Non-thermal plasma-assisted NO_x storage and reduction over cobalt-containing LNT catalysts

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Abstract

Based on their high NO oxidation capacity (NOC) and NO_x storage capacity (NSC), cobalt-containing LNT catalysts of the type Co/Ba/Al and Pd/Co/Ba/Al were tested under NO_x storage-reduction (NSR) conditions, as well as in an H₂-plasma assisted NSR process. For comparison purposes, a traditional Pt/Ba/Al catalyst was tested under the same conditions. The Co/Ba/Al catalyst exhibited similar catalytic properties to those of the Pt/Ba/Al catalyst when an H₂-plasma was employed in the rich phase to assist reduction of the stored NO_x. However, the NO_x removal efficiency was greatly depressed by the presence of H₂O and CO₂ in the feed. Notably, the addition of Pd to the Co/Ba/Al sample greatly lessened the inhibiting effects of H₂O and CO₂ on plasma-assisted cycle-averaged NO_x conversion, this being due to the excellent NO_x storage performance of the Pd/Co/Ba/Al sample even in the presence of H₂O and CO₂. The results of the present study show that by combining the high NO_x storage capacity of Pd/Co/Ba/Al in the lean phase with non-thermal plasma-assisted activation of the reductant in the rich phase, high NO_x conversion can be obtained over a broad temperature window of 150 - 350°C.

Keywords: cobalt; palladium; NO_x storage-reduction; Lean NO_x trap; non-thermal plasma

1. Introduction

Lean-burn engines are becoming increasingly popular due to their higher fuel efficiency and lower CO₂ emissions compared to stoichiometric gasoline engines. However, under lean-burn conditions, nitrogen oxide (NO_x) exhaust emissions cannot be efficiently reduced over classical three-way catalysts due to the presence of excess O₂ [1]. In order to solve this problem, Toyota developed NO_x storage and reduction (NSR) technology (otherwise known as lean NO_x trap (LNT) catalysts) in the mid-1990s [2]. LNT catalysts work under cyclic conditions of fuel-lean and fuel-rich environments. Under lean exhaust conditions, when oxygen is in excess, NO_x is adsorbed on the catalyst; under rich conditions, when an excess of reductant is present, NO_x reduction takes place. Platinum and barium deposited on γ -Al₂O₃ (Pt/Ba/Al catalyst) is the most commonly studied model composition for NO_x storage and reduction catalysis. Pt/Ba/Al exhibits good catalytic performance at temperatures higher than 300°C due to the strong surface basicity of BaO, which imparts relatively high thermal stability to the nitrates formed [3]. However, the low temperature activity of LNT catalysts is especially important for light duty diesel applications, typical engine-out temperatures in the FTP-75 (The Federal Test Procedure, commonly known as FTP-75 for the city driving cycle, are a series of tests defined by the US Environmental Protection Agency (EPA) to measure tailpipe emissions and fuel economy of passenger cars (excluding light trucks and heavy-duty vehicles)) being about 180-350°C.

In our previous study, we proposed a non-thermal plasma (NTP) assisted NO_x storage and reduction process on a LaMn_{0.9}Fe_{0.1}O₃ perovskite, combining the high NO_x storage capacity of the perovskite with non-thermal plasma-assisted activation of H₂. Using this approach, high NO_x

conversions were achieved over the $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ catalyst [4]. Aside from perovskites, a number of simple transition metal oxides with strong oxidation ability and low expense have attracted attention for LNT applications, especially cobalt oxides [5, 6]. Wang et al. [7] found that the addition of cobalt led to high NO oxidation activity for a Pt/Ba/Al catalyst, and accelerated nitrite/nitrate formation on Ba sites. Nam [8] and Kim et al. [9] also found that cobalt-containing catalysts had higher NO_x storage capacity than that of cobalt-free counterparts. In addition, Vijay et al. found that, similar to Pt, the addition of Co to Ba catalysts enhances the nitrite to nitrate transition rate and also increases the overall formation of nitrates. Therefore, the promotional effect shown by Co is the result of the combination of increased NO to NO_2 oxidation activity and improved NO_2 spillover to the Ba storage sites [10-12].

In the present study, cobalt and barium deposited on $\gamma\text{-Al}_2\text{O}_3$ (Co/Ba/Al catalyst) – without added noble metals – was investigated for application in LNT catalysis, based on its high NO_x storage capacity. Although Co/Ba/Al possesses a higher NO_x storage capacity than Pt/Ba/Al, it displays a relatively poor NO_x reduction efficiency in fuel-rich atmospheres compared with commercial Pt-based LNT catalysts. In order to overcome this problem, we attempted to employ a non-thermal plasma (NTP) to facilitate rich-phase regeneration of the catalyst [4, 13-16]. By employing an H_2 -plasma in the rich phase, the NO_x conversion is greatly improved over the Co/Ba/Al catalyst, especially in the low temperature region ($< 300^\circ\text{C}$) [4, 17]. These results indicate that the use of an H_2 -plasma in the rich phase is an effective way to regenerate the cobalt-containing catalyst, this being the rate limiting step [4]. However, when CO_2 and H_2O are present in the feed gas, the catalytic performance of Co/Ba/Al catalyst is greatly decreased, even in an H_2 -plasma assisted NSR process. Notably, this dilemma can be solved by the addition of Pd. Therefore, in the present

study, Co/Ba/Al and Pd/Co/Ba/Al catalysts were prepared and characterized, and their capacities for NO oxidation and NO_x storage were compared. In addition, their catalytic activities during typical NSR cycling as well as in H₂-plasma assisted NSR were studied in the presence and absence of H₂O and CO₂.

2. Experimental

2.1. Catalyst preparation

Catalyst samples were prepared by incipient wetness impregnation. Pd/Co/Ba/Al was prepared by the following method: the γ -Al₂O₃ support was impregnated with aqueous Ba(O₂CCH₃)₂, followed by drying and calcination at 500°C in air, after which the product was impregnated with aqueous Co(NO₃)₂, dried and calcined at 500°C in air. The resulting solid was impregnated with aqueous palladium nitrate (Pd(NO₃)₂·2H₂O dissolved in 0.1 mol/L nitric acid), dried and further calcined at 500°C for 5 h. Co/Ba/Al was similarly prepared but with omission of the palladium nitrate impregnation step. The Pt/Ba/Al reference catalyst was prepared by the incipient wetness method according to a literature procedure [4]. The target Pt or Pd, Co and Ba loadings were 1 wt.%, 5 wt.% and 10 wt.%, respectively.

2.2. Catalyst characterization

Surface area analysis was performed according to the BET method by nitrogen adsorption at -196°C using a JW-BK122W system. Prior to the measurements catalyst samples were outgassed overnight at 160°C under vacuum. Transmission electron microscopy (TEM) images of the catalysts were obtained on a JEOL JEM-2000 (EX Japan) microscope operated at 120 kV. Powder X-ray

diffraction (XRD) measurements were performed on an X-ray diffractometer (Rigaku D-Max Rotaflex) using Cu K α radiation. The actual metal content in the catalysts was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 2000DV). X-ray photoelectron spectroscopic (XPS) measurements were conducted using an Al K α source operated at 10 kV and 15 mA. Binding energies were corrected for charging effects by referencing them to adventitious carbon (284.6 eV).

2.3. NSC and NOC experiments

NO_x storage capacity (NSC) and NO oxidation capacity (NOC) experiments were performed in a microreactor using a chemiluminescence NO_x analyzer (Ecotech ML9841AS) as the detector. Prior to both sets of measurements, the catalyst (500 mg) was pretreated at 500°C in flowing 1% H₂/Ar for 1 h. NSC and NOC measurements were performed by exposing the catalyst to flowing gas containing 500 ppm NO, 8% O₂, with or without 2% H₂O and 2% CO₂ present, and balance N₂. The storage time was 10 min for the NSC experiments. NOC was measured when steady state had been achieved, i.e., when the catalyst was completely saturated with NO_x (typically requiring 2-3 h). NSC and NOC experiments were operated at a space velocity (WHSV) of 48,000 ml·g_{cat}⁻¹·h⁻¹. The NSC and NOC were calculated according to the following formulae:

$$\text{NSC} = \frac{\int_0^{t_s} (\text{NO}_{x, \text{in}} - \text{NO}_{x, \text{out}}) dt}{m_{\text{cat}}} \quad (1)$$

where t_s is the storage time (s) and m_{cat} is the mass of the catalyst (g).

$$\text{NOC} = \frac{\text{NO}_{2, \text{out}}}{\text{NO}_{\text{in}}} \times 100\% \quad (2)$$

2.4. NO_x-TPD and H₂-TPSR

The stability of adsorbed NO_x species was evaluated by means of NO_x-TPD measurements using 150 mg of catalyst contained in a microreactor. Each catalyst sample was first pretreated at 500°C for 60 min in flowing 1% H₂/Ar and then cooled to 200°C in flowing Ar. NO_x adsorption was carried out for 50 min at 200°C using feed gas containing 500 ppm NO, 8% O₂ and balance Ar, with or without 2% H₂O and 2% CO₂ present. After flushing the catalyst with Ar at 200°C for 30 min, the temperature was increased to 700°C at a rate of 10°C/min in flowing Ar. H₂-TPSR was performed after NO_x adsorption at 300°C for 50 min in a flowing gas mixture containing 2% H₂ and balance Ar. Samples were heated from room temperature to 500°C at a rate of 10°C /min. Effluent gases were analyzed on-line using a mass spectrometer (Pfeiffer Vacuum GSD 301). All flow conditions were operated at a space velocity (WHSV) of 48,000 ml·g_{cat}⁻¹·h⁻¹.

2.5. Catalyst evaluation

Catalyst evaluation was performed in the dielectric-barrier discharge (DBD) reactor as described in the literature [4], loaded with ca. 500 mg of catalyst particles (20-40 mesh). The high voltage was applied with a high-voltage generator (CTP-2000 K, Suman Electronics) working at about 40 kHz. The power was measured by voltage-charge Lissajous figures recorded with a 100 MHz digital oscilloscope (TDS 2012, Tektronix). Effluent gases were analyzed on-line using a mass spectrometer (Pfeiffer Vacuum GSD 301) and a specific FTIR (Sick Maihak S710). All flow conditions were operated at a space velocity (WHSV) of 48,000 ml·g_{cat}⁻¹·h⁻¹. Before each experiment the catalyst was pretreated in 1% H₂/Ar flow at 500°C for 1 h. Following pre-treatment, the catalyst was cooled to the measurement temperature, after which lean-rich cycling was performed until the

catalyst reached a cycle-average steady state. The NO_x concentration was averaged over 5 cycles to give a mean conversion according to the following formula:

$$\text{NO}_x \text{ conversion} = \frac{\int_0^t (\text{NO}_{x, \text{in}} - \text{NO}_{x, \text{out}}) dt}{\int_0^t \text{NO}_{x, \text{in}} dt} \times 100\% \quad (3)$$

The cycling parameters and gas composition used for the cycling experiments are summarized in Table 1.

3. Results and discussion

3.1. Catalyst characterization

X-ray diffraction (XRD) analysis (Fig. 1) showed that the main phases present in Pt/Ba/Al, Co/Ba/Al₂O₃ and Pd/Co/Ba/Al samples were BaCO₃ (JCPDS No. 45-1471) and γ -Al₂O₃ (JCPDS No. 47-1770), thereby confirming the decomposition of Ba(O₂CCH₃)₂ into crystalline BaCO₃ during catalyst calcination. The characteristic reflections of Pt or Pd and PtO_x or PdO_x were not observed due to the low concentration of Pt or Pd in the Pt/Ba/Al and Pd/Co/Ba/Al catalysts and/or the small size of the Pt or Pd particles. In the case of Co/Ba/Al, besides the major BaCO₃ and Al₂O₃ phases, trace amounts of the Co₂O₃ phase ($2\theta = 38.6$ and 58.7° , JPCDS No. 02-0770) and Co₃O₄ phase ($2\theta = 36.8$ and 65.2° , JPCDS No. 74-2120) were observed in the XRD patterns. For Pd/Co/Ba/Al, the sample showed diffraction lines for BaCO₃ and γ -Al₂O₃, although the presence of some crystalline CoO_x cannot be ruled out, given the detection limit for XRD measurements. It is also worth noting that there might have two types of BaCO₃ species present in the above samples, i.e. monoclinic and witherite. As pointed out by Baiker, the metastable monoclinic phase is readily transformed into the thermodynamically stable orthorhombic BaCO₃ (witherite) at ambient

conditions [18]. Since all the samples in the present study were aged in air for several days or weeks, the crystalline form of BaCO_3 should be witherite for the all samples[19].

The elemental compositions and surface areas of the catalysts were determined by ICP-AES and N_2 physisorption measurements, respectively, the results being collected in Table 2. The BET surface areas of the catalysts decreased slightly with respect to the bare alumina upon manganese and barium incorporation, indicative of some degree of pore filling.

Fig. 2 shows TEM images and a Pd particle size histogram of the Pd/Co/Ba/Al catalyst, the mean metal particle sizes and dispersions in Pd/Co/Ba/Al sample being given in Table 2. The Pd nanoparticles were dispersed on the support surface, an average of particle size of 3.1 nm being determined from the TEM images based on measurement of 200 Pd particles [20]. According to the TEM micrographs, the Pd dispersion is about 36.4% for the Pd/Co/Ba/Al sample.

XPS is a proven method for determining the oxidation state of elements in the top few layers of material surfaces possessing partially filled valence orbitals [21]. Fig. 3 shows the O 1s and Pd 3d XPS spectra of the Co/Ba/Al and Pd/Co/Ba/Al catalysts. By deconvoluting the O 1s signals, as shown in Fig. 3(a) and Fig. 3(b), the distribution of oxygen species was estimated. There were two kinds of oxygen species present, the peak at BE = 530.8 eV being assigned to surface lattice oxygen ($\text{O}_{\text{latt}}^{2-}$) species, while that at BE = 532.2 eV is assigned to adsorbed oxygen species (O_{ads}) [4, 19, 22]. The ratio of $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}^{2-}$ was 0.404 for Co/Ba/Al, significantly higher than that for Pd/Co/Ba/Al (0.268). This means that the Co/Ba/Al catalyst is enriched in surface oxygen compared to Pd/Co/Ba/Al. Fig. 3(c) shows the Pd 3d XPS spectra for the Pd/Co/Ba/Al sample. Two obvious peaks at 336.5 and 341.7 eV were observed, corresponding to the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies, which can be assigned to PdO [23].

3.2. NO oxidation capacity

NO oxidation capacity (NOC) was measured at different temperatures over Pt/Ba/Al, Co/Ba/Al and Pd/Co/Ba/Al in the absence and presence of H₂O and CO₂. Shown in Fig. 4(a) is the conversion of NO to NO₂ as a function of reaction temperature in the absence of H₂O and CO₂. All samples display a low NOC at below 200°C (corresponding to $\leq 10\%$ NO conversion). As the temperature was increased from 200 to 300°C, the cobalt-containing catalysts (Co/Ba/Al and Pd/Co/Ba/Al) showed enhanced NOC, the conversion increasing from 10.4% and 9.0% to 47.6% and 56.5%, respectively. However, the NO conversion over the Pt/Ba/Al catalyst was still quite low (23.2% at 300°C), suggesting that the cobalt component of the Co/Ba/Al and Pd/Co/Ba/Al samples contributed significantly to NOC at 300°C. When the temperature was raised to 350°C, NO conversion was noticeably increased over Pt/Ba/Al, although it still displayed lower activity compared with Co/Ba/Al and Pd/Co/Ba/Al. Indeed, the NO conversion approached the value predicted for thermodynamic NO/NO₂ equilibrium at this temperature for the Co/Ba/Al and Pd/Co/Ba/Al catalysts (the equilibrium NO conversion, calculated using HSC Chemistry v7.0 software, being shown by the dotted line in Fig. 4). This observation is in line with literature data which show that Pt/Ba/Al is generally a mediocre catalyst for NO oxidation, exhibiting significant activity at elevated temperatures only [7]. Fig. 4(b) shows the conversion of NO to NO₂ as a function of reaction temperature in the presence of H₂O and CO₂. Compared to the experiments performed using 500 ppm NO/ 8% O₂/N₂ as feed gas (Fig. 4(a)), the addition of H₂O and CO₂ decreased the NOC for all samples, although the Co-containing samples still exhibited better NO oxidation performance than the Pt/Ba/Al catalyst. Though there are several factors which can affect NO oxidation activity, correlating the XPS measurements with the NOC data at 300°C, it can be summarized that surface

adsorbed oxygen plays an important role in NO oxidation [24]; i.e., the cobalt-containing catalysts (Co/Ba/Al and Pd/Co/Ba/Al), containing higher amounts of surface oxygen than Pt/Ba/Al [4], exhibit higher NO oxidation capacity.

3.3 NO_x storage capacity

Fig. 5 shows NSC data collected at different temperatures in the absence/presence of H₂O and CO₂. In the absence of H₂O and CO₂ in the feed gas the NSC values span a relatively narrow range, given that the catalysts are far from saturation at this relatively short storage time. However, the presence of H₂O and CO₂ greatly reduced the NSC of the Co/Ba/Al sample, especially at lower temperatures ($\leq 300^{\circ}\text{C}$). It is worth noting that the Pd/Co/Ba/Al catalyst displays superior NSC compared with the other catalysts at all temperatures, even in the presence of H₂O and CO₂. Correlating the NOC data in previous described, although both the Co/Ba/Al and Pd/Co/Ba/Al catalysts displays the relatively high NO oxidation activity compared to Pt/Ba/Al catalyst, even in the presence of H₂O and CO₂ (Fig. 4), Co/Ba/Al shows the lowest NSC at the full temperature range in the presence of H₂O and CO₂. On this basis it can be concluded that the poor NO_x storage capacity for Co/Ba/Al in the presence of H₂O and CO₂ cannot ascribed to its lower NO oxidation activity, it must be other reasons, such as the NO_x adsorption may compete with H₂O/CO₂ adsorption more serious on Co/Ba/Al sample or NO_x storage may be accomplished via different mechanisms for different catalysts [25-27]. It has been reported that alumina is a low-temperature active storage component, however, the presence of H₂O saturates the alumina surface with hydroxyl groups, which makes it difficult for alumina to store NO_x [28, 29]. The negative impact of the CO₂ has been specifically attributed to the formation of a more thermally and chemically stable type of BaCO₃ [30,

31], often described as bulk-like, that will not readily form nitrates during the trapping phase when CO_2 is also present [32]. In addition, it has been shown that hydroxides[29, 30] and carbonates[29, 33] form over the storage components if H_2O and CO_2 are present in the gas feed and results to the lower storage capacity, which should be due to that it is more difficult to store NO_x on BaCO_3 or Ba(OH)_2 than on BaO in the presence of H_2O and CO_2 . Lindholm et al. also found that CO_2 has a greater influence on the storage compared to H_2O , which is most likely due to that BaCO_3 is more stable than Ba(OH)_2 [28], which means that it is more difficult to form nitrites and nitrates from BaCO_3 than from Ba(OH)_2 , which also has been found by Lietti et al.[30].

From the foregoing it is clear that the combination of Pd and Co greatly improves low temperature NO_x storage, even in the presence of H_2O and CO_2 . However, the Co/Ba/Al catalyst displayed the lowest NSC at all temperatures when H_2O and CO_2 were present, indicating that Pd plays an important role during NO_x storage process. Nova et al. proposed that the NO_x storage process was accomplished via two parallel routes [27]: one is the nitrate route, in which NO is oxidized (on Pt sites) to NO_2 , which is stored on BaO in the form of nitrates (nitrate formation involving a disproportionation reaction); the other route involves the stepwise oxidation of NO in the presence of oxygen to form nitrite species, which are progressively oxidized to nitrates [25-27]. Further study found that the “nitrite” pathway dominates over the disproportionation route in the case of NO/O_2 adsorption over Pt/Ba/Al at low temperatures ($\leq 200^\circ \text{C}$) [27, 34]. In the “nitrite” pathway, the cooperative effect between Pt-Ba neighboring couples plays a critical role for the trapping capacity. The presence of Pt-Ba couples favors oxygen activation on Pt sites with transfer to the neighboring Ba sites, followed by a stepwise oxidative adsorption of NO in the form of nitrite-like ad-species on the Ba sites [25, 35].

In the present study, all of the samples displaying low NO to NO₂ conversion below 250°C (about 10%). On this basis it can be concluded that NO_x storage was mainly accomplished via the nitrite route in the absence of H₂O and CO₂ for Co/Ba/Al and Pd/Co/Ba/Al, the Pd and Co functioning as active centers by supplying atomic oxygen to the nearby nitrite species to form stable nitrate species. While over Co/Ba/Al, in the absence of noble metals, which is characterized by its enrichment of active surface oxygen species, the mechanism of NO_x storage should be different. We ascribe it to “oxygen vacancy” mechanism. Co/Ba/Al catalyst is enriched of active surface oxygen species, which has been demonstrated by XPS (as shown in Fig. 3(a)), H₂ reduction in rich phase may generate more oxygen vacancies. Under lean conditions, O₂ was prone to adsorbed and dissociate on such sites. However, when there is H₂O and CO₂ coexistence in the feed gas, they are both electrophilic reagent, which could compete with O₂ for the oxygen vacancy on Co/Ba/Al surface, which results in a great decrease of NSC in the presence of H₂O and CO₂ (Fig. 5). While since gaseous oxygen is activated by Pd over Pd/Co/Ba/Al catalyst, which might not be influenced by the presence of H₂O and CO₂, and therefore it is not a significantly different on NSC in the absence/presence of H₂O and CO₂.

3.4 Thermal stability of the stored NO_x

After exposing the Pt/Ba/Al, Co/Ba/Al and Pd/Co/Ba/Al samples to a NO/O₂/Ar mixture with or without H₂O and CO₂ for 50 min at 200°C, the thermal stability of the stored NO_x was investigated by means of NO_x-TPD experiments conducted in a high purity argon flow, the results being shown in Fig. 6. For the Pt/Ba/Al sample (Fig. 6(a)), two obvious NO_x desorption peaks ($m/z = 30$) were observed at 308 and 484°C (note that the $m/z = 30$ signal can result from desorption of NO

and/or NO_2 due to the fragmentation of NO_2 to NO in the mass spectrometer [36]). The low temperature peak can be attributed to NO_x adsorbed on the Al_2O_3 support or species nearby metal sites [37], while the later peak, which was accompanied by O_2 ($m/z = 32$) formation, can be assigned to the decomposition of nitrate or nitrite at Ba sites [4, 28]. In the case of Co/Ba/Al and Pd/Co/Ba/Al, a very broad NO_x desorption peak was observed, starting at ca. 350°C and ending at ca. 650°C , with a small peak also being present at ca. 300°C . Based on the results of the literature, it is reasonable to ascribe the broad peak at high temperature to the overlap of different adsorbed NO_x species on Ba (surface and bulk $\text{Ba}(\text{NO}_3)_2$) [38]. Compared with NO_x desorption from Pt/Ba/Al, there is a remarkable shift in NO_x desorption to higher temperatures due to the incorporation of Co; specifically, deconvolution of the TPD profiles reveals the presence of a desorption maximum around $560\text{-}570^\circ\text{C}$ (Fig. 6(b) and 6(c)), close to the temperature at which bulk $\text{Ba}(\text{NO}_3)_2$ decomposes [39]. According to work by Lauterbach et al. [11], the addition of Co to the NSR catalyst can increase the number of sites available for the oxidation of NO to NO_2 ; consequently, NO_2 spillover to the Ba sites may be enhanced, with increased formation of bulk $\text{Ba}(\text{NO}_3)_2$.

NO_x -TPD experiments were also conducted over the Pt/Ba/Al, Co/Ba/Al, and Pd/Co/Ba/Al samples in which H_2O and CO_2 were added to the NO/O_2 feed during NO_x storage. Compared with the experiments in which H_2O and CO_2 were absent, the intensities of the NO_x desorption peaks significantly decreased, consistent with decreased NO_x storage. This can be attributed to the competition between CO_2 and NO_x for storage sites; furthermore, H_2O inhibits the oxidation of NO for all samples (as shown in Fig. 4). Notably, a comparison of the NO_x -TPD profiles in the absence/presence of H_2O and CO_2 for the Co/Ba/Al catalyst reveals that the high temperature NO_x desorption peak ($\sim 571^\circ\text{C}$, shown in Fig. 6(b)) was not observed in the presence of H_2O and CO_2 . This

is consistent with the significant loss of NSC in the presence of H₂O and CO₂ for the Co/Ba/Al sample. In addition, the high temperature NO_x desorption peak for Co/Ba/Al (~571 °C, shown in Fig. 6(b)) was not observed in the presence of H₂O and CO₂. This suggests that the NO_x storage process was inhibited by H₂O and CO₂ for Co/Ba/Al sample (the generation of atomic oxygen on cobalt may be inhibited by H₂O and CO₂), with the result that bulk nitrates were hardly formed. However, this was not the case for the Pd/Co/Ba/Al catalyst, due to the generation of atomic oxygen over Pd was not inhibited by H₂O and CO₂.

3.5 Reduction behavior

The reduction of stored NO_x was investigated by means of H₂-TPSR experiments in a gas mixture containing 2% H₂. The results are shown in Fig. 7. For the Pt/Ba/Al sample (Fig. 7(a)), two obvious H₂ consumption peaks accompanied by N₂ (m/e = 28) formation were observed at 90 and 249°C. These different reduction temperatures can be ascribed to NO_x stored on the Al₂O₃ support and at the Ba sites [4]. The lower basicity of Al₂O₃ compared to BaO results in a lower temperature for NO_x release (and hence reduction) from the Al₂O₃ support (90°C in this case). The position of the high temperature H₂ consumption peak (249°C) is in broad agreement with our previous study in which a temperature of 207°C was noted for NO_x release from supported BaO [4, 22]. In the case of Co/Ba/Al, the main N₂ formation peak was observed at 316°C. It is notable that the signal maximum corresponding to the N₂ formation did not line up with the maximum observed for H₂ consumption, the maximum for N₂ formation being observed at 316°C, while the H₂ consumption peaked at about 350°C. This discrepancy can be attributed to the reduction of surface or lattice oxygen on the catalyst, which evidently occurs at slightly higher temperature than NO_x reduction. In addition, significant

NO_x desorption was observed during H_2 -TPSR from 150 to 350°C (in contrast to Pt/Ba/Al), i.e., before the main reduction maximum. According to the H_2 -TPSR results over Pd/Co/Ba/Al shown in Fig. 7(a), there was an obvious H_2 consumption peak ($m/z = 2$) and accompanying N_2 ($m/e = 28$) formation at 191°C. This peak can be attributed to the reduction of adsorbed NO_x species on Ba sites as previously described. Comparing the reduction behavior of the Pt/Ba/Al, Co/Ba/Al and Pd/Co/Ba/Al catalysts, it is clear that reduction of the stored nitrates or nitrites requires much higher temperatures over Co/Ba/Al than over the Pt/Ba/Al and Pd/Co/Ba/Al catalysts.

H_2 -TPSR was also performed after NO_x storage in the presence of H_2O and CO_2 , the results being shown in Fig. 7(b). For the Pt/Ba/Al sample, there was an obvious H_2 consumption peak ($m/z = 2$) accompanied by N_2 ($m/z = 28$) formation at 231°C. Compared with the experiments conducted in the absence of H_2O and CO_2 during NO_x adsorption (Fig. 7(a)), the low temperature H_2 consumption peak was not observed. As mentioned above, this peak can be ascribed to NO_x stored on the Al_2O_3 support, NO_x storage on Al_2O_3 being inhibited in the presence of H_2O [37]. In the case of Co/Ba/Al, the majority of stored NO_x was desorbed at about 300°C, the N_2 signal being weak, i.e., most of the NO_x was desorbed without reduction. H_2 consumption appears to be associated mainly with the reduction of surface or lattice oxygen on the Co/Ba/Al sample, in addition to the reverse water gas shift (RWGS) reaction ($\text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) [40]. In the case of the Pd/Co/Ba/Al sample, compared to the experiments performed in the absence of H_2O and CO_2 (Fig. 7(a)), the H_2 consumption peak shifted to higher temperatures when NO_x storage was performed in the presence of H_2O and CO_2 . According to work by Courtois et al., reduction of CO_2 (from carbonate) via the RWGS reaction generates CO which is less efficient for the NO_x reduction than H_2 , resulting in higher reduction temperatures [41]. Notably, there was no NO_x release observed during the H_2 -TPSR

process on Pt/Ba/Al and Pd/Co/Ba/Al. However, almost all of the stored NO_x desorbed during H₂-TPSR over the Co/Ba/Al sample, this being attributed to the poor activity of Co for NO_x reduction.

3.6 NO_x storage and reduction

NO_x storage and reduction were investigated under cycling conditions over Co/Ba/Al, as well as over Pt/Ba/Al for comparison; results are shown in Fig. 8(a). For the Pt/Ba/Al catalyst, the NO_x removal efficiency increased with increasing temperature and the highest conversion of 90% was obtained at 350°C, which is consistent with results reported in the literature [4, 22]. Compared with Pt/Ba/Al, the Co/Ba/Al sample displayed much lower NO_x removal efficiency at all temperatures. The highest NO_x removal efficiency was observed at 350°C, but was only about quarter of that obtained over Pt/Ba/Al at the same temperature. As mentioned above, the Co/Ba/Al sample displays similar NSC values to those of the Pt/Ba/Al catalyst over the whole temperature range studied (Fig. 5(a)), which contrasts with its poor catalytic performance during lean-rich cycling. Given that the poor performance cannot be attributed to its NO_x storage capacity, it follows that limitations with respect to rich phase regeneration activity account for the relatively low activity of the Co/Ba/Al catalyst in NO_x storage-reduction catalysis.

Based on the promise of non-thermal plasma (NTP) assisted chemistry [4, 13-16], we opted to employ NTP in the rich phase to regenerate the Co/Ba/Al catalyst (the NO_x concentration profiles under plasma-assisted cycling being shown in Fig. S1 in the Supplementary Material, the cycle-averaged lean phase NO_x storage efficiency and rich phase NO_x release are collected in Table S1 in the Supplementary Material). In the discharge stage, the regeneration of adsorbed NO_x was

investigated using 2% H_2/Ar as the discharge gas (called H_2 -plasma), the corresponding cycle-averaged NO_x conversions at different temperatures being collected in Fig. 8(b). As indicated in Fig. 8(b), the NO_x removal efficiency of Co/Ba/Al over the temperature range 150-350°C was greatly enhanced compared with the performance obtained in the catalysis-only condition (Fig. 8(a)). Indeed, cycle-averaged NO_x conversions were higher than 80% in the temperature range 150°C-350°C. This indicates that the stored NO_x on Co/Ba/Al could be reduced by the H_2 -plasma, and that the catalyst was effectively regenerated during rich phase operation. The combination of high NO_x storage capacity and the use of the H_2 -plasma for rich phase catalyst regeneration resulted in greatly improved NO_x conversion performance.

Plasma-assisted NO_x storage and reduction experiments were also conducted over the Pt/Ba/Al and Co/Ba/Al samples in the presence of H_2O and CO_2 (Fig. 8(c)). Pt/Ba/Al and Co/Ba/Al both exhibited decreased NO_x removal efficiency compared with Fig. 8(b). Notably, the presence of H_2O and CO_2 in the feed decreased the NO_x conversion of Co/Ba/Al greatly, especially at low temperatures. This is mainly due to the fact that the NO_x storage capacity of Co/Ba/Al is significantly inhibited by the addition of H_2O and CO_2 [28, 37, 40]. In contrast, the presence of H_2O and CO_2 in the feed exerted relatively little effect on NO_x conversion over Pt/Ba/Al. This result is in accordance with NSC measurements (Fig. 5(b)), in which similar NSC was obtained for Pt/Ba/Al at above 200°C in the presence or absence of H_2O and CO_2 .

In the case of Co/Ba/Al sample, H_2O or CO_2 have only a minor effect on the conversion during H_2 -plasma assisted NO_x storage and reduction process (as shown in Fig. 8(d)) compared with Fig. 8(c). In the presence of CO_2 , this effect is attributed to the higher stability of BaCO_3 compared with BaO as well as to the conversion of H_2 to the less effective reductant CO via reverse water gas shift

chemistry. The decrease of conversion over Co/Ba/Al in the presence of H₂O more severely than CO₂ at lower temperatures ($\leq 250^{\circ}\text{C}$) and it should be due to the NO_x adsorption may compete with H₂O adsorption during lean fuel phase. Furthermore, H₂O also inhibits the oxidation of NO over Co/Ba/Al. The observed effects of H₂O or CO₂ in the feed are in good agreement with literature findings for Pt/Ba/Al[40].

As described above, the decreased NO_x removal efficiency of Co/Ba/Al in the presence of H₂O and CO₂ is mainly due to its NO_x storage capacity being significantly diminished by the addition of H₂O and CO₂. In comparison, the Pd/Co/Ba/Al sample displays superior NSC to the other catalysts at all temperatures, even in the presence of H₂O and CO₂ (as shown in Fig. 5). Therefore, the catalytic performance of the Pd/Co/Ba/Al catalyst during typical catalysis-only NSR and H₂-plasma assisted NSR was investigated in the presence and absence of H₂O and CO₂. Fig. 9(a) depicts the cycled-averaged NO_x conversion as a function of reaction temperature in catalysis-only NSR and plasma-assisted catalysis, measured in the absence of H₂O and CO₂. In the presence of the H₂-plasma, the NO_x removal efficiency of Pd/Co/Ba/Al over the temperature range 150-350°C was greatly enhanced compared with the performance obtained in the absence of the plasma in the rich phase. Pd/Co/Ba/Al exhibited slightly decreased NO_x removal efficiency at all temperatures in the presence of H₂O and CO₂ in the catalysis-only NSR process (Fig. 9(b)); this can be attributed to the fact that NO_x storage and NO_x reduction on Pd/Co/Ba/Al are slightly inhibited by the addition of H₂O and CO₂, as shown in Fig. 5 and Fig. 7. More significantly, there is almost no effect on NO_x removal efficiency for Pd/Co/Ba/Al after addition of H₂O and CO₂ to the feed in the H₂-plasma assisted NSR process (Fig. 9(b)). Indeed, the cycle-averaged NO_x conversion was greater than 95% in the temperature range 150-350°C.

Benefiting from their high NO oxidation capacity, Co-containing catalysts display superior NO_x storage capacity (relative to Pt/Ba/Al) in the absence of H₂O and CO₂. However, the presence of H₂O and CO₂ greatly reduces the NSC of the Co/Ba/Al catalyst by inhibiting the generation of activated atomic oxygen species. In contrast, it appears that generation of atomic oxygen on Pd is not inhibited by H₂O and CO₂, and thus the Pd/Co/Ba/Al catalyst displays superior NSC, even in the presence of H₂O and CO₂. By combining the high NO_x storage capacity of Pd/Co/Ba/Al in the lean phase with H₂-plasma assisted NO_x reduction in the rich phase, it follows that the Pd/Co/Ba/Al sample displays high NO_x removal efficiency in both the absence and presence of H₂O and CO₂.

4. Conclusions

A Co/Ba/Al LNT catalyst was prepared and found to exhibit higher activity for NO oxidation to NO₂ and better NO_x storage capacity than a Pt/Ba/Al reference catalyst. However, due to the difficulty in regenerating the NO_x storage sites during the rich phase, the Co/Ba/Al catalyst showed much lower activity during lean-rich cycling compared with the Pt/Ba/Al sample. By employing an H₂-plasma in the rich phase to regenerate the NO_x-saturated Co/Ba/Al, NO_x conversion was greatly improved, especially in the low temperature region. However, the presence of H₂O and CO₂ in the feed decreased the NO_x conversion of Co/Ba/Al greatly, this being mainly due to the fact that the NO_x storage capacity of Co/Ba/Al is significantly inhibited by the addition of H₂O and CO₂. In order to overcome this limitation, the addition of Pd to Co/Ba/Al was examined. The resulting Pd/Co/Ba/Al catalyst displayed high NO_x removal efficiency during plasma-assisted NO_x storage and reduction, even in the presence of H₂O and CO₂.

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Figure Captions:

Figure 1. XRD patterns of Pt/Ba/Al, Co/Ba/Al and Pd/Co/Ba/Al samples.

Figure 2. TEM images and Pd particle size distributions of Pd/Co/Ba/Al catalyst.

Figure 3. XPS spectra of Co/Ba/Al and Pd/Co/Ba/Al catalysts.

Figure 4. NO oxidation capacity at 150 to 350°C (500 ppm NO, 8% O₂, with or without 2% H₂O and 2% CO₂, N₂ balance, WHSV = 48000 ml·g_{cat.}⁻¹·h⁻¹).

Figure 5. NO_x storage capacity measured under lean conditions (500 ppm NO, 8% O₂, N₂ balance, with or without 2% H₂O and 2% CO₂, 10 min storage time, WHSV = 48000 ml·g_{cat.}⁻¹·h⁻¹).

Figure 6. NO_x-TPD profiles after NO adsorption using 500 ppm NO/8 % O₂/with or without 2% H₂O and 2% CO₂/Ar for 50 min; NO adsorption was performed at 200°C.

Figure 7. H₂-TPSR profiles after NO adsorption using 500 ppm NO/8 % O₂/ with or without 2% H₂O and 2% CO₂/Ar for 50 min; NO adsorption was performed at 300°C.

Figure 8. NO_x conversion of Pt/Ba/Al and Co/Ba/Al during lean/rich cycling at different temperatures (a) catalysis only (without H₂O and CO₂), (b) plasma assisted catalysis (without H₂O and CO₂), (c) plasma assisted catalysis (with H₂O and CO₂) and (d) plasma assisted catalysis (with or without H₂O and CO₂) for Co/Ba/Al.

Figure 9. NO_x conversion of Pd/Co/Ba/Al during lean/rich cycling at different temperatures (a) without H₂O and CO₂, (b) with H₂O and CO₂.

Table 1 Gas composition used for NO_x storage/reduction cycling experiments.

Parameter	Lean	Rich
Duration (s)	600	120
Temperature (°C)	150-350	150-350
Power input (W)	-	20
Space velocity (ml·g _{cat} ⁻¹ ·h ⁻¹)	48,000	48,000
NO (ppm)	500	-
O ₂ (%)	8	-
H ₂ (%)	-	3
H ₂ O (%)	-/2	-/2
CO ₂ (%)	-/2	-/2
Ar (%)	Balance	Balance

Table 2. Summary of ICP-AES, BET, Pd partical size and dispersion data for as-prepared catalysts.

Catalyst	Pd (wt.%)	Ba (wt.%)	Co (wt.%)	BET area (m ² /g)	Pd particle size ^a (nm)	Pd dispersion ^b (%)
γ -Al ₂ O ₃	-	-	-	198	-	-
Co/Ba/Al	-	9.47	3.01	139	-	-
Pd/Co/Ba/Al	0.64	8.48	3.08	132	3.1	36.4%

^a Average value of 200 Pd particles in TEM image.

^b Deduced from the expression $D_{\text{dispersion}} = 112/d$ for Pd. Assumes spherical particles and a Pd surface atom density of 1.27×10^{19} atoms/m² [20].

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9