Pt-free, non-thermal plasma-assisted NO_x storage and reduction over M/Ba/Al₂O₃ (M = Mn, Fe, Co, Ni, Cu) catalysts

Zhao-shun Zhang^a, Mark Crocker^b, Bing-bing Chen^a, Zhi-feng Bai^a, Xin-kui Wang^a, Chuan Shi^{a,*}

^aLaboratory of Plasma Physical Chemistry, Dalian University of Technology, Dalian, China

^bCenter for Applied Energy Research, University of Kentucky, Lexington, KY 40511, USA

* Corresponding author. Tel.: +86 411 84986083;

E-mail address: chuanshi@dlut.edu.cn (Chuan Shi).

Abstract

Based on their high NO_x storage capacities (NSCs), a series of M/Ba/Al (M= Mn, Fe, Co, Ni, Cu) catalysts were evaluated in NO_x storage-reduction catalysis. Although the M/Ba/Al catalysts exhibited high NSC values, they exhibited much lower activity during lean-rich cycling compared with a traditional Pt/Ba/Al catalyst, indicating that regeneration of stored NO_x is the rate limiting step for the M/Ba/Al samples. By employing an H₂-plasma in the rich phase to assist reduction of the stored NO_x, the NO_x conversion was greatly improved, especially at low temperature.

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

1. Introduction

The negative impact on the atmosphere, environment and human health caused by NO_x (NO , NO_2) has led to the development of a variety of technologies aimed at the control of nitrogen oxide emissions. Of these, NO_x storage/reduction technology is currently regarded as a commercially viable solution for the control of NO_x from both mobile and point sources [1, 2]. The NO_x storage and reduction (NSR, otherwise known as lean NO_x trap (LNT)) concept was originally developed by Toyota and is considered to be a particularly appropriate means to remove NO_x from light duty lean-burn engines [3]. A typical NSR catalyst, as exemplified by the model system Pt/Ba/Al (PBA), exhibits good catalytic performance at temperatures of around 300°C and higher due to the strong surface basicity of BaO, which imparts relatively high thermal stability to the stored NO_x (present as nitrate and nitrite) [4]. However, the low temperature activity of NSR catalysts is especially important for light duty diesel applications, typical engine-out temperatures in the FTP-75 (the U.S. Federal Test Procedure used to certify vehicle emissions and fuel economy) being about $180\text{--}350^\circ\text{C}$ [5]. In addition, NSR catalysts require the use of expensive precious metals such as Pt, Pd and Rh [6-8], which typically must be present in high concentrations in order to obtain satisfactory activity at low temperature. The high price of these metals provides a strong impetus to seek more economical approaches to catalytic NO_x removal.

Most of the NSR catalysts contain barium and platinum. Recently, Li et al. [9] proposed a perovskite-based, Pt free lean NO_x trap (LNT) catalyst shows promising NO_x storage capacities. However, it is limited by its regeneration during the rich phase. Malpartida et al. [10] compared the Pt/Ba/Al and Pt-free NSR catalysts, and found that that the platinum is necessary for the regeneration

in the rich phase. So it is challenging to find less expensive material that possesses high activity for the NO_x storage and reduction. In addition to focusing on searching for ideal materials, the high performance of the NSR catalyst can also be achieved through optimizing the lean/rich cycles.

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 LaMn_{0.9}Fe_{0.1}O₃ catalyst [11]. Aside from perovskites, a number of simple transition metal oxides with strong oxidation ability and low expense have attracted attention for LNT applications, especially manganese, iron, cobalt, nickel, and copper oxides [4, 12-16]. Xiao et al. found that Mn/Ba/Al exhibited good catalytic activity for NO oxidation-storage under lean burn conditions [17]. Vijay [18, 19] and Wang [20] et al. found that the addition of Co led to high NO oxidation activity for Pt/Ba/Al₂O₃ catalysts, and accelerated nitrite/nitrate formation on Ba sites. Courtois et al. [21] found that Fe addition to Pt/Ba/Al₂O₃ led to increased NO_x storage capacity, and Yamazaki et al. also pointed out that the Fe component inhibits the growth of BaSO₄ particles formed on the Pt/Ba/Fe/Al₂O₃ catalyst in the presence of SO₂ [12]. In addition, Wang et al. found that a Cu/Ba/bauxite catalyst showed superior NSR performance to Pt/Ba/Al₂O₃, even without the addition of platinum [22]. Similarly, the effect of adding Ni to Pt/Al₂O₃ and Pt/Ba/Al₂O₃ was investigated by Yamazaki et al., NO_x conversions over the fresh Ni based catalysts with or without the Ba-compound were nearly equal to that of the fresh Pt/Ba/Al₂O₃ catalyst and nearly equal or even slightly higher than that of the fresh Pt/Al₂O₃ catalyst at every temperature tested [12].

In the present paper, a series of Pt-free M/Ba/Al₂O₃ (M= Mn, Fe, Co, Ni, Cu) catalysts were investigated for application in NSR catalysis. Due to the lack of precious metal, the activity of the

M/Ba/Al₂O₃ was limited by its regeneration during the rich phase. In order to overcome this limitation, we attempted to employ a non-thermal plasma (NTP) [11, 23-28] to facilitate rich-phase regeneration of the catalyst. Due to the activation of the reductant by NTP, a combination of plasma and catalysis was expected to result in regeneration of the LNT catalyst.

2. Experimental

2.1. Catalyst preparation

Pt/Ba/Al and M/Ba/Al (M= Mn, Fe, Co, Ni, Cu) catalyst samples were prepared by incipient wetness impregnation. Taking Mn/Ba/Al as an example, γ -Al₂O₃ was impregnated with an aqueous solution of Ba(O₂CCH₃)₂, dried and calcined at 500°C for 5 h in air. The Ba-loaded γ -Al₂O₃ was subsequently impregnated with aqueous Mn(NO₃)₂, 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 [29]. The target Pt, M (M= Mn, Fe, Co, Ni, Cu) and Ba loadings were 1 wt.%, 5 wt.% and 10 wt.%, respectively.

2.2. Catalyst characterization and Catalyst evaluation

Powder X-ray diffraction (XRD) measurements were performed on an X-ray diffractometer (Rigaku D-Max Rotaflex) using Cu K α radiation (λ = 0.1542 nm), operating at 40 kV, 30 mA and at a scanning rate of 2°/min, step size = 0.04° in a 2 θ range of 10-80°. The actual metal content in the catalysts was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 2000DV).

Catalyst evaluation was performed in the dielectric-barrier discharge (DBD) reactor as

described in the literature [11], loaded with ca. 500 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 is 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 [27]:

$$\text{Energy efficiency (mmol NO}_x\text{/W} \cdot \text{h)} = \frac{NO_{x,in} \times NO_{x,conversion}}{P \times t_{discharge}} \quad (1)$$

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 $14,400 \text{ ml} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$. Before each experiment the catalyst was pretreated in 2% H_2/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. Fig. 1 shows schematically the working principle of the plasma-assisted NO_x storage and reduction process. Briefly, the NO_x is first stored on the catalyst during the fuel lean phase (plasma off) and then the stored NO_x is reduced to N_2 and H_2O by the plasma during the fuel rich phase (plasma on). The NO_x concentration was averaged over 5 cycles to give a mean conversion according to the following formula:

$$\text{NO}_x \text{ conversion} = \frac{\int_0^t (\text{NO}_{x,in} - \text{NO}_{x,out}) dt}{\int_0^t \text{NO}_{x,in} dt} \times 100\% \quad (2)$$

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

2.3. NSC and NO to NO₂ oxidation activity experiments

NO_x storage capacity (NSC) and NO to NO₂ oxidation activity experiments were performed in a microreactor using a chemiluminescence NO_x analyzer (Ecotech ML9841AS) as the detector according to a literature procedure [4]. Prior to both sets of measurements, the catalyst (150 mg) was pretreated at 500°C in flowing 2% H₂/Ar for 1 h. NSC and NO to NO₂ oxidation activity measurements were then performed by exposing the catalyst to flowing gas containing 500 ppm NO, 8% O₂, and balance N₂. The NO_x concentration was followed by chemiluminescence NO_x analyzer. NSC was then estimated by the integration of the recorded profile for the first 50 min. NO to NO₂ oxidation activity 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 NO to NO₂ oxidation activity experiments were operated at a space velocity (WHSV) of 14,400 ml·g_{cat}⁻¹·h⁻¹. The NSC and NO to NO₂ oxidation activity were calculated according to the following formulae:

$$\text{NSC} = \frac{\int_0^{t_s} (\text{NO}_{x, \text{in}} - \text{NO}_{x, \text{out}}) dt}{m_{\text{cat}}} \quad (3)$$

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

$$\text{NO to NO}_2 \text{ oxidation activity} = \frac{\text{NO}_{2, \text{out}}}{\text{NO}_{\text{in}}} \times 100\% \quad (4)$$

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 2% 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. 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 14,400 ml·g_{cat}⁻¹·h⁻¹.

3. Results and discussion

3.1. Catalyst characterization

The elemental compositions of the catalysts were determined by ICP-AES measurements, respectively, the results being collected in Table 2. X-ray diffraction (XRD) analysis (Fig. 2) showed that the main phases present in Pt/Ba/Al and M/Ba/Al (M= Mn, Fe, Co, Ni, Cu) 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 and PtO₂ were not observed due to the low concentration of Pt in the Pt/Ba/Al catalyst and/or the small size of the Pt particles. In addition, a spinel phase (MnAl₂O₄, FeAl₂O₄, CoAl₂O₄, NiAl₂O₄ and CuAl₂O₄) was observed for the transition metal containing samples (as shown in Fig. 2), indicating that the transition metal and aluminum oxides reacted to form the spinel during calcination. Furthermore, the presence of crystalline MO_x (M= Mn, Fe, Co, Ni, Cu) cannot be ruled out, given the detection limit for XRD measurements. Notably, for the Mn/Ba/Al sample, besides the BaCO₃, Al₂O₃ and MnAl₂O₄ phases, trace amounts of the BaMnO₃ phase (JCPDS No. 29-0770) were observed in the XRD patterns, implying a strong interaction between the Ba and Mn phases; it could

enhance the proximity between the NO oxidation sites (Mn) and the NO_x storage sites (Ba), which is known to be a key factor for the fast NO_x spillover and storage, this might be expected to lead to an improvement of NO_x storage capacity [4].

3.2. NO oxidation capacity

Although many factors can influence the trapping process, the oxidation of NO to NO₂ is regarded as a key step since NO₂ is more readily adsorbed than NO [20, 30]. Fig. 3 compares the conversion of NO to NO₂ over Pt/Ba/Al and M/Ba/Al (M= Mn, Fe, Co, Ni, Cu) catalysts at the end of the storage process (i.e., when the catalyst was fully saturated with NO_x), at which point the NO₂/NO_x ratio reached a steady state. On the Pt/Ba/Al catalyst, NO conversion increased with increasing temperature from 200°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 [20]. In the case of the transition metal containing catalysts (M/Ba/Al (M= Mn, Fe, Co, Ni, Cu)), NO to NO₂ oxidation activity depended on the nature of the transition metal. For the Co/Ba/Al and Mn/Ba/Al samples, excellent NO oxidation performance was obtained over the full temperature range examined (200-350°C). Indeed, the NO conversion for Mn/Ba/Al catalyst 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). For the Ni/Ba/Al catalyst, although it displayed low NO to NO₂ oxidation activity at low temperatures (<10% NO conversion at 200°C), notably, NO oxidation activity increased substantially as the temperature was increased from 200 to 300°C, the conversion increasing from 3.6% to 44.4%. For the Mn, Co, and Ni containing samples, NO oxidation

performance was in line with literature data which show that these transition metals are generally an excellent catalyst for NO oxidation [18-20, 31-35]. Finally, in the case of the Fe/Ba/Al and Cu/Ba/Al samples, both showed poor NO oxidation performance over the full operating temperature range (200-350°C).

3.3. NO_x storage capacity

NSC measurements were performed for M/Ba/Al (M = Mn, Fe, Co, Ni, Cu) from 200 to 350°C, and the results compared with a traditional LNT catalyst of the Pt/Ba/Al type. As shown in Fig. 4, the NSC of the Pt/Ba/Al catalyst is relatively low below 250°C (< 180 µmol/g) although it increased with increasing temperature, exhibiting its highest NSC value of 255.4 µmol/g at 350°C; this result can be attributed to the fact that NO_x is mainly stored as nitrate on BaO, the kinetics of NO oxidation to NO₂ being favored at the higher temperature. Furthermore, the basic nature of BaO imparts relatively high thermal stability to the nitrate [29]. Compared with Pt/Ba/Al, it is clear that the Mn, Co, and Ni containing samples possess much higher NO_x storage capacity from 200 to 350°C. Mn/Ba/Al and Co/Ba/Al in particular, exhibit relatively high NSC even at 200°C, indicating that the presence of the transition metal 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 Xiao [17] and Wang et al. [20]. The Fe/Ba/Al sample displayed the lowest NSC at all temperatures, mainly due to its poor NO oxidation performance as depicted in Fig. 3. Notably, although Cu/Ba/Al shows poor NO oxidation performance over the full operating temperature range (as shown in Fig. 3), it still showed higher NO_x storage capacity than Pt/Ba/Al. In the NO_x storage process, the proximity between the NO oxidation sites and the NO_x storage sites exerts a significant impact on the trapping

capacity. Tanaka et al. found that for copper loadings of < 5 wt. %, alumina-supported copper oxide is present in a highly dispersed, amorphous state on the Al₂O₃ support [36]. Likewise, in this work, the presence of crystalline CuO was not detected by XRD (the Cu loading being 2.91 wt.% according to ICP-AES), implying that the CuO is highly dispersed on the support surface. Given that the excellent NO_x storage capacity of the Cu/Ba/Al catalyst cannot be attributed to its NO oxidation activity, it follows that close proximity of the NO oxidation sites (Cu) and the NO_x storage sites (Ba) may be responsible, this being a key factor for efficient NO_x storage [13, 37]. Specifically, close proximity of the Cu and Ba sites would favor spillover of NO and NO₂ from Cu to the neighboring Ba sites, resulting in significant NO_x storage capacity (as compared to Pt/Ba/Al, for example), this being in agreement with the findings of Wang et al. [22].

In order to exclude the influence of surface area, the NSC per specific area of various samples were calculated, the results being shown in Table 3. The BET surface areas of the catalysts decreased slightly with respect to the bare alumina upon Pt/transition metal and barium incorporation, indicative of some degree of pore filling. The NSC per specific area data span a relatively narrow range, as might be expected given that the catalysts are far from saturation at this relatively short storage time. However, several trends are apparent, namely that: (i) Mn/Ba/Al and Co/Ba/Al displays superior NSC to the other catalysts at all temperatures; (ii) all of the catalysts reach their maximum NSC at 350°C; and (iii) Fe/Ba/Al shows the lowest NSC of all the samples over the full temperature range 200-350°C.

3.4. Thermal stability of the stored NO_x

After exposing the Pt/Ba/Al and M/Ba/Al (M = Mn, Fe, Co, Ni, Cu) samples to a NO/O₂/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. 5. For the Pt/Ba/Al sample (Fig. 5(a)), two obvious NO_x desorption peaks ($m/z = 30$) were observed at 308°C and 484°C (note that the $m/z = 30$ signal can result from desorption of NO and/or NO₂ due to the fragmentation of NO₂ to NO in the mass spectrometer [38]). The low temperature peak can be attributed to NO_x adsorbed on the Al₂O₃ support and/or NO_x species nearby metal sites [39], while the latter peak, which was accompanied by O₂ ($m/z = 32$) formation, can be assigned to the decomposition of nitrate or nitrite at Ba sites [11, 40]. Notably, almost no NO₂ ($m/z = 46$) was observed during TPD of the different samples, a fact which can be attributed, at least in part, to NO being the favored species with respect to the thermodynamic equilibrium between NO and NO₂ at high temperatures ($\geq 400^\circ\text{C}$) [41].

In the case of the transition metal containing catalysts (M/Ba/Al (M= Mn, Fe, Co, Ni, Cu)), strikingly different results were obtained depending on the metal. For Mn/Ba/Al, Co/Ba/Al and Ni/Ba/Al samples (Fig. 5(b), (d) and (e)), 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. 310°C. Based on results reported in the literature, it is reasonable to ascribe the broad peak at high temperature to the overlap of different adsorbed NO_x species on Ba (highly dispersed and bulk Ba(NO₃)₂) [42]. 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 Mn, Co or Ni; specifically, deconvolution of the TPD profiles reveals the presence of a desorption maximum around 540-570°C (Fig. 5(b), (d) and (e)), close to the temperature at which bulk Ba(NO₃)₂ decomposes [43]. According to work by Lauterbach et al. [19], the addition of Co to the NSR catalyst can increase the number of sites available for the

oxidation of NO to NO₂; consequently, NO₂ spillover to the Ba sites may be enhanced, with increased formation of bulk Ba(NO₃)₂. Similarly, high NO oxidation activity was observed for the Mn/Ba/Al, Co/Ba/Al and Ni/Ba/Al samples during NO oxidation experiments (Fig. 3), such that the formation of bulk barium nitrate may be favored. Consequently, NO_x desorption peaks ($m/z = 30$) were observed at high temperatures (540-570°C).

In the case of the Fe/Ba/Al and Cu/Ba/Al samples (Fig. 5(c) and (f)), two obvious NO_x desorption peaks were observed at 328 and 555°C for the former and 328 and 578°C for the latter. Based on the results of NO_x desorption from Pt/Ba/Al, it is reasonable to ascribe the peak at low temperature to NO_x adsorbed on the Al₂O₃ support and/or species adsorbed nearby metal sites, and the high temperature peak to NO_x adsorbed on BaO. However, compared with NO_x desorption from Pt/Ba/Al, the desorption peaks corresponding to NO_x adsorbed on Ba shifted to higher temperatures due to the incorporation of Fe and Cu, indicating that the addition of Fe and Cu results in an increase in the stability of the stored nitrate.

3.5. NO_x storage and reduction

NO_x storage and reduction performance were investigated under cycling conditions over M/Ba/Al (M = Mn, Fe, Co, Ni, Cu), as well as over Pt/Ba/Al for comparison; results are shown in Fig. 6. 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 at 350°C, which is consistent with results reported in the literature [11, 29]. Compared with Pt/Ba/Al, the M/Ba/Al (M = Mn, Fe, Co, Ni, Cu) samples displayed much lower NO_x removal efficiency at all temperatures. The highest NO_x removal efficiency for Ni/Ba/Al was observed at 350°C but was only 46.7%, i.e.,

significantly lower than that obtained over Pt/Ba/Al at the same temperature. As mentioned above, the Mn/Ba/Al, Co/Ba/Al, Ni/Ba/Al and Cu/Ba/Al samples display much higher NSC values than the Pt/Ba/Al catalyst over the whole temperature range studied, which contrasts with their poor catalytic performance during lean-rich cycling. Given that the poor performance cannot be attributed to its NO_x storage capacity, it must instead be related to its NO_x reduction properties, i.e., the efficiency with which NO_x is released from the transition metal containing catalysts and reduced [11].

3.6. 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 ($m/z = 28$) 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 [11]. 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 [11, 29]. For the Mn-, Fe- and Cu-containing samples (Fig. 7(b), (c) and (f)), the main N₂ formation peaks were observed at ~ 400°C. In the case of the Co- and Ni-containing samples (Fig. 7(d) and (e)), the main N₂ formation peaks were observed at 316°C and 257°C, respectively. It is notable that the signal maximum corresponding to the N₂ formation did not line up with the maximum observed for H₂ consumption for the transition metal containing samples. 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 H₂-TPSR from 200 to 350°C (in contrast to Pt/Ba/Al), i.e., before the main reduction maximum. Comparing the reduction behavior of the Pt/Ba/Al and M/Ba/Al (M = Mn, Fe, Co, Ni, Cu) catalysts, it is clear that reduction of the stored nitrates or nitrites requires much higher temperatures over M/Ba/Al than over the Pt/Ba/Al catalyst. This explains the poor performance of M/Ba/Al during lean-rich cycling experiments, i.e., catalyst performance was limited by its ability to be regenerated during the rich phase, as well as the inability of the transition metal sites to reduce the released NO_x.

3.7. Non-thermal plasma-assisted catalysis

As noted above (Fig. 4), it was found that transition metal containing LNT catalysts (Mn/Ba/Al, Co/Ba/Al, Ni/Ba/Al and Cu/Ba/Al) possess relatively high NO_x storage capacity at temperatures in the range 200-350°C. However, due to limitations with respect to rich phase regeneration activity (as shown in Fig. 7), the transition metal containing catalysts show relatively low activity in NO_x storage-reduction catalysis. Based on the promise of non-thermal plasma (NTP) assisted chemistry [11, 23, 27, 44, 45], we opted to employ NTP in the rich phase to regenerate the catalysts. In the discharge stage, the regeneration of adsorbed NO_x was investigated using 2% H₂/Ar as the discharge gas (i.e., a H₂-plasma was used). The input electric discharge power being fixed at 1.8 W in the present study. Fig. 8 summarizes the corresponding cycle-averaged NO_x conversions as a function of temperature. As indicated in Fig. 8, the NO_x removal efficiency over the temperature range 200-350°C was greatly enhanced compared with the performance obtained in the catalysis-only condition (Fig. 6) for all samples. Indeed, cycle-averaged NO_x conversions were higher than 80% in the temperature range 200-350°C (with the exception of the Cu/Ba/Al sample at 200°C). This

indicates that the stored NO_x on M/Ba/Al (M = Mn, Fe, Co, Ni, Cu) could be reduced by the H_2 -plasma, and that the catalysts were effectively regenerated during rich phase operation.

In the case of Pt/Ba/Al, under rich-burn conditions, the released NO_x from barium nitrates are reduced to N_2 on the Pt surface by H_2 from the rich exhaust gas. The reduction of stored nitrates with hydrogen has been found to occur by the following reactions[3, 46]:

In H_2 -plasma, 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:

In addition, it is considered that in plasma, the decomposition of NO may follows the following reactions [27]:

Notably, from the comparison of the reaction paths (catalysis only/plasma assisted catalysis) for all samples (Pt/Ba/Al and M/Ba/Al (M = Mn, Fe, Co, Ni, Cu)) 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 activity associated with the plasma. Benefitting from this improved reductant activation and enhanced NO_x storage capacity, M/Ba/Al (M = Mn, Fe, Co, Ni, Cu) samples displayed excellent NSR performance.

Consequently, the combination of high NO_x storage capacity and the use of the H₂-plasma for rich phase catalyst regeneration resulted in greatly improved NO_x conversion performance. Notably, although the Fe/Ba/Al catalyst displayed the poorest NO_x storage capacity compared with the other samples in the NO_x storage capacity experiments (Fig. 4), it showed similar NO_x removal efficiency to Pt/Ba/Al during non-thermal plasma-assisted lean/rich cycling. Roland et al. found that the introduction of ferroelectric and catalytically active materials into the discharge zone of NTP reactors considerably enhances the local electric fields in the vicinity of the edges and corners of the packed-bed grains, consequently, the energy gained by the electrons on their mean free pathway is

significantly increased, resulting in a modified energetic pattern of the reactive species and would results in a considerably higher conversion efficiency [47] In the case of the Cu/Ba/Al sample, relatively low NO_x removal efficiency (55%) was obtained at 200°C. This may be due to the poor thermal stability of adsorbed NO_x species on Cu/Ba/Al; as shown in Fig. 5(f), significant NO_x desorption was observed from Cu/Ba/Al at low temperatures (< 350°C) during TPD compared with the other catalysts. 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 [29]. During the plasma-assisted rich phase, the catalyst surface temperature is increased significantly (typically by 50-100°C, based on measurements during the cycling experiments). Hence, due to the poor thermal stability of adsorbed NO_x on Cu/Ba/Al, significant NO_x slip was generated (i.e., NO_x release without reduction), which reduced the overall NO_x removal efficiency. In the present study, the highest energy efficiency was obtained for the Co/Ba/Al and Mn/Ba/Al samples. In both cases, 100% NO_x conversion was obtained during plasma-assisted NO_x storage and reduction over the full operating temperature range of 200-350°C, the corresponding energy efficiency being 0.446 mmol NO_x/ W·h. Assuming that the concentration of NO_x in exhaust is 500 ppm, the energy efficiency equals to an energy cost of 50.05 W·h to remove the NO_x in 1 m³ exhaust. It is equivalent to an adiabatic heating of the exhaust by ca. 138°C (assuming that the specific heat and gas density of exhaust is 1.005 kJ/kg·°C and 1.29 kg/m³ respectively). Thus the energy consumption of plasma assisted NSR process is rather high compared with conventional thermal catalytic process. As previously, the input electric discharge power or the size of DBD reactor may not be appropriate to the plasma assisted catalysis process in the present paper, resulting lower energy efficiency during plasma assisted NSR process.

4. Conclusions

A series of Pt-free, transition metal containing M/Ba/Al (M = Mn, Fe, Co, Ni, Cu) LNT catalysts were 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 M/Ba/Al catalysts 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 M/Ba/Al catalysts, NO_x conversion was greatly improved, especially in the low temperature region. These results indicate that by combining the high NO_x storage capacity of the transition metal containing LNT catalysts with non-thermal plasma-assisted activation of the reductant, superior NO_x removal efficiency can be achieved over a broad temperature range.

Acknowledgement

The work was supported by the National Natural Foundation of China (Nos. 21373037, 21073024 and 21176037). MC thanks the National Science Foundation and the U.S. Department of Energy (DOE) for financial support under award no. CBET-1258742. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the DOE.

References

- [1] M. Jablonska, A.E.P. Gimeno, A. Wegrzyn, L. Chmielarz, *Acta Geodynamica Et Geomaterialia*, 11 (2014) 175-186.
- [2] K.S. Kabin, R.L. Muncrief, M.P. Harold, *Catal. Today*, 96 (2004) 79-89.
- [3] G. Liu, P.-X. Gao, *Catalysis Science & Technology*, 1 (2011) 552-568.
- [4] Z.-s. Zhang, B.-b. Chen, X.-k. Wang, L. Xu, C. Au, C. Shi, M. Crocker, *Appl. Catal. B: Environ.*, 165 (2015) 232-244.
- [5] T.W. Chan, E. Meloche, J. Kubsh, R. Brezny, *Environ. Sci. Technol.*, 48 (2014) 6027-6034.
- [6] S.S. Chaugule, A. Yezerets, N.W. Currier, F.H. Ribeiro, W.N. Delgass, *Catal. Today*, 151 (2010) 291-303.
- [7] S. Salasc, M. Skoglundh, E. Fridell, *Appl. Catal. B: Environ.*, 36 (2002) 145-160.
- [8] A. Amberntsson, E. Fridell, M. Skoglundh, *Appl. Catal. B: Environ.*, 46 (2003) 429-439.
- [9] X.-G. Li, Y.-H. Dong, H. Xian, W.Y. Hernandez, M. Meng, H.-H. Zou, A.-J. Ma, T.-Y. Zhang, Z. Jiang, N. Tsubaki, P. Vernoux, *Energy & Environmental Science*, 4 (2011) 3351-3354.
- [10] I. Malpartida, M.O. Guerrero-Perez, M.C. Herrera, M.A. Larrubia, L.J. Alemany, *Catal. Today*, 126 (2007) 162-168.
- [11] C. Shi, Z.S. Zhang, M. Crocker, L. Xu, C.Y. Wang, C.T. Au, A.M. Zhu, *Catal. Today*, 211 (2013) 96-103.
- [12] K. Yamazaki, T. Suzuki, N. Takahashi, K. Yokota, M. Sugiura, *Appl. Catal. B: Environ.*, 30 (2001) 459-468.
- [13] N. Le Phuc, X. Courtois, F. Can, S. Royer, P. Marecot, D. Duprez, *Appl. Catal. B: Environ.*, 102 (2011) 353-361.
- [14] G. Centi, G.E. Arena, S. Perathoner, *J. Catal.*, 216 (2003) 443-454.
- [15] Y. Sakamoto, K. Higuchi, N. Takahashi, K. Yokota, H. Doi, M. Sugiura, *Appl. Catal. B: Environ.*, 23 (1999) 159-167.
- [16] R.J. Hendershot, P.T. Fanson, C.M. Snively, J.A. Lauterbach, *Angewandte Chemie*, 42 (2003) 1152-1155.
- [17] J.H. Xiao, X.H. Li, S. Deng, F.R. Wang, L.F. Wang, *Catal. Commun.*, 9 (2008) 563-567.
- [18] R. Vijay, C.M. Snively, J. Lauterbach, *J. Catal.*, 243 (2006) 368-375.
- [19] R. Vijay, R.J. Hendershot, S.M. Rivera-Jiménez, W.B. Rogers, B.J. Feist, C.M. Snively, J. Lauterbach, *Catal. Commun.*, 6 (2005) 167-171.
- [20] X.Y. Wang, Y.B. Yu, H. He, *Appl. Catal. B: Environ.*, 100 (2010) 19-30.
- [21] P.N. Le, E.C. Corbos, X. Courtois, F. Can, S. Royer, P. Marecot, D. Duprez, *Top. Catal.*, 52 (2009) 1771-1775.
- [22] X. Wang, Z. Chen, Y. Luo, L. Jiang, R. Wang, *Scientific reports*, 3 (2013) 1559.
- [23] J.H. Li, W.H. Goh, X.C. Yang, R.T. Yang, *Appl. Catal. B: Environ.*, 90 (2009) 360-367.
- [24] F. Wang, X. Tang, H. Yi, K. Li, J. Wang, C. Wang, *RSC Advances*, 4 (2014) 8502-8509.
- [25] F. Thevenet, L. Sivachandiran, O. Guaitella, C. Barakat, A. Rousseau, *Journal of Physics D-Applied Physics*, 47 (2014) 14.
- [26] P. Talebizadeh, M. Babaie, R. Brown, H. Rahimzadeh, Z. Ristovski, M. Arai, *Renewable and Sustainable Energy Reviews*, 40 (2014) 886-901.
- [27] Q. Yu, H. Wang, T. Liu, L. Xiao, X. Jiang, X. Zheng, *Environ. Sci. Technol.*, 46 (2012) 2337-2344.
- [28] H.H. Kim, K. Takashima, S. Katsura, A. Mizuno, *Journal of Physics D-Applied Physics*, 34 (2001) 604-613.
- [29] C. Shi, Y. Ji, U.M. Graham, G. Jacobs, M. Crocker, Z. Zhang, Y. Wang, T.J. Toops, *Appl. Catal. B: Environ.*, 119-120 (2012) 183-196.

-
- [30] H. Mahzoul, J.F. Brillhac, P. Gilot, *Appl. Catal. B: Environ.*, 20 (1999) 47-55.
- [31] Z. Hu, K.Q. Sun, W.Z. Li, B.Q. Xu, *Catal. Today*, 158 (2010) 432-438.
- [32] M.A. Peralta, B.S. Sanchez, M.A. Ulla, C.A. Querini, *Appl. Catal. A-Gen.*, 393 (2011) 184-188.
- [33] J.H. Park, H.J. Cho, S.J. Park, I.S. Nam, G.K. Yeo, J.K. Kil, Y.K. Youn, *Top. Catal.*, 42-43 (2007) 61-64.
- [34] J.-G. Kim, H.-M. Lee, M.-J. Lee, J.-H. Lee, J.-G. Kim, J.-Y. Jeon, S.-K. Jeong, S.-J. Yoo, S.-S. Kim, *J. Ind. Eng. Chem.*, 14 (2008) 841-846.
- [35] J. Lauterbach, R. Vijay, H. Sakurai, C.M. Snively, *Top. Catal.*, 52 (2009) 1388-1399.
- [36] T. Yamamoto, T. Tanaka, S. Suzuki, R. Kuma, K. Teramura, Y. Kou, T. Funabiki, S. Yoshida, *Top. Catal.*, 18 (2002) 113-118.
- [37] B. Pereda-Ayo, R. Lopez-Fonseca, J.R. Gonzalez-Velasco, *Appl. Catal. A-Gen.*, 363 (2009) 73-80.
- [38] D.H. Kim, K. Mudiyansele, J. Szanyi, J.C. Hanson, C.H.F. Peden, *J. Phys. Chem. C*, 118 (2014) 4189-4197.
- [39] W.S. Epling, L.E. Campbell, A. Yezerets, N.W. Currier, J.E. Parks, *Catal. Rev.*, 46 (2004) 163-245.
- [40] A. Lindholm, N.W. Currier, E. Fridell, A. Yezerets, L. Olsson, *Appl. Catal. B: Environ.*, 75 (2007) 78-87.
- [41] W.B. Li, X.F. Yang, L.F. Chen, J.A. Wang, *Catal. Today*, 148 (2009) 75-80.
- [42] Y.Y. Ji, T.J. Toops, J.A. Pihl, M. Crocker, *Appl. Catal. B: Environ.*, 91 (2009) 329-338.
- [43] X.Y. Chen, J. Schwank, J. Li, W.F. Schneider, C.T. Goralski, P.J. Schmitz, *Appl. Catal. B: Environ.*, 61 (2005) 164-175.
- [44] J.H. Niu, X.F. Yang, A.M. Zhu, L.L. Shi, Q. Sun, Y. Xu, C. Shi, *Catal. Commun.*, 7 (2006) 297-301.
- [45] D.Z. Zhao, X.S. Li, C. Shi, H.Y. Fan, A.M. Zhu, *Chem. Eng. Sci.*, 66 (2011) 3922-3929.
- [46] S. Roy, A. Baiker, *Chem. Rev.*, 109 (2009) 4054-4091.
- [47] F. Holzer, F.D. Kopinke, U. Roland, *Plasma Chem. Plasma Process.*, 25 (2005) 595-611.

Figure Captions:

Fig. 1. Schematic view of plasma-assisted NO_x storage and reduction process.

Fig. 2. XRD patterns of Pt/Ba/Al and M/Ba/Al (M= Mn, Fe, Co, Ni, Cu) samples.

Fig. 3. NO conversion to NO₂ measured under lean conditions (500 ppm NO, 8% O₂, N₂ balance).

Fig. 4. NO_x storage capacity measured under lean conditions (500 ppm NO, 8% O₂, Ar balance, 50 min storage time, GHSV=14,400 ml·g_{cat.}⁻¹·h⁻¹)

Fig. 5. Evolution of NO_x and O₂ during NO_x-TPD experiments. The samples were kept under 500 ppm NO/8% O₂/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⁻¹ under Ar flow.

Fig. 6. NO_x conversion during lean/rich cycling at different temperatures (lean phase: 500 ppm NO, 8% O₂, balance Ar, duration: 10 min; rich phase: 1% H₂ balance Ar, duration: 2 min).

Fig. 7. H₂-TPSR profiles after NO adsorption using 500 ppm NO/8% O₂/Ar for 50 min; NO adsorption was performed at 300°C.

Fig. 8. NO_x conversion during non-thermal plasma-assisted lean/rich cycling at different temperatures (lean phase: 500 ppm NO, 8% O₂, balance Ar, duration: 10 min; rich phase: 2% H₂ balance Ar, discharge power: 1.8 W, duration: 2 min).

Table 1.

Gas composition used for NO_x storage/reduction cycling experiments.

Parameter	Lean	Rich
Duration (s)	600	120
Temperature (°C)	200-350	200-350
Power input (W)	-	1.8
Space velocity (ml·g _{cat} ⁻¹ ·h ⁻¹)	14,400	14,400
NO (ppm)	500	-
O ₂ (%)	8	-
H ₂ (%)	-	2
Ar (%)	Balance	Balance

Table 2.
Summary of ICP-AES data for as-prepared catalysts.

Catalyst	Pt (wt.%)	M (M= Mn, Fe, Co, Ni, Cu) (wt.%)	Ba (wt.%)
Pt/Ba/Al	0.64	-	9.95
Mn/Ba/Al	-	2.96 (Mn)	9.36
Fe/Ba/Al	-	2.65 (Fe)	8.41
Co/Ba/Al	-	3.08 (Co)	9.47
Ni/Ba/Al	-	2.42 (Ni)	9.29
Cu/Ba/Al	-	2.91 (Cu)	9.72

Table 3.

Summary of BET and NSC per specific area data for various samples.

Catalyst	BET area (m ² /g)	NSC/BET area (μmol/m ²)			
		200°C	250°C	300°C	350°C
γ-Al ₂ O ₃	198	-	-	-	-
Pt/Ba/Al	148	1.169	1.191	1.641	1.726
Mn/Ba/Al	134	1.982	1.999	1.999	1.999
Fe/Ba/Al	142	0.839	1.051	1.218	1.221
Co/Ba/Al	139	1.872	1.927	1.927	1.927
Ni/Ba/Al	137	1.540	1.894	1.955	1.955
Cu/Ba/Al	133	1.519	1.821	1.979	2.014

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Catalysis only

Plasma-assisted catalysis