Non-thermal plasma assisted NO_x storage and reduction over a cobalt-containing Pd catalyst using H₂ and/or CO as reductants

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Abstract

A catalyst of the type Pd/Co/Ba/Al was examined for lean NO_x trap (LNT) applications, and compared with Pd/Ba/Al and Pt/Ba/Al reference catalysts for NO_x storage and reduction using H₂ and/or CO as reducing agents. The activity of Pt/Ba/Al was greatly depressed when using CO as reductant at low temperatures owing to the strong poisoning effect of CO on Pt. The Pd/Co/Ba/Al catalyst exhibited higher activity for NO oxidation to NO₂ and better NO_x storage capacity than Pt/Ba/Al and Pd/Ba/Al catalysts, also showed higher NO_x reduction activity with CO compared to the other two catalysts. However, it shows relatively low NO_x removal efficiency below 250°C, especially using CO as reductants, indicating that regeneration of stored NO_x is the rate limiting step. By employing a non-thermal plasma in the rich phase to assist reduction of the stored NO_x, the Pd/Co/Ba/Al sample exhibited excellent NO_x removal efficiency under plasma assisted lean/rich cycling conditions, affording NO_x conversions close to 99% over a broad temperature window of 150-350°C, even when using CO as the reducing agent.

Keywords: cobalt; palladium; NO_x storage-reduction; carbon monoxide; non-thermal plasma

1. Introduction

Lean-burn engines are becoming increasingly popular due to their better fuel economy and lower CO₂ emissions compared to conventional Otto gasoline engines [1]. However, under lean-burn conditions, the nitrogen oxides (NO_x) exhaust emissions cannot be efficiently reduced over classical three-way catalysts due to the presence of excess O₂ [2]. In order to circumvent this problem, Toyota developed NO_x storage and reduction (NSR) technology (otherwise known as lean NO_x trap (LNT) catalysts) in the mid-1990s [3]. 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. The exhaust gas temperature of lean-burn gasoline engines is typically around ~400°C [4], Pt/Ba/Al catalysts exhibiting excellent catalytic performance at this temperature [5]. In the case of light duty diesel engines, exhaust gas temperatures are lower, corresponding to about 180-350°C in the FTP-75 (the U.S. Federal Test Procedure used to certify vehicle emissions and fuel economy) [6]. Moreover, the exhaust gas temperatures of lean-burn engines can be expected to decrease in future engine designs as thermal losses are minimized, thereby improving the fuel efficiency [7]. Consequently, the low-temperature performance of LNT catalysts is becoming increasingly important in order to facilitate the implementation of highly fuel efficient lean-burn engines [8].

Recently, non-thermal plasma (NTP) assisted catalytic processes have attracted much attention for the abatement of noxious emissions in automotive exhaust gases [9-20]. In our previous study [9], we proposed a non-thermal plasma (NTP) assisted NO_x storage and reduction process on a LaMn_{0.9}Fe_{0.1}O₃ perovskite, which combined the high NO_x storage capacity of the perovskite with non-thermal plasma-assisted activation of H₂. In this manner high NO_x conversions could be

achieved over the $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ catalyst, even at room temperature. Aside from perovskites, a number of simple transition metal oxides with strong oxidation activity and low expense have attracted attention for LNT applications, cobalt oxides being of particular interest [21, 22]. Indeed, it was found that the addition of cobalt to a Pt/Ba/Al catalyst led to high NO oxidation activity, accelerated nitrite/nitrate formation on Ba sites, and gave rise to higher NO_x storage capacity in comparison to cobalt-free counterparts [23-28]. In addition, Wang et al. noted that the synergistic effect of Pt and Co can accelerate the reduction of surface nitrites or nitrates by hydrogen and provide higher NO_x removal activity than the corresponding Pt/Ba/ Al_2O_3 catalyst [23].

Notably, whereas the reduction of stored NO_x by hydrogen as reducing agent has been widely studied over LNT catalysts, the use of reducing agents such as carbon monoxide and hydrocarbons has been investigated to a lesser degree. Unburned or partially burned hydrocarbons (HCs) and carbon monoxide (CO) present in the fuel rich phase represent a plentiful source of reducing agents [29], albeit that they are less active in NO_x reduction than H_2 . Moreover, CO exerts a poisoning effect on Pt at lower temperatures ($< 200^\circ\text{C}$). These factors limit the effectiveness of CO or HCs as reducing agents for LNT catalyst regeneration.

Based on the foregoing, the present study focused on the use of Pd, rather than Pt, as the active metal in NO_x storage-reduction catalysis owing to its lower cost and better tolerance to CO. However, while Pd is reasonably active for NO_x reduction, it possesses poor activity for NO oxidation [30, 31]. In order to improve catalyst activity for the oxidation of NO to NO_2 , cobalt oxide was added to a catalyst of the Pd/Ba/Al type (i.e., to give Pd/Co/Ba/Al), the properties of which were compared with Pd/Ba/Al and Pt/Ba/Al model catalysts. The catalytic properties of these samples were evaluated under typical NO_x storage-reduction conditions, as well as in NTP assisted NO_x storage-reduction.

Moreover, particular attention was paid to the effectiveness of NO_x reduction using different reductants, i.e., H₂, CO and H₂ mixed with CO.

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. The Pd/Ba/Al [5] and Pt/Ba/Al [32] catalysts were prepared by the incipient wetness method according to literature procedures. 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. 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). Temperature programmed reduction (H₂-TPR) experiments on the as-synthesized catalysts were performed using a Micromeritics AutoChem II Analyzer equipped with

a TCD detector to monitor H₂ uptake. Samples (about 50 mg) were heated from room temperature to 800°C at a rate of 10°C/min under flowing 5% H₂/Ar (50 ml/min). Prior to TPR, samples were pre-treated in Ar at 120°C for 1 h to remove adsorbed water.

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 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, 2% H₂O, 2% CO₂, and balance N₂. The storage time was 50 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. CO-TPSR

The reducibility of adsorbed NO_x species was evaluated by means of CO-TPSR 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, 2% H₂O, 2% CO₂ and balance Ar. After flushing the catalyst with Ar at 200°C for 30 min, CO-TPSR was performed in a flowing gas mixture containing 2% CO/2% CO₂/2% H₂O 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 [9], loaded with ca. 150 mg of catalyst particles (20-40 mesh). The high voltage was applied with a high-voltage power source (CTP-2000K, Nanjing Suman Electronic Co. Ltd) working at about 40 kHz. The power source was capable of supplying a bipolar sine wave output with 0-40 kV peak-to-peak voltage at a frequency of 10-50 kHz. The input electric discharge power was measured by voltage-charge Lissajous figures recorded with a 100 MHz digital oscilloscope (TDS 2012, Tektronix). The energy efficiency was defined as follows [14]:

$$\text{Energy efficiency (mmol NO}_x\text{/W} \bullet \text{h)} = \frac{NO_{x,in} \times NO_{x,conversion}}{P \times t_{discharge}} \quad (3)$$

where P and $t_{discharge}$ are the discharge power and discharge period at the discharge stage (rich phase), respectively. Effluent gases were analyzed on-line using a mass spectrometer (Pfeiffer Vacuum GSD 301) and a FTIR gas analyzer (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 2%

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. Briefly, the working principle of the plasma assisted NO_x storage and reduction process can be divided into two stages: (i) the NO_x is first stored on the catalyst during the fuel lean phase (plasma off) then (ii) the stored NO_x is reduced to N₂ and H₂O by the plasma during the fuel rich phase (plasma on). NO_x concentrations were averaged over 5 cycles to give a mean conversion according to the following formula:

$$\text{NO}_x \text{ conversion} = \frac{\int_0^t (\text{NO}_{x, \text{in}} - \text{NO}_{x, \text{out}}) dt}{\int_0^t \text{NO}_{x, \text{in}} dt} \times 100\% \quad (4)$$

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

2.6. In situ DRIFTS study of NO_x storage

In situ DRIFTS was performed on a Tensor 27 (Bruker) FTIR spectrometer equipped with an in situ diffuse reflection chamber with CaF₂ windows and a high-sensitivity MCT detector. The catalyst for the DRIFTS studies was finely ground and placed in a stainless steel crucible in the sample chamber. Mass flow controllers and a temperature controller were used to simulate the conditions used in the NO_x storage capacity tests. All gas mixtures were fed at a flow rate of 100 ml/min. Prior to recording each DRIFTS spectrum, the catalyst was pretreated in 1% H₂ at 500°C for 30 min and then cooled to the measurement temperature under flowing Ar in order to acquire a reference spectrum. A gas mixture of 500 ppm NO, 8% O₂, and Ar as the balance was then introduced, and a series of NO_x adsorption spectra were obtained over time. All spectra reported here were collected at

a resolution of 4 cm⁻¹ for 60 scans.

3. Results and discussion

3.1. Catalyst characterization

The elemental compositions and surface areas of the catalysts were determined by ICP-AES and N₂ physisorption measurements, respectively, the results being collected in Table 2. The catalyst carrier (γ -Al₂O₃) had the largest surface area, and the BET surface area of the catalysts decreased compared with the bare γ -Al₂O₃ as a result of sequential impregnation and calcinations. The mean Pt/Pd particle sizes determined from the TEM images [33] (based on measurement of 200 metal particles) and the corresponding Pt/Pd dispersions in these samples are also given in Table 2, the TEM images of the Pt/Ba/Al, Pd/Ba/Al and Pd/Co/Ba/Al samples being shown in Fig. S1 in the Supplementary Material. X-ray diffraction (XRD) analysis (Fig. 1) showed that the main phases present in Pt/Ba/Al, Pd/Ba/Al and Pd/Co/Ba/Al were BaCO₃ (JCPDS No. 45-1471) and γ -Al₂O₃ (JCPDS No. 47-1770), while characteristic reflections for Pt/Pd or PtO_x/PdO_x were not observed due to the low concentration of Pt/Pd in the catalyst and/or the small size of the Pt/Pd particles. In addition, a spinel phase (CoAl₂O₄, JCPDS No. 70-0753) was observed for the Pd/Co/Ba/Al sample, indicating that the cobalt and aluminum oxides reacted to form the spinel during calcination. It should be noted that the presence of crystalline CoO_x cannot be ruled out, given the detection limit for XRD measurements.

The reducibility of Pd/Co/Ba/Al was studied by H₂-TPR, the results of which are shown in Fig. 2. For comparison, the H₂-TPR profiles of Co/Al and Co/Ba/Al were also recorded (Co/Al and Co/Ba/Al were similarly prepared as described in the section 2.1, but with omission of the Pd and/or

Ba impregnation step). Over Co/Al, there are two obvious H_2 consumption peaks at ca. 407 and 453°C, the lower temperature peak being attributed to the reduction of Co_3O_4 to CoO, whereas the higher temperature peak can be attributed to the reduction of CoO to Co [34, 35]. In addition, a small peak can be observed at 715°C, which can be ascribed to the reduction of $CoAl_2O_4$ [36]. For the Co/Ba/Al sample, two H_2 consumption peaks were observed at 527 and 648°C, corresponding to the reduction sequence $Co_3O_4 \rightarrow CoO \rightarrow Co$. Notably, the H_2 consumption peaks shifted to higher temperatures for the Co/Ba/Al sample compared to Co/Al. Moreover, a peak above 700°C was also observed over the Co/Ba/Al sample (at 776°C), which again can be assigned to the reduction of the $CoAl_2O_4$ spinel (according to XRD data, the $CoAl_2O_4$ spinel is also observed for Pd/Co/Ba/Al as shown in Fig. 1). For the Pd/Co/Ba/Al sample, curve-fitting suggests the presence of three H_2 consumption peaks at 206, 315 and 418°C; the two lower temperature peaks can be assigned to the reduction sequence $Co_3O_4 \rightarrow CoO \rightarrow Co$ as described above, whereas the higher temperature peak is be attributed to the reduction of $CoAl_2O_4$ spinel. Notably, the reduction temperatures shifted to lower values compared to the other samples; this phenomenon is usually interpreted in terms of the activation and spillover of hydrogen from the initially reduced Pd to CoO_x , thereby facilitating the reduction of the oxides [37].

3.2. NO oxidation capacity

Although many factors can influence the NO_x trapping process, the oxidation of NO to NO_2 is regarded as a key step since NO_2 is more readily adsorbed than NO [23, 38]. Fig. 3 compares the conversion of NO to NO_2 over Pt/Ba/Al, Pd/Ba/Al and Pd/Co/Ba/Al catalysts at the end of the storage process (i.e., when the catalyst was fully saturated with NO_x), at which point the NO_2/NO_x

ratio reached a steady state. In the case of the Pt/Ba/Al sample, NO conversion increased with increasing temperature from 150°C to 350°C, this observation being 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 [23]. Notably, although the NO oxidation activity increased with increasing temperature for the Pd/Ba/Al catalyst, it exhibited lower activity compared to Pt/Ba/Al for NO oxidation [30, 31]. For the Pd/Co/Ba/Al catalyst, although it displayed low NOC at low temperatures (< 10% NO conversion at 250°C), NO oxidation activity increased substantially as the temperature was increased from 250 to 300°C, the conversion increasing from 9.1% to 29.4%. Indeed, the NO conversion for Pd/Co/Ba/Al approached the value predicted for thermodynamic NO/NO₂ equilibrium at 350°C (the equilibrium NO conversion, calculated using HSC Chemistry v7.0 software, being shown by the dotted line in Fig. 3). This result is in line with literature data which show that cobalt is generally an excellent catalyst for NO oxidation [23].

3.3. NO_x storage capacity

NO_x storage capacity (NSC) measurements were performed for Pt/Ba/Al, Pd/Ba/Al and Pd/Co/Ba/Al samples. As shown in Fig. 4, the NSC values of the catalysts are relatively low at 150°C (< 200 μmol/g) which can be attributed to the poor NO oxidation activity at this temperature (as shown in Fig. 3). With increase of the temperature, all of the samples showed increased NO_x storage capacity, the highest NSC values being attained at 350°C. At higher temperatures the kinetics of NO oxidation to NO₂ are favored; this, coupled with the strong surface basicity of BaO (which imparts relatively high thermal stability to the stored NO_x [32]), results in increased NSC. Unsurprisingly, the Pd/Ba/Al catalyst displayed the lowest NSC over the full temperature range, this

being mainly due to the lower NO oxidation activity of Pd/Ba/Al compared to Pt/Ba/Al [31]. Additionally, the lower precious metal dispersion of Pd/Ba/Al (Pd, 32.0%) compared to the Pt/Ba/Al sample (Pt, 41.9%, see Table 2) can also be expected to negatively impact its NO_x storage properties given that the dispersion of Pt or Pd in LNT catalysts has been shown to significantly influence NO_x storage capacity [39]. Compared with Pt/Ba/Al and Pd/Ba/Al, it is clear that the Pd/Co/Ba/Al sample possessed much higher NO_x storage capacity over the full operating temperature range (150-350°C), indicating that the presence of the cobalt as the main NO oxidation component (and barium as the chief NO_x storage component) significantly improved NO_x storage capacity, in agreement with the findings of Hu [21] and Wang et al. [23].

3.4. NO_x species studied by in situ DRIFTS

In situ DRIFTS spectra showing the evolution of surface NO_x species at 300°C are shown in Fig. 5. After exposing the Pt/Ba/Al₂O₃ and Pd/Ba/Al catalysts to a 500 ppm NO/8% O₂/Ar mixture for 5 min at 300°C, an obvious band at 1230 cm⁻¹ and a small band at 1315 cm⁻¹ were observed (Fig. 5(a) and (b)). The former can be assigned to bridged nitrite species on Al or on Ba sites [40, 41] and the latter to monodentate nitrates associated with Ba [42]. Upon increasing the exposure time, the band at 1315 cm⁻¹ significantly increased in intensity, while the band at 1230 cm⁻¹ gradually decreased and was overlapped by a new band at 1245 cm⁻¹. In addition, a band centered at 1548 cm⁻¹ grew in. These two new bands are assigned to monodentate nitrates associated with Al [43]. At 50 min of adsorption, bands between 1300 cm⁻¹ and 1450 cm⁻¹ became dominant in the spectrum and were difficult to assign due to the overlapping of nitrite/nitrate bands from both BaO and Al₂O₃ [23]. Tentatively, bands at 1338 cm⁻¹ and 1400 cm⁻¹ may be attributed to the presence of monodentate nitrates and bulk

nitrates on Ba sites, respectively [40, 44]. Notably, after 50 min the band at 1230 cm^{-1} (nitrite species) was weak for Pt/Ba/Al whereas this band was still clearly observed for Pd/Ba/Al, implying that nitrites are relatively stable on Pd-containing samples under these conditions; this is consistent with the lower NO oxidation activity of Pd/Ba/Al compared to Pt/Ba/Al (as shown in Fig. 3).

The NO_x storage process on Pd/Co/Ba/Al was similar to that on Pt/Ba/Al and Pd/Ba/Al. After exposing the Pd/Co/Ba/Al catalyst to a $\text{NO/O}_2/\text{Ar}$ mixture for 5 min at 300°C , an obvious band at 1315 cm^{-1} and a small band at 1230 cm^{-1} were observed (Fig. 5(c)). These bands are assigned to monodentate nitrates species on Ba and bridged nitrite species on Al or Ba sites, respectively, as described previously [40-42]. After exposure to the $\text{NO/O}_2/\text{Ar}$ mixture for 10 min, a new band at 1400 cm^{-1} was observed which gradually increased in intensity throughout the experiment and which can be assigned to bulk nitrate species on Ba. Moreover, the initially formed nitrite band at 1230 cm^{-1} had almost disappeared after 10 min, the observed bands being associated with the presence of nitrates.

Correlating the results obtained for Pd/Co/Ba/Al during NO_x storage with those of the Pt/Ba/Al and Pd/Ba/Al catalysts, it can be surmised that the addition of cobalt to Pd/Ba/Al significantly improved its NO oxidation activity (consistent with NOC results summarized in Fig. 3), such that NO_x was stored on the surface of Pd/Co/Ba/Al in the form of nitrates.

3.5. CO-TPSR

The reduction of stored NO_x was investigated by means of temperature programmed surface reaction in a gas mixture containing 2% CO/2% CO_2 /2% $\text{H}_2\text{O}/\text{Ar}$. The results are shown in Fig. 6. For Pt/Ba/Al, CO ($m/z = 28$) consumption commenced at $\sim 250^\circ\text{C}$ and an obvious peak at 330°C

accompanied by CO_2 ($m/z = 44$) formation was observed, which can be ascribed to the reduction of stored NO_x on Ba sites. In principle there are two main types of NO_x storage sites on the Pt/Ba/Al catalyst, i.e., Ba sites and the Al_2O_3 support. However, as noted by Epling et al. [45], the NO_x storage capacity of Al_2O_3 is limited in the presence of H_2O . Given that in this study H_2O and CO_2 were present in the feed gas during NO_x adsorption, it can be surmised that NO_x species were adsorbed mainly on the Ba sites. As the temperature was raised to $\sim 370^\circ\text{C}$, a sharp decrease in the CO ($m/z = 28$) and H_2O ($m/z = 18$) signals was observed, accompanied by CO_2 ($m/z = 44$) and H_2 ($m/z = 2$) formation, which can be attributed to the occurrence of the water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) above this temperature. According to the literature [46-48], the kinetic behavior of CO oxidation over Pd/Pt-containing catalysts can be divided into three temperature ranges: at lower temperatures, the activity is self-inhibited by a high coverage of the active sites with CO, and thus, the CO conversion is quite low. At higher temperatures, the CO conversion is significantly increased but the CO surface coverage is low; in this temperature range, the reaction rate is controlled by the diffusion of reactants to the active sites. Upon raising the temperature further, the reaction rate is accelerated by the reaction heat, water-gas shift being an exothermic reaction ($\Delta H_{298}^\circ = -41.09 \text{ kJ} \cdot \text{mol}^{-1}$), which results in a rapid increase in the conversion.

Similar trends were observed over the Pd/Ba/Al catalyst (Fig. 6(b)). However, in comparison with Pt/Ba/Al the CO consumption peak was observed at lower temperature (316°C), implying that the CO oxidation activity of the Pd catalyst was higher than the Pt analogue, in accordance with the results of Ivanova et al. [46]. In the case of Pd/Co/Ba/Al, the CO consumption peak was shifted to even lower temperature (289°C , as shown in Fig. 6(c)). Evidently, the addition of cobalt significantly enhances the reduction activity of stored NO_x by carbon monoxide. We speculate that this is likely a

consequence of enhanced CO adsorption (i.e., adsorption of CO on Co as well as on Pd), resulting in an increased rate of diffusion of CO to the stored NO_x. As noted previously, the rate of CO oxidation is controlled by the diffusion of reactants to the active sites in this temperature range [49].

3.6. NO_x storage and reduction performance

NO_x storage and reduction performance was investigated under cycling conditions using different reducing agents over Pd/Co/Ba/Al, as well as over Pt/Ba/Al and Pd/Ba/Al for comparison; results are shown in Fig. 7.

Fig. 7(a) depicts the cycled-averaged NO_x conversion as a function of reaction temperature, using 3% H₂ as the reducing agent. For the Pt/Ba/Al catalyst, the cycle-averaged NO_x removal efficiency increased with increasing temperature and the highest conversion of 90% was obtained above 300°C, which is consistent with results reported in the literature [9, 32]. Compared with Pt/Ba/Al, the Pd/Ba/Al sample displayed much lower NO_x removal efficiency at all temperatures, which is likely related to the poor NO oxidation activity and lower NO_x storage capacity compared to the Pt-containing sample (as shown in Fig. 3 and Fig. 4). Notably, in the case of Pd/Co/Ba/Al, considerably higher cycle-averaged NO_x conversions were obtained over the full operating temperature range compared to the Pd/Ba/Al sample. Indeed, Pd/Co/Ba/Al displayed comparable activity to the Pt-containing catalyst (Pt/Ba/Al). Correlating the NO_x conversion measurements with the NOC and NSC data for Pd/Co/Ba/Al, it can be inferred that the addition of cobalt to Pd/Ba/Al not only significantly improved its NO oxidation activity and NO_x storage capacity during the fuel lean phase, but also significantly promoted its NO_x removal efficiency during lean/rich cycling conditions, which is consistent with results reported in the literature [23].

When the reducing agent (3% H₂) was partly replaced by CO (1% H₂+2% CO) as shown in Fig. 7(b), NO_x conversion over Pt/Ba/Al was greatly decreased, especially at low temperatures. This is related to the coverage of Pt by CO as noted previously [50]. NO_x conversion over Pd/Ba/Al and Pd/Co/Ba/Al was also decreased at low temperatures, although not to the degree observed for Pt/Ba/Al, the Pd/Co/Ba/Al catalyst exhibiting the highest cycle-averaged NO_x conversion. When the reducing agent (3% H₂) was completely replaced by 3% CO as shown in Fig. 7(c), NO_x conversion over Pt/Ba/Al decreased further, NO_x conversion values being consistently lower (below 300°C) than those of the Pd-containing catalysts. The highest NO_x conversion was obtained over Pd/Co/Ba/Al, although a comparison of Fig. 7(a) and (c) shows that much lower NO_x conversion was obtained when using CO instead of H₂ as the reductant. For each of the catalysts, the lower NO_x reduction activity obtained with CO as the reducing agent can be attributed to the competitive adsorption of CO with NO on the precious metals [50]. Given that Pt binds CO particularly strongly, CO coverage on Pt is more extensive than on Pd [50], explaining the higher NO_x reduction activity obtained over the Pd catalysts (Fig. 7(c)) when using CO as the reducing agent.

3.7. Non-thermal plasma-assisted NSR process

As shown above, the low temperature activity of Pt/Ba/Al was greatly depressed when using CO as the NO_x reductant. Even for the most active Pd/Co/Ba/Al catalyst, the NO_x conversion in the low temperature region is still quite low. To improve the low temperature activity, we opted to employ NTP in the rich phase to facilitate catalyst regeneration.

Fig. 8(a) depicts the cycled-averaged NO_x conversion values as a function of reaction temperature, obtained using 3% H₂ as the reducing agent. From these data it is apparent that the NO_x

removal efficiency of Pt/Ba/Al, Pd/Ba/Al and Pd/Co/Ba/Al over the temperature range 150-350°C was greatly enhanced compared with the performance obtained in the absence of the NTP in the rich phase (Fig. 7(a)). In previous work we found that catalyst regeneration (i.e., the release and reduction of stored NO_x) is the rate limiting step for NSR catalysts [9]; by employing NTP in the rich phase to assist reduction of the stored NO_x, the NO_x conversion was greatly improved, especially at low temperature. In the present study, although the NO_x reduction activity was enhanced by NTP, the NO_x removal efficiency of the Pt/Ba/Al and Pd/Ba/Al catalysts was still lower than that over Pd/Co/Ba/Al below 300°C, a fact which can be explained by the lower NO_x storage capacity of Pt/Ba/Al and Pd/Ba/Al (Fig. 4).

Notably, for Pd/Co/Ba/Al, upon increasing the temperature to 350°C a slightly decreased NO_x conversion was observed, which can be attributed a small quantity of NO_x which was released during the rich phase without reduction. For LNT catalysts, the cycle-averaged NO_x removal efficiency is dependent on the lean phase NO_x storage efficiency and rich phase NO_x reduction efficiency. During the rich phase, NO_x released from barium nitrites or nitrates migrates to precious metal sites and is reduced. For optimal NO_x removal efficiency during the rich phase, the rates of nitrate decomposition and NO_x reduction should be balanced. Evidently, for Pd/Co/Ba/Al the rate of nitrate decomposition was slightly faster than that of NO_x reduction at 350°C, resulting in a small quantity of NO_x slip which decreased the NO_x removal efficiency.

Plasma-assisted NO_x storage and reduction experiments were also conducted using 1% H₂+2% CO (Fig. 8(b)) and using 3% CO (Fig. 8(c)) as the reducing agent. By comparison with the results using H₂ as reductant, Pt/Ba/Al and Pd/Ba/Al both exhibited decreased NO_x removal efficiency below 300°C, especially using CO alone as the reducing agent. In addition, Pt/Ba/Al exhibited the

poorest activity when using CO as reductant, which again can be ascribed to the strong poisoning effect of CO on Pt at lower temperatures. More interestingly, there was almost no effect on NO_x removal efficiency for Pd/Co/Ba/Al when the 3% H₂ reducing agent was partly or completely replaced by carbon monoxide (Fig. 8(b) and (c)). Indeed, the cycle-averaged NO_x conversion was greater than 95% in the temperature range 150-350°C for Pd/Co/Ba/Al. Correlating the NO_x conversion measurements with the NOC, NSC, CO-TPSR and catalysis-only NO_x conversion data (Fig. 7) for Pd/Co/Ba/Al, it can be surmised that the addition of cobalt to Pd/Ba/Al not only significantly improved its NOC, NSC and NO_x storage capacity during lean phase operation, but also significantly promoted its NO_x removal efficiency during plasma-assisted lean/rich cycling conditions.

Under rich-burn conditions, the released NO_x from barium nitrates are reduced to N₂ on the Pt or Pd surface by H₂ and/or CO from the rich exhaust gas. The reduction of stored nitrates has been found to occur by the following reactions [1, 2]:

For hydrogen,

For the catalytic oxidation reaction of carbon monoxide on Pd/Pd sites are generally by Langmuir-Hinshelwood reaction mechanisms [51]: represents a reaction between two chemically adsorbed reactants, and the reduction of NO_x may be by the following reactions [52]:

The CO can act as a direct reductant of NO_x via reactions (8)-(10); however, another route that the CO may take resulting in reduction and catalyst regeneration is the water-gas-shift (WGS) reaction, $\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$, where H₂ again acts as the ultimate reductant [45].

During plasma-assisted process, the reduction paths of stored nitrates may be different with the catalysis only system. When the plasma was introduced into the reaction system, a synergistic function occurred between the plasma and the catalyst. The interaction of plasma with the catalyst through surface discharge as well as the direct interaction of gas-phase radicals with the catalyst surface are expected to play important roles in the plasma-assisted catalytic system. The reduction paths of stored nitrates during plasma assisted catalytic system may as follow:

For hydrogen [53],

For carbon monoxide [54],

Notably, from the comparison of the reaction paths (catalysis only/plasma assisted catalysis) for all samples (Pt/Ba/Al, Pd/Ba/Al and Pd/Co/Ba/Al) it is clear that plasma addition greatly increased the NO_x removal efficiency, especially at low temperatures. This can be attributed to the enhanced H₂ → H + H or CO dissociation/desorption activity associated with the plasma. Benefitting from this improved reductant activation and enhanced NO_x storage capacity, all samples displayed excellent NSR performance.

In the present study, the highest energy efficiency was obtained for Pd/Co/Ba/Al using H₂ and/or CO as the reducing agent. In both cases, complete NO_x conversion was obtained during plasma-assisted NO_x storage and reduction over the full operating temperature range of 150-350°C, the corresponding energy efficiency being 0.446 mmol NO_x/ W·h which is comparable with

literature results[14, 16]. Since the large amount of adsorbed NO_x on the catalysts (lean phase, plasma off) is converted to N₂ in a very short period of time in the discharge stage (rich phase, plasma on), the energy efficiency is high compared with other studies in which NTP was employed during the whole process [15, 20, 55]. Therefore, combining the high NO_x storage capacity of transition metal-containing LNT catalysts with non-thermal plasma assisted activation of H₂ and/or CO reductants is potentially promising for practical applications.

4. Conclusions

A Pd/Co/Ba/Al LNT catalyst was prepared and found to exhibit higher activity for NO oxidation and better NO_x storage capacity than Pt/Ba/Al and Pd/Ba/Al catalysts. Moreover, compared to the Pd/Ba/Al sample, the Pd/Co/Ba/Al catalyst was shown to achieve significantly improved NO_x conversion under lean/rich cycling conditions, especially using carbon monoxide as the reducing agent. This is attributed to its increased activity for CO activation, which combined with the high NO_x storage efficiency, results in superior NO_x removal efficiency. Furthermore, benefitting from the improved reductant activation ($\text{H}_2 \rightarrow \text{H} + \text{H}$ or CO dissociation/desorption) associated with the plasma, NO_x conversion was greatly improved, especially in the low temperature region. Using carbon monoxide as the reducing agent, NO_x conversions of close to 99% were obtained over a broad temperature window (150-350°C) over the Pd/Co/Ba/Al catalyst.

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Figure Captions:

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

Fig. 2. H₂-TPR profiles of Co/Al, Co/Ba/Al and Pd/Co/Ba/Al samples.

Fig. 3. NO conversion to NO₂ measured under lean conditions (500 ppm NO, 8% O₂, 2% H₂O, 2% CO₂, N₂ balance, WHSV = 48,000 ml·g_{cat.}⁻¹·h⁻¹).

Fig. 4. NO_x storage capacity measured under lean conditions (500 ppm NO, 8% O₂, 2% H₂O, 2% CO₂, Ar balance, 50 min storage time, WHSV = 48,000 ml·g_{cat.}⁻¹·h⁻¹).

Fig. 5. In situ DRIFTS spectra of Pt/Ba/Al, Pd/Ba/Al and Pd/Co/Ba/Al catalysts after 50 min NO adsorption at 300°C.

Fig. 6. CO-TPSR profiles after NO adsorption using 500 ppm NO/8% O₂/2% H₂O /2% CO₂/Ar for 50 min; NO adsorption was performed at 200°C.

Fig. 7. NO_x conversion during lean/rich cycling at different temperatures (lean phase: 500 ppm NO/8% O₂/2% H₂O/2% CO₂/Ar balance, duration: 80 s; rich phase: (a) **3% H₂**/2% H₂O/2% CO₂/Ar balance, or (b) **1% H₂/2% CO**/2% H₂O/2% CO₂/Ar balance, or (c) **3% CO**/2% H₂O/2% CO₂/Ar balance, duration: 20 s, WHSV = 48,000 ml·g_{cat.}⁻¹·h⁻¹).

Fig. 8. NO_x conversion during non-thermal plasma-assisted lean/rich cycling at different temperatures (lean phase: 500 ppm NO, 8% O₂, 2% H₂O, 2% CO₂, balance Ar, duration: 10 min; rich phase: (a) **3% H₂**/2% H₂O/2% CO₂/Ar balance, or (b) **1% H₂/2% CO**/2% H₂O/2% CO₂/Ar balance, or (c) **3% CO**/2% H₂O/2% CO₂/Ar balance, discharge power: 1.8 W, duration: 2 min, WHSV = 48,000 ml·g_{cat.}⁻¹·h⁻¹).

Table 1.

Gas composition used for NO_x storage/reduction cycling experiments.

Parameter	Lean	Rich
Temperature (°C)	150-350	150-350
Power input (W)	-	-/1.8
Space velocity (ml·g _{cat} ⁻¹ ·h ⁻¹)	48,000	48,000
NO (ppm)	500	-
O ₂ (%)	8	-
H ₂ (%)	-	0-3
CO (%)	-	0-3
H ₂ O (%)	2	2
CO ₂ (%)	2	2
Ar (%)	Balance	Balance

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

Catalyst	Pt/Pd (wt.%)	Ba (wt.%)	Co (wt.%)	BET area (m ² /g)	Pt/Pd particle size ^a (nm)	Pt/Pd dispersion ^b (%)
γ -Al ₂ O ₃	-	-	-	198	-	-
Pt/Ba/Al	0.71	9.95	-	153	2.7	41.9
Pd/Ba/Al	0.62	8.41	-	148	3.5	32.0
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 $D_{\text{dispersion}} = 113.2/d$ for Pt and $112/d$ for Pd. Assumes spherical particles and a Pt or Pd surface atom density of 1.31×10^{19} atoms/m² or 1.27×10^{19} atoms/m² [33].

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.