Non-thermal plasma enhanced NSR performance over Pt/M/Ba/Al₂O₃ (M = Mn, Co, Cu) catalysts

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Abstract

To improve the NO_x storage capacity (NSC) of lean NO_x trap (LNT) catalysts of the Pt/BaO/Al₂O₃ type, the catalyst was doped with redox active transition metals of Mn, Co, or Cu, respectively. Due to differences in the chemical states of the doped metals, the catalysts exhibited different catalytic behaviors. Co and Mn doped catalysts showed improved NO to NO₂ oxidation ability, and therefore enhanced NO_x storage capacities, which led to the increased cycle averaged NO_x conversions as compared to a Pt/Ba/Al₂O₃ reference. However, being limited by NO_x reduction in rich phase, the NO_x conversions were still poor at low temperatures (<250°C). By employing an H₂-plasma in rich phase to assist NO_x reduction, NO_x conversions were greatly enhanced especially for low temperatures (≤250°C). The best properties were achieved over Pt/Co/Ba/Al₂O₃ catalyst which exhibited NO_x conversions higher than 80% in the whole temperature range (150 to 350°C) and best SO₂ resistance abilities.

Keywords: transition metal oxide; NO_x storage-reduction; non-thermal plasma

1. Introduction

The push for better fuel economy and lower vehicular CO₂ emissions has led to increased deployment of lean-burn engines, the lean burn engine is widely used in heavy duty diesel and light duty gasoline engine. However, exhaust gases from these engines contain NO_x and excess O₂, which renders NO_x reduction into N₂ impractical over conventional three-way catalysts (TWCs) [1]. Consequently, selective catalytic reduction (SCR) of NO_x using urea as a reductant has been developed for mobile lean NO_x removal [2, 3]. While this technology is well suited for heavy duty diesel applications, for light duty applications lean NO_x trap (LNT) catalysts (otherwise known as NO_x adsorber or NO_x storage-reduction catalysts) offer a cheaper and more practical alternative in some cases [4]. NSR operation is cyclic: during the lean part of the cycle, NO_x is trapped on the catalyst; intermittent rich excursions are used to reduce the NO_x to N₂ and restore the original catalyst surface, after which lean operation resumes [5]. Platinum and barium deposited on γ -Al₂O₃ (Pt/Ba/Al₂O₃ catalyst) is the most commonly studied model composition for NO_x storage-reduction catalysis [6]. Pt/Ba/Al₂O₃ 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 nitrate [7]. However, the low temperature activity of LNT catalysts is especially important for light duty diesel applications, typical engine-out temperatures in the EOC (Efficiency Optimization Control) and FTP-75 (Regulatory Vehicle Mode) being about 180-350°C [8]. 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.

A number of efforts have been made to improve the low temperature activity of LNT catalysts.

Doping transition metal oxides into Pt/Ba/Al₂O₃ catalysts is one such approach. Kim et al. [9] found that 2 wt% cobalt loaded onto Pt/BaO/Al₂O₃ improved NO_x uptake during the lean phase, this being ascribed to the formation of Co₃O₄ on the catalyst surface (identified by XRD), which functions as a catalyst for NO oxidation to NO₂. A study by Le Phuc et al. [10] showed that Mn addition to Pt/BaO/Al₂O₃ improved NO_x storage capacity and led to an improvement in NO_x reduction at 400°C, although the presence of Mn inhibited activity at low temperatures (<300°C), being attributed to Pt-Mn interactions which inhibit the reduction function of the catalyst. In our previous study, we found that Pd/Mn/Ba/Al showed significantly improved NO_x conversion compared to Pd/Ba/Al as a consequence of its increased activity for NO oxidation and hence, its superior NO_x storage efficiency [7]. We also observed that ceria-containing catalysts Pt/BaO/CeO₂ and Pt/BaO/CeO₂/Al₂O₃ exhibited better NO_x storage capacity at 200 and 300°C relative to the ceria-free Pt/Ba/Al₂O₃ catalyst. Furthermore, regeneration behavior at 200-400°C was greatly improved by the presence of ceria [11]. Based on the foregoing, it is evident that doping Pt(Pd)/Ba/Al catalysts with redox active metal oxides can improve their NO_x storage capacity at low temperature (<300°C). However, NO_x conversions obtained under lean-rich cycling conditions are still quite low, which can be attributed to the inability to fully regenerate the catalysts at low temperatures.

Electrically produced plasma-based processes have been reported as an attractive alternative to conventional thermally activated reactions, which stems from the fact that the highly reactive species in the plasma are not in thermodynamic equilibrium, especially for non-thermal plasma (NTP). We have previously studied the use of NTP to facilitate rich-phase regeneration of LNT catalysts. By combining the high NO_x storage capacity of a perovskite-based catalyst in the lean phase with non-thermal plasma-assisted activation of the reductant in the rich phase, high NO_x conversions

were obtained at low temperatures [12]. However, when H₂O and CO₂ were present in the feed gas catalytic activity was greatly depressed, even in H₂-plasma assisted NSR. Consequently, a catalyst with higher NO_x storage capacity in the presence of H₂O and CO₂ is especially desirable for such an H₂-plasma enhanced NSR process.

In the present study, we prepared a series of Pt/M/Ba/Al₂O₃ (M = Co, Mn, Cu) catalysts designed to achieve improved NSC in the presence of H₂O and CO₂ at low temperatures. Redox active metal oxides (CoO_x, MnO_x and CuO_x) act as catalysts for NO oxidation with NO_x storage occurring on the Ba phase. In the case of Pt/Co/Ba/Al₂O₃ and Pt/Mn/Ba/Al₂O₃, the combination of these two features is indeed found to confer enhanced NO_x storage capacity. Furthermore, when an H₂-plasma is applied during rich phase regeneration, the Pt/Co/Ba/Al₂O₃ catalyst exhibits high NO_x conversions ($\geq 80\%$) from 150°C to 350°C and best SO₂ resistance abilities.

2. Experimental

2.1. Catalyst preparation

Catalyst samples were prepared by incipient wetness impregnation. Taking Pt/Co/Ba/Al as an example, 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 again calcined at 500°C in air. The resulting solid was impregnated with aqueous chloroplatinic acid (H₂PtCl₆·6H₂O), dried and further calcined at 500°C for 5 h. The Pt/Ba/Al reference catalyst was prepared by the incipient wetness method according to a literature procedure [11]. The target Pt, M (M=Co, Mn, Cu) and Ba loadings were 1 wt%, 10 wt% and 20 wt%, respectively. The obtained catalysts are noted Pt/Ba/Al, Pt/10Co/20Ba/Al, Pt/10Mn/20Ba/Al and Pt/10Cu/20Ba/Al. They exhibit

BET specific surface areas of $156 \text{ m}^2 \cdot \text{g}^{-1}$, $136 \text{ m}^2 \cdot \text{g}^{-1}$, $138 \text{ m}^2 \cdot \text{g}^{-1}$ and $135 \text{ m}^2 \cdot \text{g}^{-1}$, respectively.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were performed on an X-ray diffractometer (Rigaku D-Max Rotaflex) using Cu K α radiation ($\lambda = 0.1542 \text{ nm}$) in a 2θ range of $10\text{--}80^\circ$.

Hydrogen temperature programmed reduction (H_2 -TPR) measurements were performed on a Micromeritics AutoChem II 2920 chemisorption analyzer. Samples (about 50 mg) were heated from room temperature to 800°C at a rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ under flowing 5% H_2/Ar ($50 \text{ ml} \cdot \text{min}^{-1}$). Prior to TPR, samples were pre-treated in Ar at 120°C for 1 h to remove adsorbed water.

Surface area analysis was performed according to the BET method by nitrogen adsorption at -196°C using a JW-BK 122W system. Prior to the measurements samples were outgassed overnight at 160°C under vacuum.

The platinum dispersion was determined by CO chemisorption. After in situ reduction under 5% H_2/Ar at 500°C for 1 h, the sample was flushed at the same temperature under He for 30 min. The 2% CO/He was dosed on the sample at room temperature until saturation.

Scanning transmission electron microscopy (STEM) images of the catalysts were obtained on a Tecnai F30 microscope operated at 300 Kv in the dark field.

X-ray photoelectron spectroscopic (XPS) measurements were conducted using an Al K α source operating at 10 kV and 15 mA. Binding energies were corrected for charging effects by referencing them to adventitious carbon (284.6 eV).

CO chemisorption/DRIFTS measurements were conducted to investigate the chemical state of Pt in the catalysts, and were performed using a Tensor 27 (Bruker) FTIR spectrometer equipped with

an in situ diffuse reflection chamber with CaF_2 windows and a high-sensitivity MCT detector. Catalyst samples were finely ground and placed in a stainless steel crucible in the sample chamber. After the catalysts were pretreated at 500°C in flowing 5% H_2/Ar for 1 h, samples were held at 500°C for 1 h in flowing helium (99.999%, $50\text{ ml}\cdot\text{min}^{-1}$) and then cooled to 20°C . Next, the samples were exposed to flowing 3% CO/He ($50\text{ ml}\cdot\text{min}^{-1}$) for 15 min in order to saturate them and were then flushed with flowing helium. DRIFT spectra were then recorded. All spectra reported here were collected at a resolution of 4 cm^{-1} for 30 scans.

2.3. Catalytic properties

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 (150 mg) was pretreated at 500°C in flowing 3% H_2/Ar for 1 h. NSC and NOC measurements were performed by exposing the catalyst to flowing gas containing 500 ppm NO, 8% O_2 , with 2% H_2O and 2% CO_2 present, and balance N_2 . 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), that means the data was collected only when adsorption reached saturation, the concentration of NO_2 did not change with time any more. NSC and NOC experiments were performed at a space velocity (WHSV) of $48,000\text{ ml}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$. The NSC and NOC were calculated according to the following formulae:

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

where t_s is the storage time (s), m_{cat} is the mass of the catalyst (g), $C_{\text{NO}_x, \text{in}}$ is the NO_x concentration in the feed gas (μmol) and $C_{\text{NO}_x, \text{out}}$ is the NO_x concentration in the outlet gas ($\mu\text{mol}/\text{min}$).

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

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 3% H_2/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% O_2 , 2% H_2O , 2% CO_2 and Ar as a balance. After flushing the catalyst with Ar at 200°C for 30 min, the temperature was increased to 700°C at a rate of $10^\circ\text{C}/\text{min}$ in flowing Ar.

Catalyst evaluation was performed in a dielectric-barrier discharge (DBD) reactor as described in the literature [12], loaded with ca. 150 mg of catalyst particles (20-40 mesh). The 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 consumption is defined as follows [13]:

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

where P and $t_{\text{discharge}}$ 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 specific FTIR (Sick Maihak S710). All flow conditions were operated at a

space velocity (WHSV) of $48,000 \text{ ml} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$. The lean and rich cycling was controlled by solenoid valve. Before each experiment the catalyst was pretreated in 3% H_2/Ar flow at 500°C for 1 h. Following pre-treatment, the catalysts were degreened at 500°C for 1 h in lean-rich cycles of 500ppmNO/8% O_2 /2% H_2O /2% CO_2/Ar (lean phase: 5 min) and 3% H_2 /2% H_2O /2% CO_2/Ar (rich phase: 1 min), then cooled to the measurement temperature, after which lean-rich cycling was performed until the catalyst reached a cycle-average steady state (it typically requires 3-4 h, in terms of cycles is about 30-40). NO_x was stored on the catalyst during the fuel lean phase (plasma off), after which the stored NO_x was reduced to N_2 and H_2O by the plasma during the fuel rich phase (plasma on). For calculation, at least 5 cycles were average to give a mean conversion according to the following formula:

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

The cycling parameters and gas composition used for the cycling experiments are summarized in Table 1. NO_x was determined by mass spectrometry ($m/z=30$, contributing both from NO and NO_2), N_2O and NH_3 were measured by specific FTIR (Sick Maihak S710). The N_2 selectivity is calculated assuming no other N-compounds than NO , NO_2 , N_2O , NH_3 .

The effect of SO_2 on NO_x storage and reduction was investigated without the presence of H_2O and CO_2 in the feed gases (lean: 500 ppm NO / 8% O_2 / Ar , 5 min; rich: 5% H_2/Ar , 1 min). After the catalyst reached a cycle-averaged steady state, 8 cycles were collected to determine the averaged NO_x conversions without SO_2 , and then another 8 cycles were collected to determine NO_x conversions in presence of 80 ppm SO_2 both in lean and rich phase.

3. Results

3.1. Catalyst characterization

X-ray diffractograms of Pt/Ba/Al, Pt/Co/Ba/Al, Pt/Mn/Ba/Al and Pt/Cu/Ba/Al catalysts are shown in Fig. 1. The characteristic reflections of Pt and PtO_x are not observed due to the low concentration of Pt in the catalysts and/or the small size of the Pt particles. XRD analysis shows that the main phases present in Pt/Ba/Al and Pt/M/Ba/Al ($M = \text{Co}, \text{Mn}, \text{Cu}$) are BaCO_3 (JCPDS No. 45-1471) and $\gamma\text{-Al}_2\text{O}_3$ (JCPDS No.47-1770), thereby confirming the decomposition of $\text{Ba}(\text{O}_2\text{CCH}_3)_2$ into crystalline BaCO_3 during catalyst calcination. In the case of Pt/Co/Ba/Al, besides the major BaCO_3 and $\gamma\text{-Al}_2\text{O}_3$ phases, a trace amount of the Co_3O_4 phase (JPCDS No. 74-2120) and CoAl_2O_4 spinel (JCPDS No. 44-0160) are observed. For Pt/Mn/Ba/Al, diffraction lines ascribed to BaMnO_3 (JCPDS No.26-0168) are detected, implying a strong interaction between the Ba and Mn phases. In the case of Pt/Cu/Ba/Al, diffraction lines are observed corresponding to BaCO_3 , $\gamma\text{-Al}_2\text{O}_3$, CuO (JCPDS No.45-0937) and CuAl_2O_4 (JCPDS No.01-1153). Notably, the decrease in the intensity of BaCO_3 phase for the Pt/M/Ba/Al ($M=\text{Co}, \text{Mn}, \text{Cu}$) samples is suggestive of a chemical interaction between Ba and the transition metals.

Fig. 2 shows the H_2 -TPR profiles recorded for Pt/Ba/Al, Pt/Co/Ba/Al, Pt/Mn/Ba/Al and Pt/Cu/Ba/Al. As expected the Pt/Ba/Al catalyst does not exhibit significant H_2 consumption, which reflects the low concentration of PtO_x in the sample. For Pt/Co/Ba/Al, there are three H_2 consumption peaks at 257, 433 and 743°C . The peaks at 257 and 433°C are assigned to the sequential reduction of Co^{3+} to Co^{2+} and Co^{2+} to metallic Co, respectively [14, 15]. The peak at 743°C can be attributed to reduction of the CoAl_2O_4 spinel [16] observed by XRD. For Pt/Mn/Ba/Al, an H_2

consumption peak is observed at 305°C, with a second smaller H₂ consumption peak at high temperature (>700°C). The low temperature peak is attributed to the reduction of MnO_x to MnO [10], whereas the high temperature peak can be attributed to the reduction of BaMnO₃ (as detected by XRD, see Fig. 1) [7, 10]. In the case of Pt/Cu/Ba/Al, there are two reduction peaks at 272 and 743°C. The former is assigned to the reduction of well dispersed CuO to Cu⁰ [17, 18], while the latter is associated with the reduction of CuAl₂O₄ (also detected by XRD, see Fig. 1).

DRIFTS of CO adsorbed on the reduced Pt/Ba/Al, Pt/M/Ba/Al (M = Co, Mn, Cu) catalysts was used to probe the oxidation state of Pt on the supports, the results being shown in Fig. 3. For Pt/Ba/Al, a strong peak is observed at 2068 cm⁻¹, with a shoulder at 2046 cm⁻¹. Given that the alkaline BaO/Al₂O₃ support is electron-rich, electron density is donated from the support to the Pt 5d orbital [19, 20]. As a result, upon CO chemisorption back-donation of electron density from the Pt 5d orbital to CO (2π*) is increased, leading to a red shift in the CO vibration [19]. On this basis, the band at 2046 cm⁻¹ can be assigned to CO linearly (L-CO) adsorbed on Pt sites close to Ba species, and the other band at 2068 cm⁻¹ is assigned to CO chemisorbed on Pt in contact with Al₂O₃.

When Mn or Co is added to Pt/Ba/Al, in addition to the above mentioned bands, there is a new band at 2085 cm⁻¹. Such a blue shift in the CO vibration indicates that CO is chemisorbed on positively charged Pt (Pt^{δ+}), which results from charge transfer from Pt to CoO_x or MnO_x oxide.

In the case of Pt/Cu/Ba/Al, the CO bands at 2068 and 2046 cm⁻¹ are very weak, while a strong band at 2115 cm⁻¹ is observed. This band can be ascribed to CO chemisorbed on Cu [21, 22], since as indicated by H₂-TPR, the copper oxide is easily reduced directly to Cu⁰. Based on the literature, Pt-Cu alloy formation can result, which in turn can lead to the Pt surface always enriched with Cu, similar to the observation on Pt/Fe-Ba/Al₂O₃ catalyst [19].

The surface chemical states of the samples were analyzed by XPS, the results being collected in Fig.4. Due to the overlapping peaks for Al 2p and Pt 4f, as well as the difference in concentration between Al and Pt (weight ratio of 0.007), the Pt 4f peaks are not observed. Fig.4 (A) shows the O 1s spectra of the Pt/Ba/Al and Pt/M/Ba/Al samples. By deconvoluting the O 1s signals, the distribution of oxygen species can be estimated, the results being given in Table 2. There are two kinds of oxygen species, the peak at BE = 530.5-531.4 eV being assigned to surface lattice oxygen (O_{latt}^{2-}) species, while that at BE = 532.0-532.9 eV is assigned to adsorbed oxygen species (O_{ads}) [12, 23]. As indicated in Table 2, for the Pt/Co/Ba/Al and Pt/Mn/Ba/Al samples, the ratio of O_{ads}/O_{latt}^{2-} is 0.85 and 0.52, respectively, higher than that in Pt/Ba/Al (0.10), indicating that there is an increase in the concentration of surface oxygen species after Co and Mn addition to Pt/Ba/Al. The ratio of O_{ads}/O_{latt}^{2-} is 0.04 for Pt/Cu/Ba/Al, lower than that in the Pt/Ba/Al catalyst.

Mn 2p, Co 2p and Cu 2p XPS spectra of the reduced Pt/Mn/Ba/Al, Pt/Co/Ba/Al and Pt/Cu/Ba/Al samples are shown in Fig. 4 (B). For Pt/Co/Ba/Al, there are two kinds of cobalt species, the peak at BE = 780.8 eV being assigned to Co (II), while that at BE = 781.2 eV is assigned to Co (III) [24, 25]. The ratio of Co^{2+}/Co^{3+} is 0.38. Over Pt/Mn/Ba/Al, it is evident that there are also two kinds of Mn species present; one, with a Mn 2p binding energy at 641.1 eV, is assigned to Mn^{2+} , while that at 642.8 eV is ascribed to Mn^{3+} [26, 27], the Mn^{2+}/Mn^{3+} ratio being 2.9. In the case of Pt/Cu/Ba/Al, metallic Cu (B.E = 932.5 eV) and Cu^{2+} (B.E = 934 eV) [17] are found, the ratio of Cu/Cu^{2+} being 2.0. The Cu^{2+} species may result from the slight oxidation of the metallic Cu by air during XPS measurements.

STEM observation of the Pt/Ba/Al and Pt/M/Ba/Al (M=Co, Mn, Cu) catalysts are shown in Fig. 5. It is found that the Pt nanoparticles observed as light spots are highly dispersed on the substrates.

The Pt particle size of Pt/Ba/Al, Pt/Co/Ba/Al, Pt/Mn/Ba/Al and Pt/Cu/Ba/Al catalysts is estimated to be 2.1 nm, 1.6 nm, 1.8 nm and 2.1 nm, respectively. Meanwhile, Pt dispersion was also determined by CO chemisorption. For Pt/Ba/Al, Pt/10Co/20Ba/Al, Pt/10Mn/20Ba/Al and Pt/10Cu/20Ba/Al catalysts, platinum dispersion is 11.6%, 19.8%, 17.0% and 5.7%, respectively. The order of the dispersion obtained from CO chemisorption measurements is consistent with results of STEM. It is indicated that the addition of Co and Mn contributed to better dispersion of Pt, which might facilitate catalytic oxidation of NO to NO₂ as well as NO_x reduction in rich phase.

3.2. Catalytic properties

Although many factors can influence the NO_x trapping process, the oxidation of NO to NO₂ is regarded as a key step since NO₂ is more readily adsorbed than NO [28, 29]. Fig. 6 compares the conversion of NO to NO₂ over Pt/Ba/Al and Pt/M/Ba/Al (M = Mn, Co, Cu) catalysts as a function of reaction temperature in the presence of H₂O and CO₂. On the Pt/Ba/Al catalyst, NO conversion increased with increasing temperature from 150 to 350°C, this observation being consistent with literature data which shows that Pt/Ba/Al possesses limited activity for NO oxidation, exhibiting enhanced activity at elevated temperatures only [7]. In the case of the transition metal containing catalysts (Pt/M/Ba/Al (M = Mn, Co, Cu)), NO to NO₂ oxidation activity depends on the nature of the transition metal. For the Pt/Co/Ba/Al and Pt/Mn/Ba/Al samples, much better NO oxidation performance is obtained over the examined temperature range 200–350°C, suggesting that the oxides of cobalt and manganese in Pt/Co/Ba/Al and Pt/Mn/Ba/Al contribute significantly to NOC. For the Pt/Cu/Ba/Al catalyst, lower NO to NO₂ oxidation activity is observed compared with Pt/Ba/Al. Correlating the XPS measurements with the NOC data, it can be summarized that surface adsorbed

oxygen plays an important role in NO oxidation; i.e., Pt/Co/Ba/Al and Pt/Mn/Ba/Al catalysts, containing higher amounts of surface oxygen than Pt/Ba/Al, exhibit higher NO oxidation capacity. However, Pt/Cu/Ba/Al has less surface oxygen than Pt/Ba/Al and exhibits correspondingly lower NO oxidation capacity.

NO_x storage capacity (NSC) was evaluated for the catalysts from 100 to 400°C using a continuously flowing feed of 500 ppm NO, 8% O₂, 2% H₂O and 2% CO₂. As shown in Fig. 7, the NSC of Pt/Ba/Al increases with increasing temperature, exhibiting its highest NSC value of 331.6 μmol/g at 400°C; this result can be attributed to the fact that the basic nature of BaO imparts relatively high thermal stability to the nitrate [11]. For the Pt/Co/Ba/Al and Pt/Mn/Ba/Al samples much higher NO_x storage capacity is obtained in the temperature range of interest, indicating that the presence of transition metal oxides as the NO oxidation component and barium as the chief NO_x storage component significantly improves NO_x storage capacity at all temperatures, in agreement with the findings of Xiao [30] and Wang et al. [28]. Moreover, the highest NSC value is obtained at 300°C over Pt/Co/Ba/Al and Pt/Mn/Ba/Al, the value decreasing at 400°C. This may be due to the reduced thermal stability of nitrate due to the presence of the Co and Mn oxides. In contrast, such obvious improvement in NSC is not observed for Pt/Cu/Ba/Al, this being ascribed to its poor NO oxidation activity.

After exposing the Pt/Ba/Al and Pt/M/Ba/Al (M = Mn, Co, Cu) samples to a NO/O₂/H₂O/CO₂/Ar mixture 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. 8. For the Pt/Ba/Al sample (Fig. 8(a)), an obvious NO_x desorption peak ($m/z = 30$) is observed at 490°C, accompanied by O₂ ($m/z = 32$) formation, which can be assigned to the

decomposition of nitrate or nitrite at Ba sites [12, 31]. For the Pt/M/Ba/Al catalysts, two obvious NO_x desorption peaks are observed. The first is detected at ca. 320°C, while the other appears at ca. 450°C. The higher temperature peak is accompanied by O₂ formation, which is consistent with the decomposition of adsorbed nitrites or nitrates at this temperature. The low temperature peak, which is not accompanied by the evolution of O₂, may be associated with the release of NO₂ (m/e=30) adsorbed on the transition metal oxides (CoO_x, MnO_x and CuO_x) [14, 28]. In addition, the presence of the transition metals is observed to cause a shift in the position of the high temperature NO_x desorption peak to lower temperature. Evidently, the interaction of the transition metal with Ba [28] decreases the thermal stability of nitrates associated with the Ba phase. Compared with the Pt/Ba/Al catalyst, the intensities of the NO_x desorption peaks for Pt/M/Ba/Al (M = Co, Mn, Cu) are significantly increased, which is in accordance with the finding that NSC is enhanced over the doped Pt/Ba/Al₂O₃ catalysts (see Fig 7).

NO_x storage and reduction activity was investigated under cycling conditions as shown in Fig. 9, and the NO_x concentration profiles being shown in Fig. S3 (A). For the Pt/Ba/Al catalyst the NO_x removal efficiency increases with increasing temperature and the highest conversion is obtained at 350°C, which is consistent with results reported in the literature [11]. Over the Pt/M/Ba/Al catalysts the NO_x conversion initially increases with temperature and then decreases at 350°C. Compared with Pt/Ba/Al, the Pt/Co/Ba/Al and Pt/Mn/Ba/Al catalysts display enhanced NO_x removal efficiency above 200°C. But below 200°C, the activity was not significantly enhanced. While Pt/Cu/Ba/Al displays much lower NO_x removal efficiency at all temperatures.

Catalyst performance during the lean phase was evaluated in terms of the NO_x storage efficiency (NSE), representing the amount of NO_x stored divided by the total amount of NO_x

supplied to the catalyst during the lean phase. Similarly, the rich phase performance of the catalysts was characterized in terms of the percentage of NO_x released (NRE), i.e., the amount of NO_x released during the rich phase (without reduction) divided by the total amount of NO_x stored during the lean phase (see Table 3). From the results collected in Table 3, it is clear that the NSE values of Pt/Co/Ba/Al and Pt/Mn/Ba/Al samples are higher than that of Pt/Ba/Al above 200°C. With respect to the NRE values, the NO_x release percentage is the highest for Pt/Cu/Ba/Al, which can be ascribed to an imbalance between the rates of nitrate decomposition and NO_x reduction, i.e., the rate of NO_x reduction is too slow for the liberated NO_x to be fully consumed. Due to the good oxidation ability of MnO_x , better NO oxidation and storage capacity have been achieved over Pt/Mn/Ba/Al catalyst. However, Pt/Mn/Ba/Al exhibits poorer NO_x conversions in the lean-rich cycles than Pt/Co/Ba/Al. As revealed by NO_x -TPD (Fig. 8) and DRIFTS results in our previous paper [7], the adsorbed NO_x on Mn are mainly nitrite species, which are only stable at low temperatures, and apt to decompose at temperatures higher than 300°C, which caused the decreased NSE but higher NRE, and therefore the dropped NO_x conversions. However, it is not the case for Pt/Co/Ba/Al, nitrates instead of nitrites adsorbed on the Pt/Co/Ba/Al catalyst; which exhibits higher NSE at high temperatures, and therefore better NO_x conversions are obtained. In addition, NRE values are consistently higher for the Mn- and Co-doped catalysts than for Pt/Ba/Al, which suggests that the interaction of Pt with the MnO_x and CoO_x phases (characterized by charge transfer from Pt to the oxide phases) is deleterious for the NO_x reduction activity of Pt in these catalysts. Combining the NSE and NRE data with the measured NO_x conversions during lean-rich cycling, it is clear that the enhanced NO_x removal efficiency above 200°C over Pt/Co/Ba/Al and Pt/Mn/Ba/Al catalysts results from the enhancement of NO_x storage

efficiency, while the poor activity of Pt/Cu/Ba/Al is related to its poor NO_x reduction performance during the rich phase.

Although the Pt/Co/Ba/Al and Pt/Mn/Ba/Al catalysts have enhanced NO_x storage capacity compared with Pt/Ba/Al, they exhibit poor NO_x removal efficiency at low temperatures, i.e., 150-250°C. Based on the promise of non-thermal plasma assisted catalysis, we opted to employ NTP in the rich phase to assist regeneration of the catalysts, as indicated in Fig. 10 and the NO_x concentration profiles being shown in Fig. S3 (B). From the figure it is evident that the NO_x removal efficiency of Pt/Ba/Al, Pt/Co/Ba/Al, Pt/Mn/Ba/Al and Pt/Cu/Ba/Al is enhanced over the whole temperature range. Indeed, in the case of Pt/Co/Ba/Al, the NO_x conversion is greater than 80% over the whole temperature range from 150 to 350°C. For Pt/Ba/Al the NO_x removal efficiency is still lower as compared to Pt/Co/Ba/Al and Pt/Mn/Ba/Al, this being a consequence of the comparatively lower NO_x storage capacity. Pt/Cu/Ba/Al again exhibits the poorest activity, even when NO_x reduction is H₂-plasma assisted.

Table 4 shows that the cycle-averaged lean phase NO_x storage efficiency and rich phase NO_x release values for the H₂-plasma assisted process. For Pt/Co/Ba/Al and Pt/Mn/Ba/Al, higher NSE and lower NRE is obtained compared to Pt/Ba/Al. Notably, for Pt/Co/Ba/Al the NSE value is 88.5% at 150°C, significantly higher than that obtained in the absence of the rich phase NTP (49.1%). This indicates that application of the NTP not only improves NO_x reduction activity but also promotes the release of stored NO_x, thereby increasing the extent of catalyst regeneration and improving subsequent lean phase NSE. The fact that NRE values for the Co- and Mn-doped catalysts are higher than those of the Pt/Ba/Al reference in the absence of the NTP but are lower than the reference in the presence of the NTP in the low temperature (<250°C), this may be ascribed to the reduction of PtO_x

(formed in the lean phase) to Pt (0) is faster in the presence of the NTP , and this is particularly beneficial for the Pt which is in a more highly oxidized state when Co or Mn is present (as detected by DRIFTS of CO adsorbed, see Fig. 3). From the NO_x concentration profiles under cycling being shown in Figure 10, the results show that the NO_x slip is being decreased at the start of the rich phase for the Co- and Mn- doped catalysts in the presence of the NTP than that in the absence of NTP, it indicating that the fast reduction of the PtO_x when the NTP is applied.

For Pt/Ba/Al, the comparatively higher NO_x release at 150 and 200°C can be ascribed to an imbalance between the rates of nitrate decomposition and NO_x reduction, i.e., the rate of NO_x reduction is too slow for the liberated NO_x to be fully consumed. For Pt/Cu/Ba/Al catalyst, even with the help of the rich phase NTP, the NRE value is the largest, indicating that the NO_x reduction step is still kinetically limited.

NO_x reduction product speciation during regeneration has been investigated, the results being shown in Table 3 and Table 4. The reduction of stored nitrates and nitrites leads to the formation of different nitrogen containing species, such as N₂, NH₃ and N₂O along with H₂O, as described by the following reactions:

For all samples (as shown in Table 3), NH₃ and N₂O were both observed during the regeneration phase, and at significant levels at low temperature (200°C). Formation of N₂ increased with

increasing temperatures, mainly due to N_2 formation was promoted due to reaction (4) and (5) where the formed NH_3 and N_2O continued to react further with stored nitrates or H_2 to form nitrogen, which is consistent with results reported in the literature [7].

Notably, it is clear that employing NTP improved the N_2 selectivity, especially at low temperatures, mainly due to N_2 formation was promoted due to reaction (4) and (5) where the formed NH_3 and N_2O continued to react further with stored nitrates or H_2 to form nitrogen. So employing H_2 -plasma in rich phase provides an effective means of facilitating both NO_x reduction and N_2 selectivity at low temperatures.

The effect of SO_2 on NO_x storage and reduction was also investigated. After the catalyst reached a cycle-average steady state, 80 ppm SO_2 was dosed, the results being shown in Table 5 and the NO_x concentration profiles being shown in Fig. 11. For all samples, NO_x removal efficiency was lowered in comparison with SO_2 -absent samples, being ascribed to the competitive adsorption of SO_2 with NO_x on the storage components. While, it is noted that the degree of sulfur poisoning was apparently retarded over Pt/Co/Ba/Al and Pt/Mn/Ba/Al catalysts, being consistent with previous report that Co, Mn addition could enhance the catalysts' sulfur resistance [37].

Based on the promise of non-thermal plasma assisted catalysis, NTP assisted regeneration of the catalysts were also conducted with presence of SO_2 , the data being depicted in Table 5, and NO_x concentration profiles being shown in Fig. 11. It is clear that employing NTP in rich phase enhanced the cycle-averaged NO_x conversions both with and without the presence of SO_2 in the feed gas. Moreover, the degree of sulfur poisoning was further slowed down by H_2 plasma. The best performance was achieved over Pt/Co/Ba/Al catalyst. This can be attributed to the enhanced H_2

dissociation by DBD plasma, which promoted the reduction of stored sulfates with hydrogen based on the following proposed reactions [38]:

From the foregoing, it is clear that employing H_2 -plasma in rich phase provides an effective means of facilitating sulfur desorption and regenerating of sulfated samples.

4. Discussion

The low temperature performance of NSR catalysts is becoming increasingly important in order to facilitate the implementation of highly fuel efficient lean-burn engines [32]. Model Pt/Ba/Al₂O₃ type catalysts exhibit good catalytic performance only at temperatures higher than 300°C, the low temperature activity being relatively poor. As a consequence, significant effort has been made to improve the low temperature activity of LNT catalysts. One approach is to dope transition metals such as CoO_x, MnO_x or CuO_x into Pt/Ba/Al₂O₃ [7, 10, 11, 33]. Typically the low temperature activity is enhanced to some degree, although it is still quite low below 250°C.

To design a NSR catalyst with good performance at low temperatures (<300°C), the material must in the first instance possess sufficient NSC. Due to the strong basicity of barium, Pt/Ba/Al₂O₃ shows desirable NSC above 300°C. To improve NSC at lower temperatures, in this study Pt/Ba/Al was doped with Co, Mn and Cu in an effort to exploit their excellent redox properties. Catalyst characterization data indicate that the chemical states of these doped metals are quite different. Even upon H_2 pretreatment at 500°C, Co and Mn are only partially reduced (to Co(II) and Mn(II)), as

directly proved by XPS data and indirectly suggested by H_2 -TPR. However, due to the facile reduction of CuO to Cu (0), under rich phase conditions the chemical state of copper in Pt/Cu/Ba/Al mainly corresponds to Cu (0). Analysis of the O1s region of the XPS spectra was also informative. Higher O_{ads}/O_{latt}^{2-} ratios were observed for Pt/Co/Ba/Al and Pt/Mn/Ba/Al than for Pt/Cu/Ba/Al, indicating that higher concentrations of surface oxygen species existed on the catalysts, these generally playing an important role in catalytic oxidation reactions [7]. Moreover, such doping changes the chemical environment of Pt. Pt shows an electronic interaction with doped CoO_x and MnO_x , as evidenced by the presence of $Pt^{\delta+}$. For the Pt/Cu/Ba/Al catalyst it is speculated that Pt is covered by Cu, as indicated by a strong IR band corresponding to CO adsorbed on Cu(0) instead of on Pt (see Fig. 3).

These differences in chemical states lead to different catalytic properties. Both Pt/Co/Ba/Al and Pt/Mn/Ba/Al catalysts exhibit good NO oxidation activity due to the enrichment of surface oxygen species. Accordingly, they show obviously enhanced NSC, especially for the Pt/Co/Ba/Al catalyst. The experimental data is consistent with the theoretical data, where the highest possible NSC was calculated by assuming each Ba and the dopants could store NO_x as nitrates, the results were shown in Table S1. It can be seen the Pt/Co/Ba/Al catalyst showed the highest theoretical NSC, that can be explained as nitrite/nitrate species directly stored on CoO_x and MnO_x counterparts [28], which were easily desorbed as NO_2 at ca. 320°C as shown in Fig. 8.

Although the improved NSC leads to enhanced NO_x conversion in the 250-350°C temperature range during lean-rich cycling as shown in Fig. 9, NO_x conversions below 250°C are still quite low. This is a consequence of the fact that low temperature NO_x conversion is limited by rich phase NO_x reduction rather than NO_x storage capacity. As revealed by Table 3, NRE values are consistently

higher for the Mn- and Co-doped catalysts than for Pt/Ba/Al at low temperatures (<250°C). However, by employing an H₂-plasma in the rich phase to assist NO_x reduction, NO_x conversions are greatly enhanced at low temperatures (≤250°C), especially for the Pt/Co/Ba/Al catalyst which exhibits the highest NSC. However, due to the coverage of Pt by Cu, limited NO_x reduction activity was obtained over Pt/Cu/Ba/Al, even in the plasma assisted reduction process; this is evidenced by the large rich phase NO_x release.

Regarding the mechanism of NO_x storage and reduction reaction, the reduction of the stored nitrates has been proposed to occur through the following steps [3]:

By employing Ar plasma instead of H₂/Ar plasma in rich phase, it's shown in Fig. S2 that only a small amount of N₂ was produced during the rich phase, almost all of the inlet NO_x was released during the lean phase. These results show that the sample could not be regenerated with Ar plasma, but by H₂-plasma. Non-thermal Plasma (NTPs) employed here is characterized by its high temperature electrons of several thousands of degrees, but the gas molecules/ions are close to ambient temperature. Measurements showing the temperature rise in the reactor with H₂ plasma was about 5-30°C as indicated in Fig. S1. However, the averaged electron energy of DBD plasma is 1-5 eV, which could dissociate of H₂ into H atoms (note that the binding energy of H₂ is ca. 4.4 eV).

Therefore, it is generally considered that electrons' assistance in H_2 dissociation is the major contributions from plasma. Following this key step, H adsorbed on the catalyst reduces the stored NO_x to N_2 and H_2O to regenerate the catalyst for the subsequent storage-reduction cycle. The reduction paths of stored nitrates during plasma assisted catalytic system may be ascribed as follows:

As a consequence of the improved reductant activation and its enhanced NO_x storage capacity, the Pt/Co/Ba/Al catalyst displays excellent NSR performance. The highest energy consumption obtained over Pt/Co/Ba/Al is 0.446 mmol/Wh at 250-350°C, which is comparable with literature results [13, 34]. Assuming that the concentration of NO_x in combustion gas is 500 ppm, the energy consumption equals to an energy cost of 50.05 W·h to remove completely the NO_x in 1 m³ combustion gas. Since the large amount of adsorbed NO_x on the catalysts (lean phase, plasma off) is converted to N_2 in a very short period of time in the discharge stage (rich phase, plasma on), the energy consumption is high compared with other studies in which NTP was employed during the whole process [35, 36]. Therefore, combining the high NO_x storage capacity of transition metal-containing LNT catalysts with non-thermal plasma assisted activation of H_2 is potentially promising for practical applications.

5. Conclusions

The design of LNT catalysts possessing adequate low temperature performance is becoming increasingly important in order to facilitate the implementation of highly fuel efficient lean-burn engines. As shown in this study, employing an H_2 -plasma in the rich phase provides an effective means of facilitating both NO_x release and reduction at low temperatures during lean-rich cycling. Equally important is the ability of the LNT catalyst to store NO_x at such temperatures. Doping redox active transition metal oxides into LNT catalysts provides one possible approach. In this work, Pt/Co/Ba/Al and Pt/Mn/Ba/Al were found to exhibit improved NSC, and consequently superior cycle-averaged NO_x conversion, as compared to a Pt/Ba/Al reference catalyst. In contrast, doping with Cu was found to be deleterious to both NO_x storage efficiency and NO_x reduction activity, as the probable consequence of Pt-Cu alloying. The best performances were achieved over Pt/Co/Ba/Al₂O₃ catalyst which exhibited NO_x conversions higher than 80% in the whole temperature range (150 to 350°C) and best SO₂ resistance abilities. Overall, this dual approach to optimizing low temperature LNT performance appears promising, albeit the durability of such transition metal-doped LNT catalysts under realistic operating conditions remains unproven.

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recommendations expressed herein are those of the authors and do not necessarily reflect the views of the DOE.

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Figure Captions:

Figure 1 XRD patterns of Pt/Ba/Al, Pt/Co/Ba/Al, Pt/Cu/Ba/Al and Pt/Mn/Ba/Al catalysts

Figure 2 H₂-TPR profiles obtained at a rate of 10°C/min under flowing 5% H₂/Ar

Figure 3 DRIFT spectra in the 2200-1800 cm⁻¹ region for Pt/Ba/Al, Pt/Mn/Ba/Al, Pt/Cu/Ba/Al and Pt/Co/Ba/Al after CO adsorption. Samples were kept under 3% CO/He for 15 min at 20°C and then purged with He for 20 min at 20°C

Figure 4 XPS spectra of (A) O 1s region and (B) Co 2p, Mn 2p and Cu 2p regions

Figure 5 STEM images of Pt/Ba/Al and Pt/M/Ba/Al (M=Co, Mn, Cu) catalysts

Figure 6 NO conversion to NO₂ measured under lean conditions (500 ppm NO, 8% O₂, 2% CO₂ and 2% H₂O, N₂ balance, GHSV= 30,000 h⁻¹)

Figure 7 NO_x storage capacities (NSCs) measured under lean conditions (500 ppm NO, 8% O₂, 2% CO₂ and 2% H₂O, Ar balance, 50 min storage, GHSV= 30,000 h⁻¹)

Figure 8 Evolution of NO and O₂ during NO_x-TPD experiments. The samples were kept under 500 ppm NO/8%O₂/2%H₂O/2%CO₂/Ar for 50 min at 200°C. After Ar purging at 200°C for 30 min, the temperature was increased to 700°C at 10°C/min under Ar flow.

Figure 9 NO_x conversion under cyclic lean-rich conditions at different temperatures. Lean (5 min): 500ppm NO, 8% O₂, 2% CO₂ and 2% H₂O, Ar balanced; Rich (1 min): 3% H₂, 2% CO₂ and 2% H₂O, Ar as balance, GHSV= 30,000 h⁻¹.

Figure 10 Plasma-assisted NO_x conversion during lean/rich cycling at different temperatures (lean phase: 500ppmNO/8%O₂/2%H₂O/2%CO₂/Ar, duration: 5 min; rich phase: 3%H₂/2%H₂O/2%CO₂/Ar, non-thermal plasma-assisted, duration: 1 min)

Figure 11 NO_x concentration profiles during lean-rich cycling at 200°C with/ without SO₂ in the

presence or absence of H₂-plasma in rich phase

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

Parameter	Lean	Rich	Specify quality	Supplier	Flow rate /ml
Duration (s)	300	60	-	-	-
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	-	2%NO/Ar	Dalian Special Gases Co., Ltd Gas station of	3
O ₂ (%)	8	-	99.99%	Dalian Institute of Chemical Physics Gas station of	9.6
H ₂ (%)	-	2	5%H ₂ /Ar	Dalian Institute of Chemical Physics	48
H ₂ O (%)	2	2	-	-	2.4
CO ₂ (%)	2	2	99.99%	Dalian Institute of Chemical Physics Gas station of	2.4
Ar (%)	Balance	Balance	99.99%	Dalian Institute of Chemical Physics	81.0 (lean) 45.6 (rich)

Table 2 Binding energies (eV) of O_{ads} and O_{latt}^{2-}

Catalysts	Peak position(eV)		$O_{\text{ads}}/O_{\text{latt}}^{2-}$ (%)
	O_{latt}^{2-}	O_{ads}	
Pt/Ba/Al	531.3	533.0	10
Pt/10Co/20Ba/Al	531.1	532.6	85
Pt/10Mn/20Ba/Al	530.9	532.6	52
Pt/10Cu/20Ba/Al	531.5	533.0	4

Table 3 Comparison of NO_x storage, release and selectivity of N₂, NH₃ and N₂O during NO_x storage/reduction cycling

Temperature (°C)	Catalyst	NO _x conversion (%)	NSE (%)	NRE* (%)	N ₂ selectivity (%)	N ₂ O selectivity (%)	N ₂ O selectivity (%)
150	Pt/Ba/Al	43.82	45.42	3.53	52.08	25.10	22.82
	Pt/Co/Ba/Al	42.09	49.12	14.32	61.99	16.63	21.38
	Pt/Mn/Ba/Al	43.30	48.53	10.77	60.73	16.17	23.10
	Pt/Cu/Ba/Al	13.28	29.36	54.76	17.17	0	82.83
200	Pt/Ba/Al	47.12	48.36	2.56	66.05	21.22	12.73
	Pt/Co/Ba/Al	51.28	57.53	10.87	68.8	23.40	7.80
	Pt/Mn/Ba/Al	38.75	43.66	11.24	71.62	15.48	12.90
	Pt/Cu/Ba/Al	21.75	30.87	29.54	72.41	0	27.59
250	Pt/Ba/Al	60.00	62.87	4.56	71.67	20	8.33
	Pt/Co/Ba/Al	96.98	100.00	3.02	73.19	20.62	6.19
	Pt/Mn/Ba/Al	77.77	81.19	4.21	76.85	19.29	3.86
	Pt/Cu/Ba/Al	38.99	55.88	30.23	84.61	0	15.39
300	Pt/Ba/Al	76.00	78.77	3.51	90.79	6.58	2.63
	Pt/Co/Ba/Al	98.65	100.00	1.35	88.85	2.03	9.12
	Pt/Mn/Ba/Al	97.00	98.64	1.67	95.88	2.06	2.06
	Pt/Cu/Ba/Al	46.84	69.01	32.13	93.6	0	6.40
350	Pt/Ba/Al	80.07	81.24	1.53	93.75	1.25	5
	Pt/Co/Ba/Al	90.90	100.00	9.10	95.6	0	4.40
	Pt/Mn/Ba/Al	95.00	97.53	2.60	95.79	1.05	3.16
	Pt/Cu/Ba/Al	17.90	78.37	77.16	83.24	5.59	11.17

*(NO_x released in rich purge/NO_x stored in lean phase)*100%

Table 4 Comparison of NO_x storage, release and selectivity of N₂, NH₃ and N₂O during NO_x storage/reduction cycling with application of H₂-plasma in rich phase

Temperature (°C)	Catalyst	NO _x conversion (%)	NSE (%)	NRE (%)	N ₂ selectivity (%)	N ₂ O selectivity (%)	N ₂ O selectivity (%)
150	Pt/Ba/Al	51.00	57.76	11.72	85.78	8.89	5.33
	Pt/Co/Ba/Al	83.70	88.49	5.42	91.44	4.28	4.28
	Pt/Mn/Ba/Al	61.00	63.98	4.66	87.15	4.28	8.57
	Pt/Cu/Ba/Al	24.00	33.92	29.24	97.02	0	2.98
200	Pt/Ba/Al	56.00	62.10	9.83	88.20	3.93	7.87
	Pt/Co/Ba/Al	93.40	96.82	3.53	92.84	3.58	3.58
	Pt/Mn/Ba/Al	70.00	72.64	3.63	86.98	1.63	11.38
	Pt/Cu/Ba/Al	34.00	40.58	16.21	95.81	0	4.19
250	Pt/Ba/Al	78.00	80.00	2.50	92.31	5.13	2.56
	Pt/Co/Ba/Al	98.91	100.00	1.65	94.95	1.01	4.04
	Pt/Mn/Ba/Al	86.00	88.09	2.37	94.21	0	5.79
	Pt/Cu/Ba/Al	41.00	54.43	24.68	92.67	0	7.33
300	Pt/Ba/Al	87.00	88.30	1.47	93.15	1.14	5.71
	Pt/Co/Ba/Al	98.78	100.00	1.30	95.96	1.01	3.03
	Pt/Mn/Ba/Al	97.00	98.36	1.38	95.86	0	4.14
	Pt/Cu/Ba/Al	52.00	71.62	27.40	94.21	0	5.79
350	Pt/Ba/Al	92.00	93.10	1.18	93.5	1.08	5.42
	Pt/Co/Ba/Al	98.62	100.00	1.38	95.94	2.03	2.03
	Pt/Mn/Ba/Al	96.00	97.94	1.98	96.86	0	3.14
	Pt/Cu/Ba/Al	63.00	80.74	21.97	93.63	0	6.37

Table 5 Comparison of NO_x conversions with / without SO₂ during NO_x storage/reduction cycling with / without application of H₂-plasma in rich phase

Catalysts	Conditions	NO _x conversions with/without SO ₂ / %
Pt/Ba/Al	Catalysis only	54.8 / 73.6
	Plasma-assisted	61.6 / 74
Pt/Co/Ba/Al	Catalysis only	76.2 / 93
	Plasma-assisted	93.9 / 98.5
Pt/Mn/Ba/Al	Catalysis only	56.8 / 68.6
	Plasma-assisted	80.6 / 86.7
Pt/Cu/Ba/Al	Catalysis only	37.5 / 50.1
	Plasma-assisted	73.8 / 79.6

Fig. 1

Fig. 2

Fig. 3

Fig. 4 (A)

Fig. 4 (B)

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig.11