 200 °C over Rh/CZ and Rh/K/CZ, in-situ Drift spectra during C3H6/Ar over 15NO pre-nitrated (B) Rh/K/CZ and (D) 15NO Rh/CZ. (C) isotope gas switching experiment over Rh/K/CZ.

Fig. 11. H2 over NO pre-oxidised (A) and 15NO pre-nitrated Rh/K/CZ at 450 °C, Ar was used as internal standard.

Fig. 12. C3H6 over 15NO pre-nitrated Rh/K/CZ at 450 °C, Ne was used as internal standard.
4.1. The effect of potassium on the stability of catalyst performance

C\textsubscript{3}H\textsubscript{6} was used to reduce the catalyst to mimic the consequence of fuel injection in the Di-Air system [14]. The Rh lowered the C\textsubscript{3}H\textsubscript{6} oxidation temperature over the CZ [14]. At the temperature below 450 °C, the reduction of CZ support was not favoured [14]. By loading Rh, the reduction of CZ by C\textsubscript{3}H\textsubscript{6} at 450 °C was obtained around 3 hypothetical reduced CZ layers with additional carbon deposition.

The reactivity of NO reduction was investigated in a flow reactor under atmospheric pressure. Prior to the NO reduction experiments, 1.25% C\textsubscript{3}H\textsubscript{6}/He was used to pre-treat the Rh/K/CZ and Rh/CZ at 450 °C for 2 h before each cycle of NO experiments, as shown in the experimental scheme (Scheme 1). The pre-treatment by C\textsubscript{3}H\textsubscript{6} led to the reduction of CZ support and deposition of carbon on the catalyst surface [16]. The H\textsubscript{2}-TPR experiment (Fig. 2B) showed significant changes in reduction peak position between Rh/CZ and Rh/K/CZ. Therefore, the addition of potassium hardly changed the lattice oxygen reactivity. The amount of H\textsubscript{2} consumption over Rh/K/CZ was almost two times of that over Rh/CZ. For K-containing NSR catalyst, several kinds of K species can be existed in the form of K\textsubscript{2}O, KOH, and K\textsubscript{2}CO\textsubscript{3} [28]. The K\textsubscript{2}CO\textsubscript{3} could be reduced to CO\textsubscript{2} and H\textsubscript{2}O at lower temperature, around 200 °C, initiated by surface hydroxyl groups [29,30]. Therefore, separately from the contribution of the reduction of CZ support, the H\textsubscript{2} consumption was accounted for the reduction of surface carbonate.

The results of Fig. 3A showed the reduction of NO into N\textsubscript{2} over the C\textsubscript{3}H\textsubscript{6} pre-reduced Rh/CZ. The FT-IR spectra (Fig. 3B) confirmed the formation of CO and CO\textsubscript{2} and excluded the formation of NO\textsubscript{2} and N\textsubscript{2}O during the first 460 s, where NO was completely converted. The conversion of NO into N\textsubscript{2} was confirmed by the \textsuperscript{15}NO experiment, as reported in our previous work [17].

The oxygen vacancies were the catalytic sites for the NO reduction into N\textsubscript{2}. The reduction of NO resulted in a re-oxidation of the reduced Rh/CZ. Subsequently, the oxygen from the (re-oxidised) CZ lattice was further reacted with the deposited carbon to form CO and CO\textsubscript{2}, thus additional oxygen vacancies were created and the new oxygen vacancies were used for additional NO reduction. NO appeared in the exit exhaust stream after 460 s. In the time frame from 450 s till 1500 s, the rest of carbon deposited was oxidised. From 1500 s onwards NO was partially converted into N\textsubscript{2}O. As shown in Fig. 3D, the complete NO conversion time interval remained the same during the 4 cycles and indicated the high stability of Rh/CZ sample during the C\textsubscript{3}H\textsubscript{6} pre-treatment and NO reduction process.

In the presence of potassium the overall product evolution profile for the C\textsubscript{3}H\textsubscript{6} reduced Rh/K/CZ catalyst during the NO reduction was similar to that of Rh/CZ over fresh sample. This was due to the oxygen vacancies playing a role in NO reduction. The NO, however, started to break through at t = 750 s (Fig. 4), which was 290 s longer than the NO over Rh/CZ. The extended duration of the NO conversion was due to the presence of potassium, which could adsorb additional NO as potassium nitrite and nitrate [31]. The difference between the fresh and the used Rh/K/CZ was significant. The NO breakthrough time dropped from 750 s for the 1st cycle to 450 s for the 4th cycle (Fig. 5). Potassium was common ingredient in the NSR system to store NO\textsubscript{x} during the fuel lean stage.

For the Rh/K/CZ catalyst the fresh and pre-nitrated surface affected the C\textsubscript{3}H\textsubscript{6} reactivity. Apparently, less CO was formed during the NO gas stream over the used Rh/K/CZ sample (Fig. 4 and 5). The less CO formation indicated the low reactivity of C\textsubscript{3}H\textsubscript{6} for a recycled ‘potassium’ catalyst. The BET surface of Rh/K/CZ before and after the reaction remained similar, therefore, the reactivity difference between the fresh
and used Rh/K/CZ was ascribed to the nitrate or nitrite formation. The formation of nitrate or nitrite was confirmed by the in-situ Drift as shown in Fig. 10B. A long NO admission time led to nitrites and slowly transformation into nitrites. The formation of nitrate and nitrite species stabilised the CZ lattice oxygen reducibility, which caused to a low C3H6 reactivity. The addition of alkali metals into V2O5/CeO2 catalysts led also to the deactivation for the selective catalytic reduction of NOx with NH3 in the SCR reaction. Potassium decreased the surface acidity and lowered the reducibility of the ceria and V2O5, both suppressing the NH3 adsorption and NH4 activity for the SCR reaction [32]. Therefore, the addition of potassium into the Rh/CZ system will lower the C3H6 reactivity by the stabilisation of the ceria lattice oxygen.

In our TAP study, different reductant reactivity’s over pre-oxidised and pre-nitrated Rh/K/CZ were observed. The pulsing of even the most active reductant, H2, showed different reactivity over the fresh and pre-nitrated Rh/K/CZ samples. H2 showed a full conversion to H2O over the oxidised Rh/K/CZ sample, but around 80% conversion over the pre-nitrated sample (Fig. 11). The presence of nitrate/nitrite inhibited the CZ support reduction reactivity.

In the presence of gas-phase oxygen, NO transformed in nitrate-like species over the potassium sample [33]. At the temperature of 450 °C, a stronger stability of nitrate species in the form of polydentate species was formed [34]. The formation of such stable species during a long NO exposure inhibited the reaction between C3H6 and Rh/CZ. As shown in Fig. 9, the NO started to breakthrough from 45 s at the 4th cycle experiment, as compared to 340 s at the 1st cycle experiment. Additionally, the NO2 breakthrough time dropped. With the cycles of (NO + O2) experiments, the NO adsorption on the potassium led to a more stable polydentate nitrate species that deteriorated the reversible NO2 storage capacity. More importantly, unlike the Rh/K/CZ, the NO breakdown for Rh/CZ remained the same temperature during the whole NO exposure cycles (69 s), as shown in Fig. 6D. The difference behaviours in the NO breakthrough time (Figs. 6D and 9) indicated clearly that the potassium was the component for the deactivation of Rh/K/CZ in NO reactivity in cycles of NO reduction experiment. To validate this conclusion, the stability of stored NOx over Rh/K/CZ was studied both by NOx-TPD in He (Fig. 10A) and under reductant gas stream (Fig. 10B and C). The NOx-TPD showed that a broad temperature window of NOx desorption till 700 °C. The desorbed NOx up to 380 °C was likely related to the decomposition of nitrates, whereas those desorption species above 380 °C were more related to the desorption of nitrates [35]. During this temperature ramp, the nitrite species also transformed into the nitrate species. Apparently, significant amount of the adsorbed NOx was strongly adhesive to the Rh/K/CZ, which required temperature above 700 °C to completely regenerate the catalyst to be free of adsorbed NOx. Additionally, in-situ Drift experiments were performed to investigate the thermal stability of adsorbed NOx in the presence of reductant. As shown in Fig. 10B, the exposure of pre-nitrated Rh/K/CZ under C3H6 environment led to the formation of peaks at 2143 and 1971 cm⁻¹, which was further confirmed in Fig. 10C that these two peaks contained both N and H atoms. During the C3H6 exposure, only the chelating nitrite peaks disappeared. The in-situ Drift experiments demonstrated that C3H6 was not able to completely regenerate the N storage over the surface at the temperature of 450 °C.

H2 and CO were regarded to have a relatively high nitrate reduction efficiency compared to that of C3H6 and C2H4 [36]. In the Di-Air system, fuel was used as reductant and was directly injected over the catalyst. The reaction between C3H6 and pre-nitrated Rh/K/CZ showed similar reaction step. As shown in Fig. 12, the pulses of C3H6 firstly led to the formation of H2O, 15NH3, 15N2, and 15NO. The formation of CO2 was secondly followed by the formation of H2 and CO from pulse number 90 indicated the participation of CZ lattice oxygen in C2H4 complete reaction and cracking reaction. Therefore, C3H6 needed to react with the adsorbed nitrate and nitrite species before the CZ lattice oxygen could participate in the C2H4 reaction. The low reactivity of hydrocarbon towards the nitrate(s) would eventually affect the life time of the catalyst.

4.2. The effect on potassium on the NH3 formation and NO slip

Regarding the ammonia formation, ammonia evolution occurred after introducing the H2 and hydrocarbons over the NSR catalyst. The formation of ammonia could act as reductant to reduce NOx into N2, especially for the SCR reaction of NOx with NH3. It was well-known that both the NOx slip and NH3 formation were main hurdles to the tackle in the NSR system. Therefore, a combined NSR (upstream) and SCR (downstream) DeNOx system was developed, aiming to solve the NH3 and NOx challenges [37].

The pulsing of H2 over a 15NO pre-nitrated Rh/K/CZ led to an initial reaction between H2 and surface nitrate/nitrite with formation of H2O, 15NH3, 15N2, and 15NO (Fig. 11B). The 15N2 and 15NO formation diminished after the pulse number 400. The reduction of CZ support led to the water formation after pulse number 400. Therefore, the reduction of pre-nitrated Rh/K/CZ by H2 firstly led to the reduction of surface absorbed nitrite and subsequently to the CZ support reduction. The formation of ammonia depended on the local coverage of chemisorbed N and H atoms [38]. The introduction of H2 initially led to the NOx slip that was due to the fast NOx desorption at the temperature of 450 °C. The formation of ammonia favoured when the NOx desorption rate dropped down (from pulse number 80 to 800) and the concentration of surface H species increased. In our TAP experiment, the introduction of H2 firstly led to the 15NH3 formation and some NO slip. The reduction of NOx into N2 started from pulse number 80. 15N2 was formed during the pulse number 80 to 400, which could be due to the decomposition of NOx over the reduced site of Rh/K/CZ or the reduction of NOx by the formed ammonia. Similarly, the introduction of C3H6 over the pre-nitrated Rh/K/CZ also led to the 15NO slip and 15NH3 formation (Fig. 12).

4.3. The effect of potassium on the N2O formation and N2 formation rate

N2O formation has a large impact the NO reduction over a NSR catalyst. In our study, N2O formation was only observed over the potassium containing samples.

For Rh/CZ, during the full NO conversion time interval (t = 0–460 s), neither N2 and NO was formed (Fig. 3). The observation of m/e = 28 indicated the reduction of NO into N2. Even 1 ppm N2O coming from the impurity in of NO gas bottle was reduced. Therefore, a reduced ceria, acting as ‘oxygen black hole’ [16], selectively reduced NO and traces of N2O into N2.

When the Rh/CZ was reduced, most probably associated with an oxygen vacancy linked to a Ce3+ cation. The adsorption of NO over the reduced site of Ce led to NO dissociation, as described in Eq. (1), and recombination of Nads into N2, as described in Eq. (2).

\[ \text{NO} + \text{Ce}^{3+} \rightarrow \text{Ce}^{4+} + O + \text{Nads} \]  
\[ \text{Nads} + \text{Nads} \rightarrow \text{N}_2 \] (1)

Reading the N2O formation during the NO reduction process, two steps were proposed for the formation of N2O over Pt and Rh in the literature [39]:

\[ \text{NO} + 2\text{N} \rightarrow \text{NM} + \text{N} + \text{N} \rightarrow \text{O} \]  
\[ \text{N} + \text{N} + \text{O} \rightarrow \text{N}_2 + \text{N} \] (3)

Over the Rh/CeO2-ZrO2 system hardly any N2O formation was observed [40]. In the presence of noble metal, the combination of Nads into N2 step was faster than the reaction between NO and Nads.

For the fresh Rh/K/CZ, a level of 25 ppm of N2O was, however, observed from t = 500 s, where a full NO conversion was observed (Fig. 4). Over the used Rh/K/CZ sample, N2O was instantly formed during the NO exposure (Fig. 5). When an excess of oxygen vacancies was available over the nitrate free Rh/K/CZ catalyst, e.g., t < 500 s in Fig. 4, NO was selectively reduced into N2 and no N2O was observed.
The decreasing of the CO formation from t = 400 s onwards indicated the depletion of the deposited carbon over the Rh/K/CZ sample and the largely (re-)oxidised of CZ support. N₂O started to be formed, when CO intensity largely decreased, i.e., N₂O was formed over a less reduced Rh/K/CZ sample. This hypothesis/observation was in line with the observation over the used Rh/K/CZ, as shown in Fig. 5. The difference between the fresh and used Rh/K/CZ sample was the adsorption of NO over the K on the used Rh/K/CZ, which had a significant influence on the C₃H₆ reactivity and the CZ support reduction, as described in Section 4.1. To sum up, the addition of potassium into the CZ catalyst clearly led to a significant N₂O formation.

For a NSR catalyst, the stored NOₓ over potassium or barium component was supposed to be converted into N₂, but N₂O was commonly observed. N₂O was formed during the lean/rich switching transient. The formation of N₂O during the rich fuel conditions was attributed to either the incomplete reduced catalyst sites or the reaction between reductants and intermediates. While the N₂O formation during the rich to lean switching originated from the oxidation of the reduction intermediates remaining on the surface, which included adsorbed ammonia, NH₄NO₃, or isocyanates. In our experimental protocol, lean/rich switching transients were not really existed and the N₂O formation was also not only observed during the switching of reaction conditions. Therefore, the formation of N₂O could not completely be attributed to the decomposition of ammonia, NH₄NO₃, or isocyanates.

Different reaction rates of NO dissociation and N_ads combination into N₂ might explain the N₂O formation by the addition of potassium to Rh/CZ catalyst, as shown in Eqs. (1–4). N₂O can be formed via recombination of NO adsorption over the surface, and with N left over the surface. Therefore, the relative reaction rate among the N recombination into N₂, surface concentration of NO, and NO dissociation rate are critical to the N₂O formation. In order to understand the process of the NO reduction over the potassium containing sample, NO pulses experiments over a H₂ reduced Rh/CZ and Rh/K/CZ were performed. The N₂ response during the 1⁵NO pulses can provide information on the NO reduction process.

The results of TAP experiment by pulsing ¹⁵NO over a H₂ reduced Rh/CZ showed that a fast N species (re)combination into N₂. There was hardly N-species left over the Rh/CZ surface during each NO injection. However, the injection of ¹⁵NO over a H₂ reduced Rh/K/CZ led to a slower N₂ formation rate as compared to that over the Rh/CZ sample (Fig. 13). The N₂ formation slowed down during the ¹⁵NO pulses. Since no ¹⁵NO was observed by the MS during the ¹⁴NO injection, the slower N₂ formation rate was due to slow N-species (re)combination process. Therefore, when the reaction was performed under the atmosphere pressure and under high space velocity, the adsorbed N-species combined with the NO to form N₂O over the potassium containing catalyst.

5. Conclusions

To summarise the addition of potassium into the Rh/CZ catalyst deteriorated performance of the catalysts. Over a clean Rh/K/CZ catalyst, the initial NO conversion performance, including the NO reduction and storage, was determined both by the rate of NOₓ storage capacity and the oxygen vacancies capacity. The NOₓ stored over Rh/K/CZ in the previous lean phase could not be regenerated sufficiently upon C₃H₆ exposure and the levels of stored (unreduced) NOₓ gradually increased from one cycle to the next, resulting in deteriorating performance of the potassium containing catalysts. Besides, the well-known problems of NOₓ slip and NH₃ formation over the NSR the addition of potassium led to the NOₓ formation and slowed down the reaction rate of N_ads combination into N₂. It is, therefore, recommended for an efficient Di-Air NOₓ abatement technology to avoid the addition of potassium to the noble metal ceria (Rh/CZ) catalyst system.

Declaration of Competing Interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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