Environ Sci Pollut Res (2017) 24:21496–21508
DOI 10.1007/s11356-017-9785-8

RESEARCH ARTICLE

Combined fast selective reduction using Mn-based catalysts and nonthermal plasma for NOx removal

Jun Xiang Chen[1] · **Kuan Lun Pan**[1] · **Sheng Jen Yu**[2] · **Shaw Yi Yen**[2] · **Moo Been Chang**[1]

Received: 11 March 2017 / Accepted: 19 July 2017 / Published online: 26 July 2017

Abstract In this study, the concept of fast SCR for NO reduction with NH_3 as reducing agent is realized via the combination of nonthermal plasma (NTP) with Mn-based catalyst. Experimental results indicate that 10% wt. Mn-Ce-Ni/TiO_2 possesses better physical and chemical properties of surface, resulting in higher NO removal efficiency if compared with 10% wt. Mn-Ce/TiO_2 and 10% wt. Mn-Ce-Cu/TiO_2. Mn-Ce-Ni/TiO_2 of 10% wt. achieves 100% NO_x conversion at 150 °C, while 10% wt. Mn-Ce/TiO_2 and 10% wt. Mn-Ce-Cu/TiO_2 need to be operated at a temperature above 200 °C for 100% NO_x conversion. However, NO conversion achieved with 10% wt. Mn-Ce-Ni/TiO_2 is significantly reduced as $H_2O_{(g)}$ and SO_2 are introduced into the SCR system simultaneously. Further, two-stage system (SCR with DBD) is compared with the catalyst-alone for NO_x conversion and N_2 selectivity. The results indicate that 100% NO_x conversion can be achieved with two-stage system at 100 °C, while N_2 selectivity reaches 80%. Importantly, NO_x conversion achieved with two-stage system could maintain >95% in the presence of C_2H_4, CO, SO_2, and $H_2O_{(g)}$, indicating that two-stage system has better tolerance for complicated gas composition. Overall, this study demonstrates that combining NTP with Mn-based catalyst is effective in reducing NO_x emission at a low temperature (≤200 °C) and has good potential for industrial application.

Keywords Nitrogen oxides (NO_x) · Selective catalytic reduction (SCR) · Nonthermal plasma (NTP) · Plasma catalysis

Responsible editor: Suresh Pillai

✉ Moo Been Chang
mbchang@ncuen.ncu.edu.tw

[1] Graduate Institute of Environmental Engineering, National Central University, No.300, Jhongda Road, Jhongli District, Taoyuan City 32001, Taiwan

[2] Green Energy and Environment Institute, Industrial Technology Research Institute, Hsinchu, Taiwan

Introduction

Continuous emission of large quantity of NO_x into atmosphere has caused various environmental problems, such as acid rain, photochemical smog, and visibility degradation. Also, it is harmful to human health. Several post-combustion methods including selective catalyst reduction (SCR), selective non-catalyst reduction (SNCR), and non-selective catalyst reduction (NSCR) are available to control NO_x emissions. Among them, selective catalyst reduction (SCR) is of the highest NO_x removal efficiency and NH_3 is commonly applied as a reducing agent to reduce NO_x to form N_2 in the presence of O_2 (Jun et al. 2015). Generally, NO_x removal efficiency achieved with SCR process could reach 90% if appropriate catalyst is applied (Wu et al. 2007). The main reaction of SCR is described as rReaction (1).

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

V_2O_5-WO_3/TiO_2 is typically used in SCR process; however, it needs to be operated within the temperature range of 250–350 °C for high efficiency. The narrow reaction temperature window is considered as one of the main disadvantages of SCR. In addition, the catalyst deactivation always takes place, because SCR catalyst is generally placed before particle removal equipment and flue gas desulfurization (FGD) (Phil et al. 2008). Also, SCR process shows good efficiency for

NO_x removal with urea as a reducing agent for the treatment of flue gas from diesel engine (Choi and Woo 2015; Cimino et al. 2016). Urea has several advantages such as easier transportation, higher safety of storage, and higher stability if compared with NH_3 (Feng and Lü 2015). However, the temperature of low-loading diesel engine exhaust is relatively low (100–200 °C). As mentioned previously, the most disadvantage of applying SCR in controlling diesel emission is that the catalysts have to be operated at a temperature higher than 200 °C. As a result, conventional SCR could not be applied for removing NO_x from diesel engine exhaust (Chen et al. 2016; Yoshida et al. 2012). Therefore, how to develop a low-temperature SCR has become an emerging issue. Recently, relevant study indicated that SCR catalyst has good potential to convert the NO_x to N_2 at lower temperatures; further, it can be placed downstream of the particle control device such as bag filter and the desulfurization system to avoid the deactivation of catalyst (Huang et al. 2016).

Manganese-based (Mn-based) catalysts such as MnO_x, MnO_x/TiO_2 (Jin et al. 2014), Mn-Ce/TiO_2 (Cao et al. 2015), and Mn-Ce-Fe/γ-Al_2O_3 (Thirupathi and Smirniotis 2011a) have attracted much attention due to their high capability in converting NO_x at low temperatures (≦200 °C). Previous studies indicated that applying different metals as promoters can enhance the activity of Mn-based catalyst, such as Ce, Cu, Fe, and Ni. Especially Ce is most applied for developing low-temperature catalysts (Liu et al. 2017). Kwon et al. (2015) reported that Ce has good activity toward NO_x reduction due to its redox properties. Additionally, Ce could store and release oxygen via the transformation between Ce^{4+} and Ce^{3+} to promote SCR reaction (Kwon et al. 2015). Zhou et al. (2016) investigated Ce-based catalysts with different Ce valences (Zhou et al. 2016) and indicated that catalyst has a higher sulfur dioxide resistance as the ratio of $Ce^{4+}/(Ce^{4+}+Ce^{3+})$ is increased. Thirupathi et al. (2011) indicated that activity of Mn-based catalyst can be promoted by adding Ni for SCR process, because Ni can also enhance redox capacity of catalyst (Thirupathi and Smirniotis 2011b).

However, Mn-based catalysts still face serious drawbacks although it has potential to be operated at a lower temperature for SCR process (Yang et al. 2016). For example, N_2O is the inevitable product in a low-temperature SCR process, resulting in a lower N_2 selectivity. Niu et al. (2016) indicated that N_2O may be generated from direct oxidation of NH_3 in the excess O_2 via reaction (2) at a low temperature (≤150 °C) or NO would react with adsorbed NH_3 on catalyst surface via reaction (3) (Niu et al. 2016).

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \quad (2)$$

$$4NO + 4NH_{3(ads)} + 3O_2 \rightarrow 4N_2O + 6H_2O \quad (3)$$

Similarly, Mn-based catalysts have poor durability and resistance in complicated gas composition (especially in the presence of SO_2 and $H_2O_{(g)}$); Mn-based catalysts could be seriously poisoned by formation of ammonia bisulfate (NH_4HSO_4 and $(NH_4)_2SO_4$) on the catalyst. On the other hand, SCR performance could be significantly enhanced as fast-SCR is applied. Especially, fast-SCR is effective to reduce NO to N_2 at a low temperature. Generally, fast-SCR has a higher reaction rate and wider reaction temperature window if compared with conventional SCR. Fast-SCR was first investigated by Koebel et al. (2001, 2002) and Madia et al. (2002) and can be described as reaction (4). Relevant study indicated that redox mechanism in fast-SCR is similar to the standard SCR reaction (Grossale et al. 2008). For fast-SCR process, NO_2 plays a crucial role which serves as a more efficient oxidizing agent than O_2 in the redox process of the SCR reaction. In fast-SCR, NH_4NO_3 is formed via the reaction between NH_3 and NO_2, and subsequently, NH_4NO_3 will be decomposed by NO described in reactions (5) and (6). Relevant study indicated that reactions (5) and (6) are closely related to the fast-SCR chemistry (Grossale et al. 2008). The vital process is the redox reactions as indicated in reactions (5) and (6), which dominate the reaction rate of fast-SCR. It has been proved that existence of NO_2 in the exhaust gas is essential and the content of NO_2 approximately equals to that of NO favors fast-SCR reaction (Iwasaki and Shinjoh 2010).

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \quad (4)$$

$$2NH_3 + 2NO_2 \rightarrow N_2 + NH_4NO_3 + H_2O \quad (5)$$

$$NH_4NO_3 + NO \rightarrow N_2 + NO_2 + 2H_2O \quad (6)$$

However, NO_x in the typical flue gas of combustion system is composed of 95% NO and 5% NO_2; therefore, fast-SCR process is difficult to be applied. How to effectively convert NO into NO_2 is an important step for fast-SCR process (Jõgi et al. 2016; Kang et al. 2006a). Nonthermal plasma (NTP) has been demonstrated as an effective technology to oxidize NO into NO_2 or NO_3^- via the collision with highly active radicals generated, i.e., O and OH (Patil et al. 2016). Combining catalyst with NTP to form plasma catalysis is a novel reaction system, which is regarded as feasible technology for reducing the emission of gaseous pollutants. Generally, plasma catalysis system can be distinguished into two configurations, i.e., in-plasma catalysis (IPC) and post-plasma catalysis (PPC). The former is similar to a packed-bed reactor, namely, catalyst is directly packed into the discharge zone. The latter implies that catalyst is located downstream NTP reactor, and catalysis system and plasma reactor are operated separately.

Bröer and Hammer (2000) reported that NO_x conversion can reach 90% at 160 °C by combining dielectric barrier discharges (DBD) with V_2O_5-WO_3/TiO_2 catalyst to form two-stage system (Bröer and Hammer 2000). Tran et al. (2004) applied DBD and In-doped γ-alumina catalyst to form a two-stage system for reducing of NO_x and indicated that 100% NO_x conversion could be achieved at 350 °C (Tran

et al. 2004). Cho et al. (2012) also applied plasma to assist the HC-SCR and indicated that NO_x conversion reached 100% with the operating temperature of 300 °C and applied voltage of 16 kV (Cho et al. 2012). Hence, PPC has good potential to reduce the emission of NO_x.

As mentioned previously, Mn-based catalysts have potential to be applied for NO_x reduction at a temperature below 200 °C. The aim of this study is to develop low-temperature SCR catalysts through various Mn-modified catalysts, which are Mn-Ce/TiO_2, Mn-Ce-Ni/TiO_2, and Mn-Ce-Cu/TiO_2, respectively. Additionally, a lab-scale two-stage system consisting of NTP and low-temperature SCR catalysts is developed to reduce NO from simulated gas streams. In this two-stage system, NTP can be regarded as an oxidation system to achieve $NO_2/NO \approx 1$. It is expected that combining Mn-based catalyst with plasma would enhance NO_x conversion and reduce the formation of N_2O. Furthermore, the effects of operating parameters on NO_x removal efficiency are extensively evaluated via a lab-scale experimental setup, and gas streams with complicated gas compositions are applied to evaluate the practical application of this two-stage system for NO removal.

Experimental

Catalyst preparation

A series of Mn-based catalysts including 10% wt. Mn-Ce/TiO_2, 10% wt. Mn-Ce-Ni/TiO_2, and 10% wt. Mn-Ce-Cu/TiO_2 were prepared by wet impregnation method. First of all, corresponding metal nitrates (including $Mn(NO_3)_2{\cdot}4H_2O$ (purity: 98%, Showa), $Ce(NO_3)_3{\cdot}6H_2O$ (purity: 99%, ACROS), $Ni(NO_3)_2{\cdot}6H_2O$ (purity: 99%, Showa), and $Cu(NO_3){\cdot}3H_2O$, (purity: 100%, Showa) as precursors were dissolved in deionized water to prepare aqueous solution with appropriate stoichiometry. All ratios of active phases of catalysts (i.e., Mn-Ce, Mn-Ce-Ni, and Mn-Ce-Cu) were controlled at 1. Subsequently, corresponding P25-type TiO_2 (purity: 100%, Degussa) used as support was added into mixture solution and mixed completely at 80 °C until water was evaporated. Secondly, the residual solid precursor was placed into an oven to dry overnight, and then calcined in air at 400 °C for 4 h with the heating rate of 5 °C/min. Finally, all catalysts were sieved to 30–70 mesh for catalytic test.

Catalyst characterization

The crystal structures of catalysts were characterized by powder X-ray diffraction (XRD). The XRD (D8AXRD BRUKER, Germany) profiles were obtained using an X-ray diffractometer, operated at 40 kV and 40 mA using Cu-Kα radiation with a nickel filter, diffraction with 2θ were recorded over the range of 10–80°. The specific surface areas, total pore volume, and average pore diameter of the catalysts were measured by N_2 adsorption at −196 °C with a Micromeritics ASAP 2010 (ASAP2010 Micromeritics, USA). Field-emission scanning electron microscopy (FE-SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) was used to examine the micro-structure of catalyst surface and the elemental composition of catalysts by S80 JEOL (SEM, S80 JEOL, Japan). X-ray photoelectron spectroscopy (XPS, Sigma Probe VG, UK) was used to analyze the chemical state of elements of the catalysts, and XPS spectra were recorded with monochromatic Al anode X-ray which was equipped with a concentric hemispherical analyzer. Al Kα (1486.6 eV) X-ray source was used for excitation. The binding energies were referenced to the C1s line at 284.5 eV. Thermogravimetric analysis (TGA, Pyris 1 TGA PERKIN ELMER, USA) was carried out to investigate the thermal stability of sulfate species in a static N_2 atmosphere, with Hitachi STA7300. The TGA experiments were conducted with 10–20-mg catalysts, and it was analyzed with the temperature ranging from room temperature to 900 °C at a rate of 10 °C/min.

Activity test

Low-temperature reduction of NO with ammonia was first performed with SCR process at a fixed-bed quartz reactor (I.D.= 20 mm) containing 6 g catalyst in excess oxygen. The SCR process was carried out with the temperature ranging from 50 to 200 °C and the total gas flow rate was fixed at 1500 sccm, corresponding to a gas hourly space velocity (GHSV) of 20,000 h^{-1}. Typical gas mixture consisted of NO = 300 ppm, NH_3 = 300 ppm, O_2 = 10%, $H_2O_{(g)}$ = 10% (when used), SO_2 = 100 ppm (when used), and N_2 as balance. Various gases were provided by gas cylinders and a set of mass flow controllers (MFC) were used for regulating the gas flow rates, while $H_2O_{(g)}$ was introduced into the system by a peristaltic pump. For the analysis of exhaust, a condensation system was used to capture $H_2O_{(g)}$ in order to avoid the damage to instruments. An NO_x analyzer (Testo 350, Germany) was used to measure NO and NO_2 concentrations while N_2O was analyzed by Fourier transform infrared spectrophotometer (FTIR, Nicolet 6700 Thermo Scientific, USA).

Further, the two-stage system was constituted by combining DBD-type (dielectric barrier discharge) NTP with Mn-based catalyst, and it was evaluated for the effectiveness in removing NO_x. As shown in Fig. 1, the catalysis system (SCR process) was placed downstream of the NTP (similar to PPC system). Likewise, the total gas flow rate of two-stage system was controlled at 1500 sccm. In two-stage system, all operating conditions were similar to SCR process. For NTP system, the DBD-type reactor was constituted of a quartz tube (I.D. = 10 mm) filled with glass beads, a stainless steel rod,

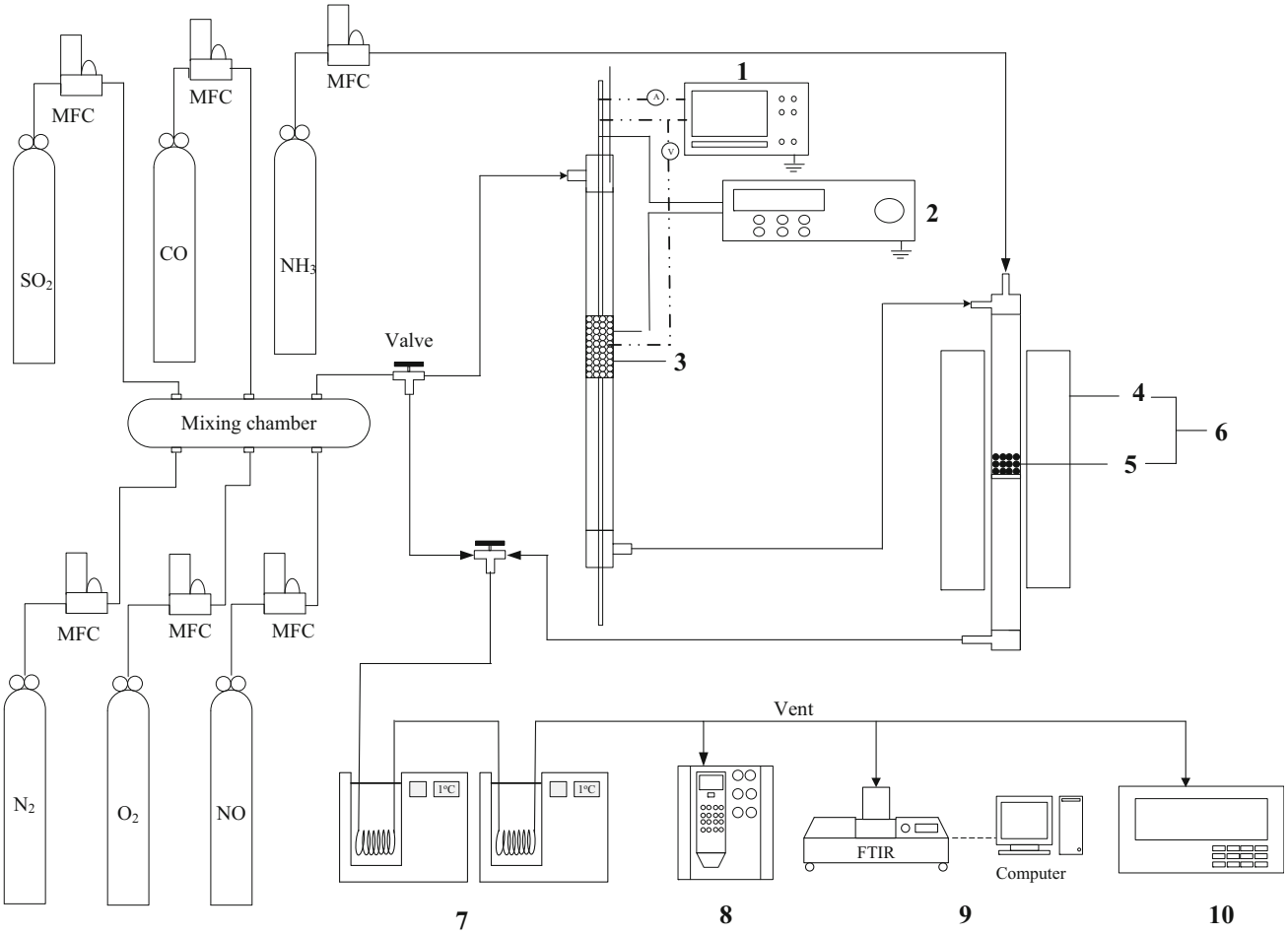

Fig. 1 Schematic of the two-stage system for NO_x reduction

and a stainless steel wire mesh, where stainless steel rod and a stainless steel wire mesh were used as the inner and outer electrodes, respectively. The operating temperature and pressure of NTP were 25 °C and atmospheric pressure, respectively. The DC pulse power was applied to generate plasma, and the applied voltage and frequency were controlled at 12–20 kV and 8–10 kHz, respectively, for test. The discharge power was measured by a digital oscilloscope equipped with a current probe and a high-voltage probe. The NO_x conversion and N_2 selectivity are calculated via Eqs. (7) and (8), respectively:

$$\mathrm{NO}\ \ conversion(\%) = \frac{[\mathrm{NO}]_{in} - [\mathrm{NO}]_{out}}{[\mathrm{NO}]_{in}} \times 100(\%) \tag{7}$$

$$SN_2 = \frac{[\mathrm{NOin} - \mathrm{NOout}] - [\mathrm{NO_2}] - 2[\mathrm{N_2O}]}{[\mathrm{NOin} - \mathrm{NOout}]} \times 100\% \tag{8}$$

Results and discussion

Catalyst characterizations—XRD, BET, and SEM

The XRD patterns of Mn-Ce/TiO_2, Mn-Ce-Ni/TiO_2, and Mn-Ce-Cu/TiO_2 are presented in Fig. 2, and the result indicates that all catalysts prepared present strong diffraction peaks of TiO_2, being mainly contributed by anatase crystalline. It is observed that three Mn-based catalysts have basically amorphous peaks of MnO_x on the catalyst surface. Previous studies reveal that amorphous MnO_2 is of higher activity if compared with crystalline MnO_2 for NO reduction (Boningari et al. 2015; Tang et al. 2007). The presence of amorphous manganese oxide in Mn-based catalysts may be one of the key factors for their excellent activities in removing NO_x (Kang et al. 2006b; Peña et al. 2004). In addition, Cu and Ni are not

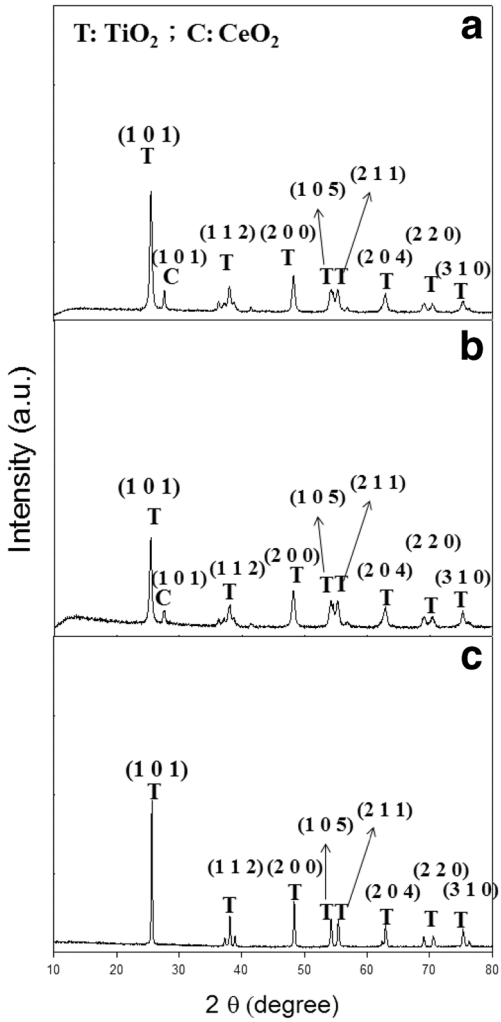

Fig. 2 XRD patterns of Mn-based catalysts. **a** Mn-Ce-Ni/TiO_2. **b** Mn-Ce/TiO_2. **c** Mn-Ce-Cu/TiO_2

observed in XRD profiles of Mn-Ce-Cu/TiO_2 and Mn-Ce-Ni/TiO_2, respectively. It is speculated that they may be incorporated into Mn lattice to form solid solution. The diffraction peaks of CeO_2 are not present in Mn-Ce-Cu/TiO_2 due to less Ce content. As shown in EDS results (see Table 1), Mn-Ce-Cu/TiO_2 has lower contents of Cu, Mn, and Ce, and it is speculated that active phase (Mn-Ce-Cu) is not well supported on TiO_2 due to the addition of Cu.

The specific surface areas (S_{BET}), average pore diameter, and pore volume of catalysts and TiO_2 are summarized in Table 2.

Table 1 Elemental compositions of the catalysts prepared

Catalyst	EDS (atomic %)					
	Mn	Ce	Ni	Cu	Ti	O
Mn-Ce/TiO_2	4.31	5.04	–	–	55.26	35.39
Mn-Ce-Ni/TiO_2	4.22	4.27	4.06	–	50.03	37.42
Mn-Ce-Cu/TiO_2	3.24	3.28	–	3.33	61.05	29.10

The results indicate that BET surface areas of Mn-Ce/TiO_2, Mn-Ce-Ni/TiO_2, and Mn-Ce-Cu/TiO_2 are 48, 50, and 30 m^2/g, respectively. Obviously, BET surface areas of catalysts prepared decrease as TiO_2 is impregnated with various metal elements. Possibly, parts of TiO_2 pores are covered. Also, it is found that pore volume of TiO_2 decreases to some extent after impregnation. Among Mn-based catalysts, Mn-Ce-Ni/TiO_2 shows the largest BET (~50 m^2/g) and average pore diameter (8.6 nm), and it may correspond to the highest activity due to smaller diffusion limitation. As shown in Table 1, EDS analysis indicates that the elemental composition of the catalysts prepared deviates a little from the designated formula of catalysts. In addition, it is observed that Mn-Ce-Ni/TiO_2 has the highest oxygen content among three catalysts prepared. According to SCR mechanism, NH_3 is first adsorbed on reactive oxygen of catalyst. Hence, it is speculated that higher oxygen atom content may result in higher NO conversion. Figure 3 displays the SEM images of Mn-Ce-Ni/TiO_2, Mn-Ce/TiO_2, and Mn-Ce-Cu/TiO_2, respectively. The results reveal that three Mn-based catalysts are mainly constituted by pseudo-spherical particles; they are composed of irregular small particles corresponding to the prepared method. The average particle sizes of 3 Mn-based catalysts were calculated by Sherr's equation, and their particle sizes are Mn-Ce-Ni/TiO_2 = 25 nm, Mn-Ce/TiO_2 = 28 nm, and Mn-Ce-Cu/TiO_2 = 31 nm, respectively. The particle sizes of catalysts rank in the order of Mn-Ce-Cu/TiO_2 > Mn-Ce/TiO_2 > Mn-Ce-Ni/TiO_2. Especially, Mn-Ce-Cu/TiO_2 reveals severe sintering after calcination (see Fig. 3), resulting in lower BET (30 m^2/g). On the other hand, sintering of Mn-Ce-Ni/TiO_2 is not significant if compared with Mn-Ce/TiO_2 and Mn-Ce-Cu/TiO_2. Previous study indicated that addition of Ni to Mn-based catalysts can prevent its sintering, and higher catalytic activity is obtained (Thirupathi et al. 2011). Overall, Mn-Ce-Ni/TiO_2 presents better surface characteristics if compared with Mn-Ce/TiO_2 and Mn-Ce-Cu/TiO_2.

SCR performance

Low-temperature SCR performance

Catalytic activities of three Mn-based catalysts prepared are first evaluated for NH_3-SCR reaction at various temperatures.

Table 2 BET, pore diameter, and pore volume of TiO_2 and three Mn-based catalysts

Catalyst	BET (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3/g)
TiO_2	60	6.8	0.36
Mn-Ce/TiO_2	48	7.8	0.30
Mn-Ce-Ni/TiO_2	50	8.6	0.28
Mn-Ce-Cu/TiO_2	30	8.0	0.25

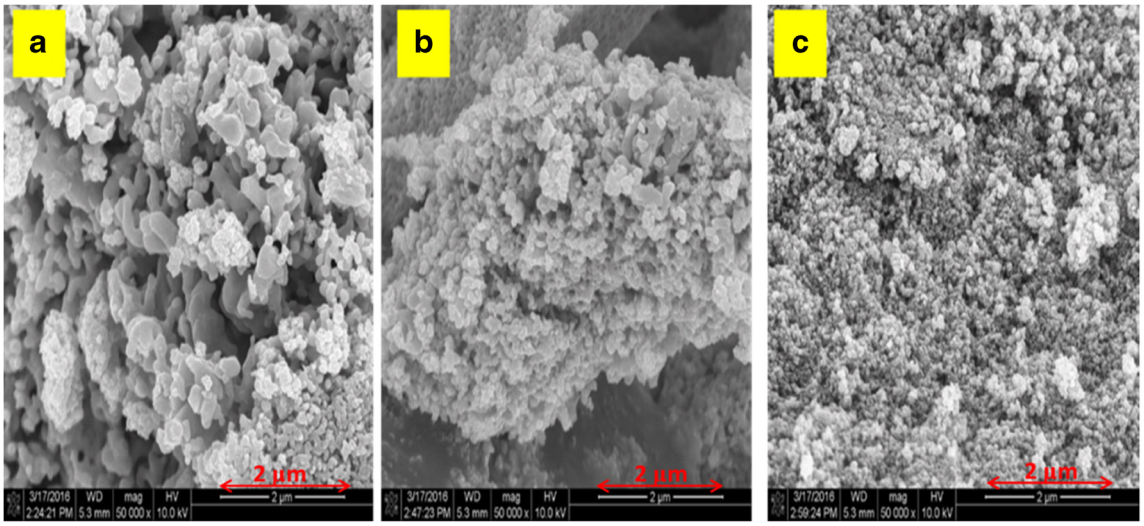

Fig. 3 SEM images of Mn-based catalysts. **a** Mn-Ce-Ni/TiO_2. **b** Mn-Ce/TiO_2. **c** Mn-Ce-Cu/TiO_2

As shown in Fig. 4, the NO_x conversions achieved increase with increasing temperature for three Mn-based catalysts. At 50 °C, NO_x conversion achieved with Mn-Ce-Ni/TiO_2, Mn-Ce/TiO_2, and Mn-Ce-Cu/TiO_2 are 58, 31, and 30%, respectively. As temperature is increased to 150 °C, NO_x conversions achieved with Mn-Ce-Ni/TiO_2 and Mn-Ce/TiO_2 reach 100% while Mn-Ce-Cu/TiO_2 needs to be operated at 200 °C for reaching 95% NO_x conversion. Activities of three Mn-based catalysts for NO reduction rank in the order of Mn-Ce-Ni/TiO_2 > Mn-Ce/TiO_2 > Mn-Ce-Cu/TiO_2. For the effect of Ni on activity of Mn-based catalyst, previous study indicated that Mn/TiO_2 has positive interaction if doped with Ni (Thirupathi et al. 2011). This interaction may lead to the enhancement of the oxygen mobility, resulting in higher activity for SCR process.

Additionally, the kinetics is investigated by the power rate law model. The activation energies are calculated on the basis of the conversion smaller than 20% by increasing GHSV. The kinetics study is conducted by assuming steady-state before and after reaction, and a mathematical model of a differential-type reactor is used for determining the reaction rates ($-r_i$) at different temperatures (T) and inlet NO concentrations (C_i). Subsequently, regression straight lines of $1/r_i$ versus $1/C_i$ are plotted to obtain the values of rate constant (k) with different temperatures. Then, a regression line is obtained by plotting ln k versus 1/T, and activation energy (E_a) is calculated by Arrhenius equation (see Fig. 5). The result indicates that activation energy with Mn-Ce-Ni/TiO_2 as catalyst for SCR process is 23.1 kJ/mol.

XPS analysis of catalysts

XPS spectra are used to understand the chemical bonding states on the catalyst surface for analysis of mechanism. XPS Mn 2p spectra of three fresh catalysts are presented in Fig. 6a. For all three catalysts, two main peaks corresponding to Mn $2p_{3/2}$ and Mn $2p_{1/2}$ are located at 642 and 653 eV, respectively. Among them, Mn $2p_{3/2}$ can be separated into

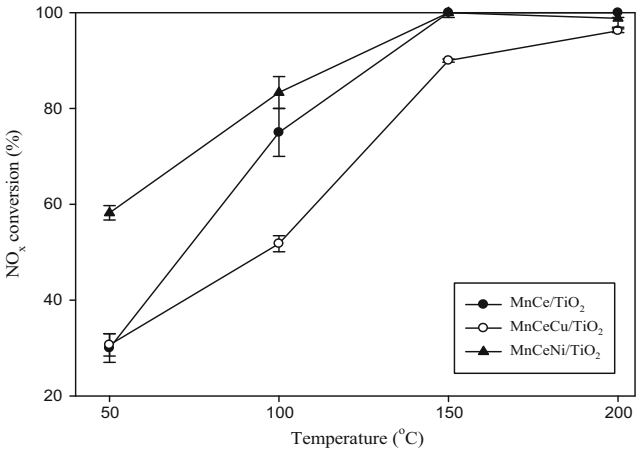

Fig. 4 The performance of three Mn-based catalysts (NO: 300 ppm, NH_3: 300 ppm, O_2: 10%, balance: N_2 and GHSV = 20,000 h^{-1})

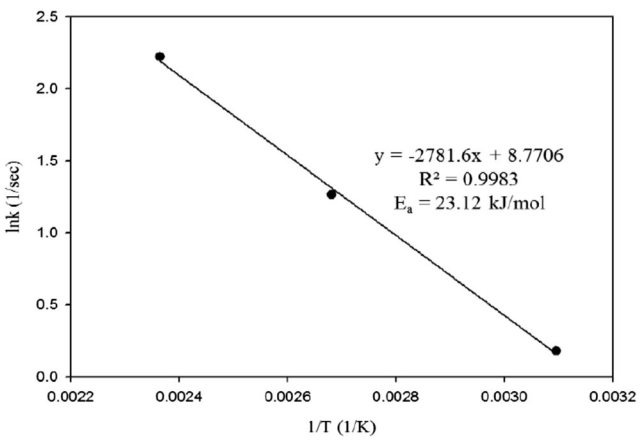

Fig. 5 Arrhenius plot for rate constant of NO conversion with Mn-Ce-Ni/TiO_2 as catalyst

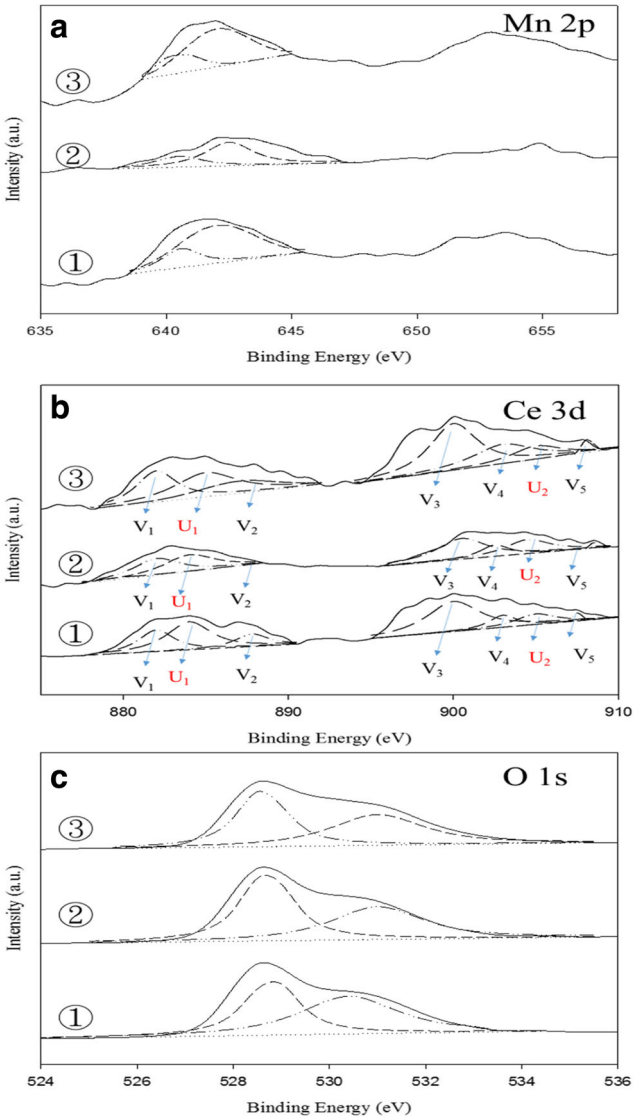

Fig. 6 XPS analysis of three catalysts. **a** Mn 2p. **b** Ce 3d. **c** O 1s (①$MnCeNi/TiO_2$, ② $MnCe/TiO_2$, ③ $MnCeCu/TiO_2$)

two peaks, corresponding to Mn^{4+} (642.0–642.5 eV) and Mn^{3+} (641.0–641.3 eV), respectively (Chang et al. 2013; Shaju et al. 2002).

Figure 6b shows the valence state of Ce 3d of three catalysts. The Ce 3d peaks were fitted into the sub-bands, and those marked as U_1 and U_2 represent Ce^{+3} species. The sub-bands marked as V_1, V_2, V_3, V_4, and V_5 are attributed to Ce^{4+} species. In addition, XPS spectra of the O 1s of three Mn-based catalysts are presented in Fig. 6c. The results indicate that the two main peaks appeared at 529~530 and 531~532 eV, corresponding to lattice oxygen (O_β) and adsorbed surface oxygen (O_α), respectively (Peng et al. 2013).

Fang et al. (2015) indicated that Mn^{4+} has a higher activity than Mn^{3+} and Mn^{2+} toward NO_x removal (Fang et al. 2015). Wang et al. (2016) mentioned that Mn^{4+} species could enhance the oxidation of NO to NO_2, further promote SCR performance at a low temperature (Wang et al. 2016). Wan et al. (2014) indicated that the surface Mn^{4+} species is the predominant valence state of the Mn-based catalysts and the activity of Mn-based catalysts increases with increasing Mn^{4+}. To summarize above results, Mn^{4+} has better electron mobility and thus higher production of oxygen defect (Wan et al. 2014). Regarding the effect of Ce, previous study indicated that the activity of SCR catalyst increases with increasing $Ce^{4+}/(Ce^{4+}+Ce^{3+})$ ratio. As shown in Fig. 6c, O 1s of three catalysts have two peaks, which are O_β and O_α, respectively. Relevant study indicated that the catalyst activity is related to ratio of $O_\alpha/(O_\alpha + O_\beta)$ in SCR process (Shu et al. 2014). Generally, O_α has a higher mobility than O_β, leading to the enhancement of SCR catalytic activity (Ma et al. 2015). Indeed, the results of three Mn-based catalyst are similar to that reported in literature, and the ratios of $Mn^{4+}/(Mn^{4+}+Mn^{3+})$, $Ce^{4+}/(Ce^{4+}+Ce^{3+})$, and $O_\alpha/(O_\alpha + O_\beta)$ of three catalysts are summarized at Table 3. Mn-Ce-Ni/TiO_2 reveals the best SCR performance of three catalysts, and it also has the highest $Mn^{4+}/(Mn^{4+}+Mn^{3+})$, $Ce^{4+}/(Ce^{4+}+Ce^{3+})$, and $O_\alpha/(O_\alpha + O_\beta)$ ratios. Previous study indicated that addition of Ni to Mn-based catalyst improves surface properties of Mn-based catalyst, resulting in better catalysis, because Ni has good interaction with Mn and Ti (Thirupathi et al. 2011). Conversely, the performance of Mn-Ce-Cu/TiO_2 decreases due to weak or no interaction of Cu with Ti (Boccuzzi et al. 1997). The results indicate that Ni is a good promoter, and it could increase the formation of Mn^{4+}, resulting in higher SCR performance. With the addition of nickel into Mn-Ce/TiO_2 catalyst, the ratio of $Mn^{4+}/(Mn^{4+}+Mn^{3+})$ increases from 72 to 79%. Obviously, the activity of Mn-Ce/TiO_2 is significantly improved by modification with Ni. Experimental results indicate that Mn-Ce-Ni/TiO_2 has the highest activity on NO_x reduction. Therefore, Mn-Ce-Ni/TiO_2 is mainly applied for further tests.

Effect of SO_2 and $H_2O_{(g)}$ on low temperature SCR

As reported previously, Mn-Ce-Ni/TiO_2 catalyst is demonstrated with the highest activity in SCR process. The long-term activity is further investigated for NO_x removal, and the results indicate that NO_x conversion maintains above 99% in the time course over 80 h at 150 °C, indicating high stability of Mn-Ce-Ni/TiO_2 for NO reduction.

It is important to evaluate the effects of $H_2O_{(g)}$ and SO_2 on the catalytic activity(Shen et al. 2014). Figure 7 illustrates the effects of 10% $H_2O_{(g)}$ and 100 ppm SO_2 on SCR performance at 150 °C. The NO_x conversion decreases from 100 to 80% as 100 ppm SO_2 and 10% $H_2O_{(g)}$ are introduced into the gas stream simultaneously. As SO_2 and $H_2O_{(g)}$ feedings are turned off, the NO_x conversion gradually increases to 90%. These results indicate that the activity of Mn-Ce-Ni/TiO_2 could be inhibited as $H_2O_{(g)}$ and SO_2 are simultaneously present in flue gas. Possibly, SO_2 are oxidized into SO_3 or sulfate species on

Table 3 Percentages of different valence states for Mn and Ce of three catalysts

Catalysts	$Mn^{4+}/(Mn^{4+}+Mn^{3+})$ (%)	$Ce^{4+}/(Ce^{4+}+Ce^{3+})$ (%)	$O_\alpha/(O_\alpha + O_\beta)$ (%)
$MnCeNi/TiO_2$	79	64	50
$MnCe/TiO_2$	72	61	30
$MnCeCu/TiO_2$	64	59	46

MnO_x during SCR process, then SO_3 or sulfate species move to Ce or Ni to form bulk-sulfate species. Yu et al. (2010) mentioned that the NO conversion can be recovered to 90%, being attributed to decomposition of adsorbed ammonium sulfate when $H_2O_{(g)}$ and SO_2 are turned off (Yu et al. 2010).

To confirm SCR behaviors in the presence of SO_2 and $H_2O_{(g)}$, used Mn-Ce-Ni/TiO_2 catalysts were analyzed by thermogravimetric analysis. The sulfate species and $H_2O_{(g)}$ adsorbed on the surface of catalysts would lead to weight increase. As shown in Fig. 8, the TGA curve presents three major weight losses for Mn-Ce-Ni/TiO_2. The first one appears at 100 °C, which can be attributed to the evaporation of water. The second and third losses appear at approximately 400 and 800 °C, respectively, which are originated from the decomposition of sulfate species, such as NH_4HSO_4 and $(NH_4)_2SO_4$ (Putluru et al. 2015).

NO_x reduction via two-stage system

The system combining NTP and Mn-Ce-Ni/TiO_2 catalyst is evaluated for the effectiveness in reducing NO_x. In order to elucidate the effects of NTP on catalytic performance, the gas compositions are kept the same as that listed in section "SCR performance." The DBD experiment is conducted with the applied voltage of 15.5 kV and a frequency of 10,000 Hz to generate plasma. The NO and NO_2 concentrations after plasma are measured as 165 and 153 ppm, respectively, and the ratio of NO_2/NO is about 0.93. Figure 9 shows the SCR performances of the Mn-Ce-Ni/TiO_2 catalyst without and with DBD, respectively. At 50 °C, the NO_x conversion achieved with two-stage system reaches 80%, indicating that the NO_x conversion achieved with t two-stage system is higher than that achieved with the catalyst alone by 20%. When temperature is increased to 100 °C, two-stage system reaches 100%. The experimental results indicate that combining Mn-Ce-Ni/TiO_2 with NTP is more effective in reducing NO_x compared with the catalysis alone at a low temperature. Hence, it can be applied for controlling NO_x emission from low-loading diesel engine in which the temperature of exhaust gas ranges from 100 to 200 °C (Xie et al. 2012).

As NO reacts with NH_3, N_2O is an important by-product. Thus, N_2O is also measured in this study and the results indicate that the two-stage system produced a lower N_2O concentration if compared with catalysis alone. At various temperatures tested, the N_2O concentration generated by two-stage system are all below 30 ppm, while the catalysis-alone generates 90 ppm of N_2O at 150 °C. The N_2O concentration of catalyst alone is significantly higher than that generated by the two-stage system. Niu et al. (2016) indicated that N_2O may be generated from the direct oxidation of NH_3 in the excess O_2 via reaction (2) or NO would react with adsorbed NH_3 on surface of catalyst via reaction (3) at a low temperature (≤150 °C). Also, the N_2O formation pathway in SCR reaction is the decomposition of intermediate NH_4NO_3 via reaction (9) (Grossale et al. 2008).

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \quad (9)$$

In two-stage system, the plasma can assist the reaction of SCR to induce fast-SCR reaction, achieving a higher NO conversion and a lower N_2O generation at a temperature ranging

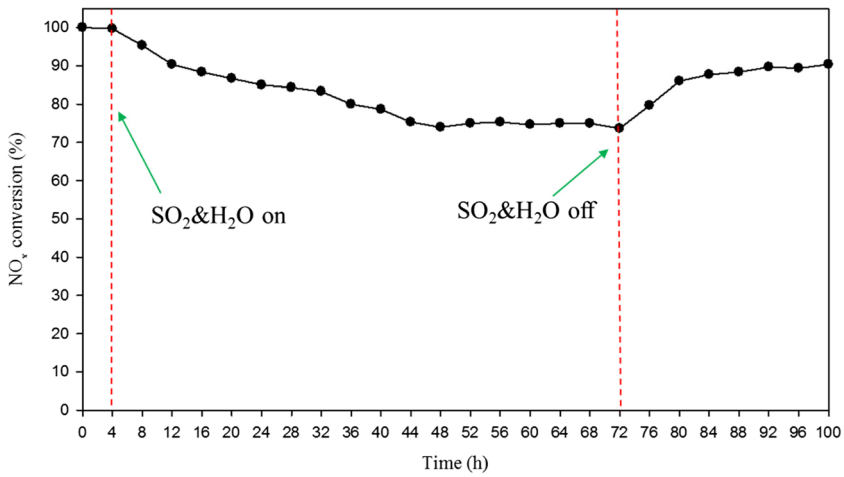

Fig. 7 The durability test and tolerance of SO_2 and $H_2O_{(g)}$ for SCR reaction

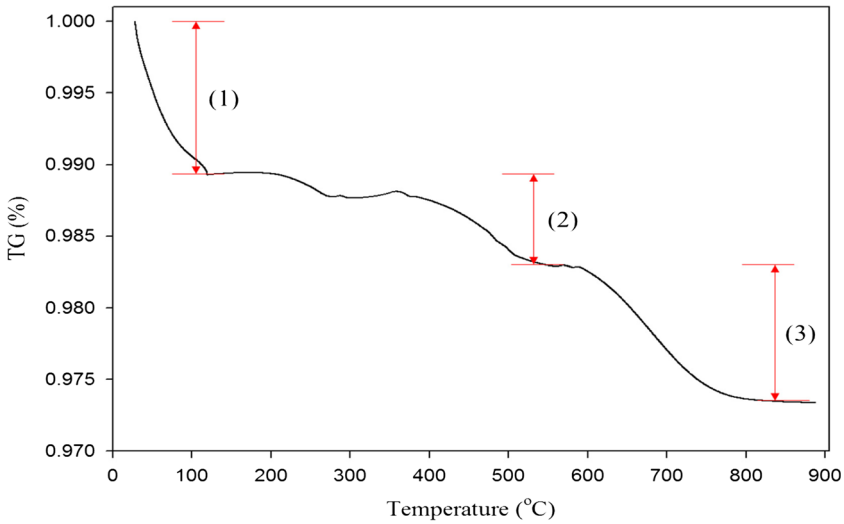

Fig. 8 TGA curve of used Mn-Ce-Ni/TiO_2 catalyst subjected to $H_2O_{(g)}$ and SO_2

from 50 to 200 °C. The two-stage system can also make SCR reaction more complete than catalyst alone. Moreover, NH_3 would be effectively consumed by reaction with NO_2 to form NH_4NO_3. Subsequently, NH_4NO_3 is reduced with NO via

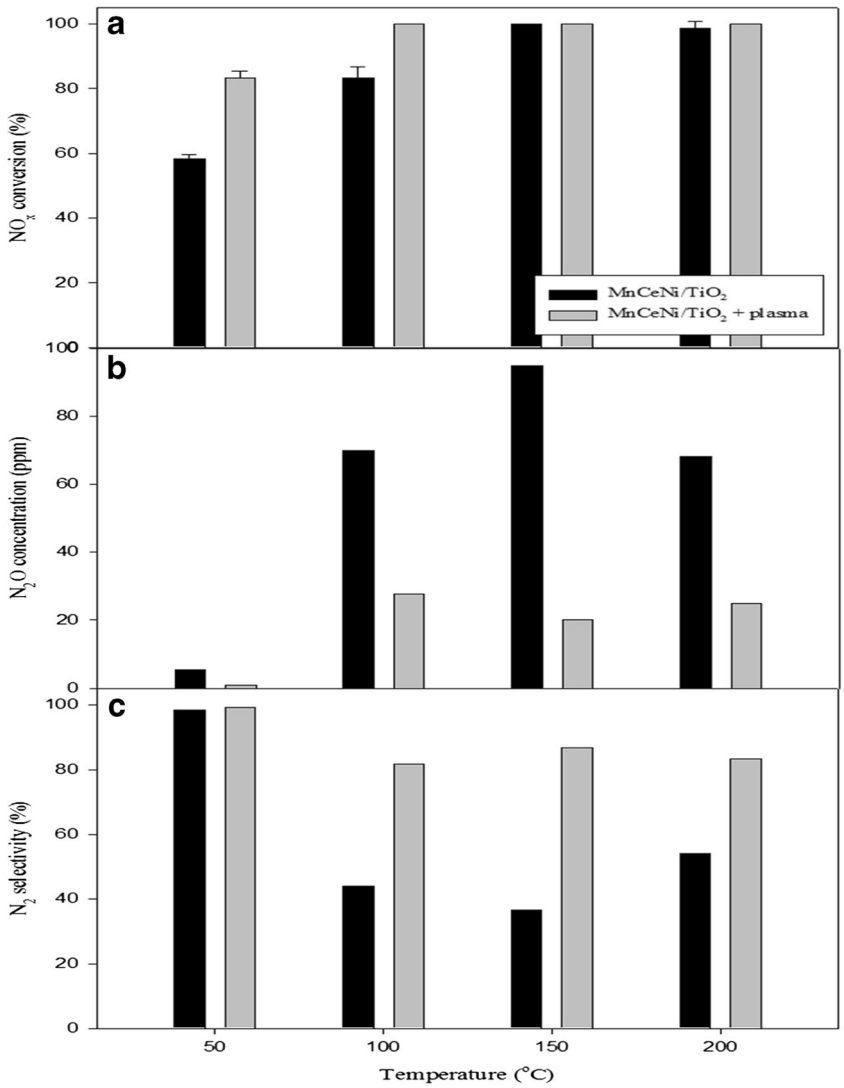

Fig. 9 Comparison of MnCeNi/TiO_2 alone ■ and MnCeNi/TiO_2 + plasma ▒, **a** NO_x conversion, **b** N_2O concentration, and **c** N_2 selectivity (300 ppm NO, 300 ppm NH_3, 10% O_2, applied voltage: 15.5 kV, frequency: 10 kHz and packed with glass beads)

reaction (10) to inhibit N_2O formation. In addition, N_2 selectivity of the two-stage system is higher than that of catalyst alone at a temperature range of 50–200 °C because two-stage system generates a lower N_2O concentration if compared with the catalyst-alone.

$$NO + NH_4NO_3 \rightarrow NO_2 + N_2 + 2H_2O \quad (10)$$

Effect of gas composition on two-stage system

In order to understand the effect of gas composition on the ratio of NO_2/NO, Fig. 10a–c shows the variation of NO_2/NO ratio with different gas compositions. The complicated gas compositions are added (including 10% CO_2, 0.5% CO, and 300 ppm C_2H_4) individually, for test. The concentrations of different compositions are chosen based on typical exhaust of diesel engine. As shown in Fig. 10, the NO_2/NO ratio still can reach 1 for different gas compositions. With the existence of 300 ppm C_2H_4, 0.5% CO, and 10% CO_2, the applied voltage needed to achieve NO_2/NO = 1 increases to 16.5, 16.5, and 17.5 kV, respectively, if compared with the NO + O_2 only. The gas composition with CO_2 has the most effect on the NO_2/NO ratio because the concentration of CO_2 is the highest than others. In addition, CO_2 belongs to electronegative characteristic gas which further forms negative ions such as CO_2^- to inhibit gas discharge. Generally, existence of electronegative characteristic gas may consume energetic electron in NTP system, resulting in the reduction of discharge performance and a lower ratio of NO_2/NO. Figure 10d shows that the variation of NO_2/NO ratio with applied voltage when C_2H_4, CO, CO_2, SO_2, and H_2O are present in the flue gas simultaneously. Obviously, the applied voltage has to be increased raise from 15.5 to 18 kV to achieve the fast-SCR condition (NO_2/NO ≈ 1).

To evaluate the performance of two-stage system to reduce NO_x to N_2 with complicated gas compositions, the reaction condition is as follows: 300 ppm NO, 300 ppm NH_3, 300 ppm C_2H_4, 0.5% CO, 10% CO_2, 2% $H_2O_{(g)}$, and 100 ppm SO_2. Results indicate that 300 ppm NO in complicated gas compositions could be converted into 156 ppm NO and 152 ppm NO_2 with the applied voltage of 18 kV and frequency of 10 kHz (as presented in Fig. 10d). As shown in Fig. 11, the NO_x reduction performance reveals an increased trend with increasing temperature and NO_x conversion reaches 90% at 100 °C. The two-stage system of this study shows better performance for SCR process if compared with literature (as summarize at Table 4).

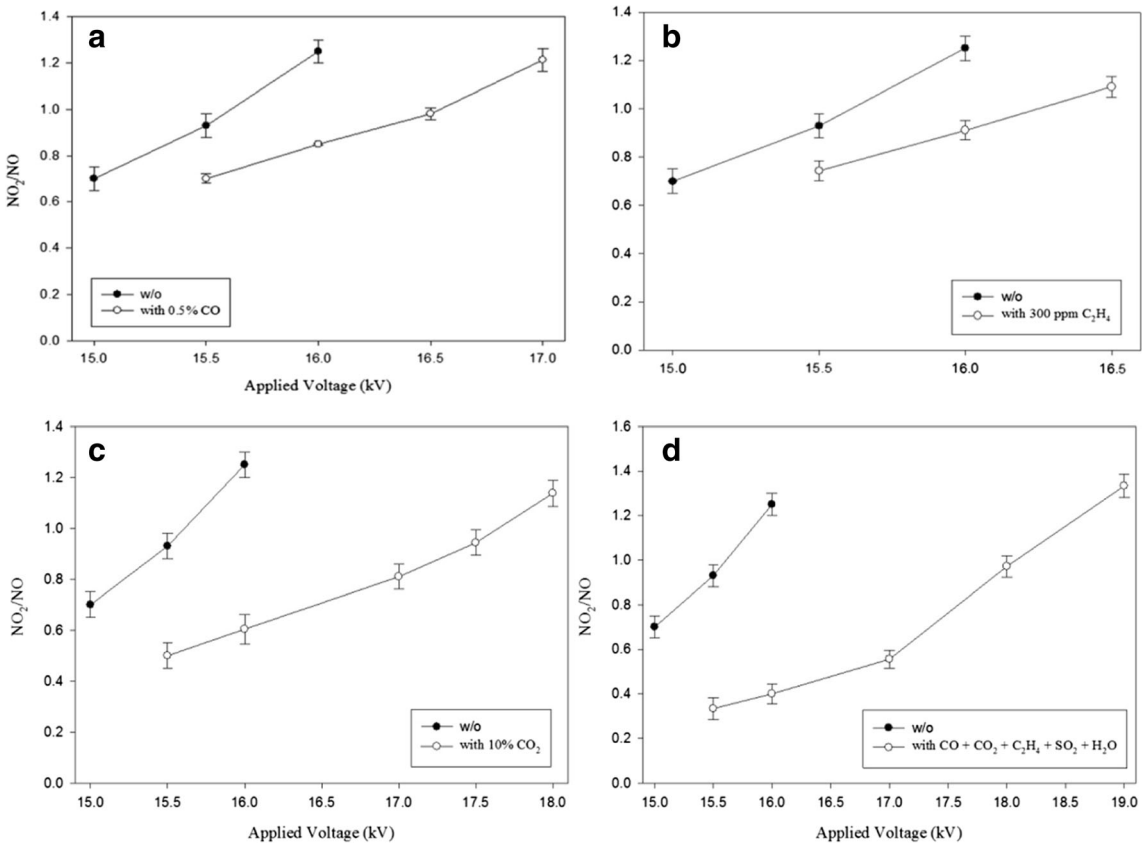

Fig. 10 Variation of NO_2/NO with different gas composition **a** NO + O_2 + CO, **b** NO + O_2 + C_2H_4, **c** NO + O_2 + CO_2, **d** NO + O_2 + CO+ CO_2 + C_2H_4 + SO_2 + H_2O

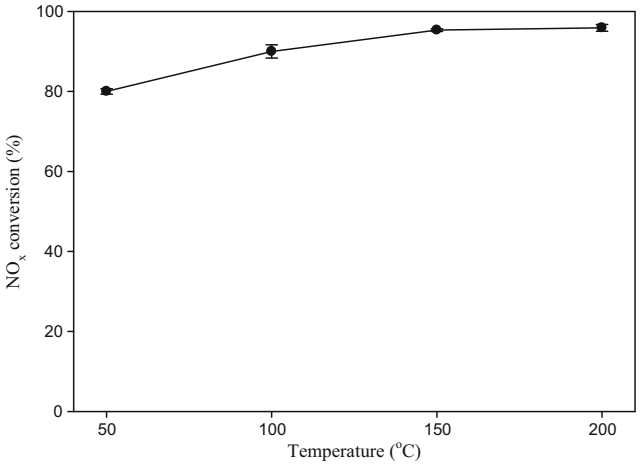

Fig. 11 Dependence of NO_x reduction activity on temperature of two-stage system

In addition, it is found that SO_2 concentration is reduced from 100 to 63 ppm as the gases pass through the NTP reactor, and it may be oxidized into SO_3 or H_2SO_4 by O, OH, or O_3. Relevant study indicated that the removal process of SO_2 involves oxidation of SO_2 by O, OH, and O_3, forming SO_3 and H_2SO_4 in the NTP system (Obradović et al. 2011). The results indicate that NO_x conversion reaches 95% at 150 °C by two-stage system and it has a good tolerance for $H_2O_{(g)}$ and SO_2 if compared with catalyst-alone. In the two-stage system, NTP system plays an essential role which can effectively oxidize NO to NO_2 for fast-SCR process. Goo et al. (2007) use V_2O_5-WO_3-MnO_2/TiO_2 with NH_3 as a reducing agent to conduct conventional SCR and fast-SCR for NO removal with the temperature ranging from 200 to 400 °C. The results indicate that fast-SCR has better tolerance for $H_2O_{(g)}$ if compared with conventional SCR. They suggest that the effect of water presence is marginal due to high reaction rate of fast SCR (Goo et al. 2007). In addition, they point out that >90% conversion could be achieved with fast-SCR (with V_2O_5-WO_3-MnO_2/TiO_2 as catalyst) in the presence of 8% $H_2O_{(g)}$ and 100 ppm SO_2 at 200 °C. Based on literature and the results obtained, it is speculated that fast-SCR has better NO conversion in the presence of $H_2O_{(g)}$ and SO_2 due to high reaction rate. Also, addition of another reducing agent (C_2H_4) in simulated gas streams may help increase NO conversion. These results indicate that the two-stage system has a high NO_x conversion at a low temperature, and it can operate not only at simple gas composition but also complicated gas condition. The two-stage plasma catalysis system has good potential to improve the activity of NO reduction at a low temperature.

Conclusions

Conventional SCR process still faces some challenges, for example, it needs to be operated within the temperature range of 250–350 °C for high efficiency. SCR catalyst suffers from deactivation, because conventional SCR process is typically installed before dust removal equipment and flue gas desulfurization (FGD) due to temperature limit. In addition, conventional SCR process cannot be applied for effective removal of NO_x from diesel engine exhaust due to its low temperature (100–200 °C). In this study, NTP and Mn-based catalyst are combined to form a two-stage system for NO reduction. First, three Mn-based catalysts including Mn-Ce/TiO_2, Mn-Ce-Ni/TiO_2, and Mn-Ce-Cu/TiO_2 are evaluated for SCR performance. Experimental results indicate that Mn-Ce-Ni/TiO_2 owns the best activity for SCR reaction among three Mn-based catalysts prepared. However, Mn-Ce-Ni/TiO_2 still needs to be operated at 150 °C for 100% NO_x conversion, and it also generates significant N_2O. Further, NTP is placed upstream of SCR system to transform part of NO into NO_2 for achieving fast-SCR. Results indicate that the NO_x conversion and N_2 selectivity achieved can reach 100 and 80%, respectively, and the N_2O concentration measured is lower than that of catalysis alone at 100 °C. The condition of NO_2/NO = 1 can be achieved for fast SCR by applying appropriate voltage with plasma system. This study demonstrates that combining Mn-based catalysts with NTP can successfully achieve fast SCR reaction to reduce NO_x to N_2, with a high efficiency and N_2 selectivity. This study indicates that plasma-assisted system

Table 4 Comparison of performance of the NTP enhanced SCR with literature

Catalysts	Plasma type	Voltage (kV)	Frequency (kHz)	Reducing agent	NO conc. (ppm)	SCR Temp. (°C)	Removal efficiency (%)	Reference
Mn-Ce-Ni/TiO_2	DBD	15.5	10	NH_3	300	150	>99	This study
H-mordenite	DBD	20	–	NH_3	500	160	76	Miessnera et al. (2002)
V_2O_5-WO_3/TiO_2	DBD	10	1	NH_3	500	200	>99	Bröer and Hammer (2000)
Co-HZSM-5	DBD	–	–	C_2H_2	500	300	90	Niu et al. (2006)
NH_4-mordenite	DBD	–	–	C_3H_6	500	200	>100	Chae (2003)
BaY + CuY	–	16	–	C_xH_y	182	200	95	Cho et al. (2012)

can improve the performance of SCR catalyst, and it has high performance at a low temperature (≦200 °C).

Nomenclature

Item
10% wt. Mn-Ce/TiO_2 = Mn-Ce/TiO_2
10% wt. Mn-Ce-Ni/TiO_2 = Mn-Ce-Ni/TiO_2
10% wt. Mn-Ce-Cu/TiO_2 = Mn-Ce-Cu/TiO_2
Dielectric barrier discharge = DBD
Nonthermal plasma = NTP
Selective catalytic reduction = SCR
SCR system + NTP = two-stage system

References

Boningari T, Ettireddy PR, Somogyvari A, Liu Y, Vorontsov A, McDonald CA, Smirniotis PG (2015) Influence of elevated surface texture hydrated titania on Ce-doped Mn/TiO_2 catalysts for the low-temperature SCR of NO_x under oxygen-rich conditions. J Catal 325: 145–155

Boccuzzi F, Chiorino A, Martra G, Gargano M, Ravasio N, Carrozzini B (1997) Preparation, characterization, and activity of cu/TiO_2 catalysts. I. Influence of the preparation method on the dispersion of copper in cu/TiO_2. J Catal 165:129–139

Bröer S, Hammer T (2000) Selective catalytic reduction of nitrogen oxides by combining a non-thermal plasma and a V_2O_5-WO_3/TiO_2 catalyst. Appl Catal B Environ 28:101–111

Cao F, Su S, Xiang J, Wang P, Hu S, Sun L, Zhang A (2015) The activity and mechanism study of Fe–Mn–Ce/γ-Al_2O_3 catalyst for low temperature selective catalytic reduction of NO with NH_3. Fuel 139: 232–239

Chang H, Li J, Yuan J, Chen L, Dai Y, Arandiyan H, Xu J, Hao J (2013) Ge, Mn-doped CeO_2–WO_3 catalysts for NH_3–SCR of NO_x: effects of SO_2 and H_2 regeneration. Catal Today 201:139–144

Chae JO (2003) Non-thermal plasma for diesel exhaust treatment. J Electrost 57:251–262

Chen H-Y, Wei Z, Kollar M, Gao F, Wang Y, Szanyi J, Peden CHF (2016) NO oxidation on zeolite supported cu catalysts: formation and reactivity of surface nitrates. Catal Today 267:17–27

Cho BK, Lee J-H, Crellin CC, Olson KL, Hilden DL, Kim MK, Kim PS, Heo I, Oh SH, Nam I-S (2012) Selective catalytic reduction of NO_x by diesel fuel: plasma-assisted HC/SCR system. Catal Today 191: 20–24

Choi B, Woo S-M (2015) Numerical analysis of the optimum heating pipe to melt frozen urea-water-solution of a diesel urea-SCR system. Appl Therm Eng 89:860–870

Cimino S, Lisi L, Tortorelli M (2016) Low temperature SCR on supported MnO_x catalysts for marine exhaust gas cleaning: effect of KCl poisoning. Chem Eng J 283:223–230

Fang D, Xie J, Hu H, Yang H, He F, Fu Z (2015) Identification of MnO_x species and Mn valence states in MnO_x/TiO_2 catalysts for low temperature SCR. Chem Eng J 271:23–30

Feng T, Lü L (2015) The characteristics of ammonia storage and the development of model-based control for diesel engine urea-SCR system. J Ind Eng Chem 28:97–109

Grossale A, Nova I, Tronconi E, Chatterjee D, Weibel M (2008) The chemistry of the NO/NO_2–NH_3 "fast" SCR reaction over Fe-ZSM5 investigated by transient reaction analysis. J Catal 256:312–322

Goo JH, Irfan MF, Kim SD, Hong SC (2007) Effects of NO_2 and SO_2 on selective catalytic reduction of nitrogen oxides by ammonia. Chemosphere 67:718–723

Huang L, Wang X, Yao S, Jiang B, Chen X, Wang X (2016) Cu–Mn bimetal ion-exchanged SAPO-34 as an active SCR catalyst for removal of NO_x from diesel engine exhausts. Catal Commun 81:54–57

Iwasaki M, Shinjoh H (2010) A comparative study of "standard", "fast" and "NO_2" SCR reactions over Fe/zeolite catalyst. Appl Catal A Gen 390:71–77

Jõgi I, Erme K, Raud J, Laan M (2016) Oxidation of NO by ozone in the presence of TiO_2 catalyst. Fuel 173:45–51

Jin R, Liu Y, Wang Y, Cen W, Wu Z, Wang H, Weng X (2014) The role of cerium in the improved SO_2 tolerance for NO reduction with NH_3 over Mn-Ce/TiO_2 catalyst at low temperature. Appl Catal B Environ 148-149:582–588

Jun L, Liwei J, Weiyang J, Feng X, Jiaming W (2015) Effects of Ce-doping on the structure and NH_3-SCR activity of Fe/Beta catalyst. Rare Metal Mater Eng 44:1612–1616

Kang M, Kim DJ, Park ED, Kim JM, Yie JE, Kim SH, Hope-Weeks L, Eyring EM (2006a) Two-stage catalyst system for selective catalytic reduction of NO_x by NH_3 at low temperatures. Appl Catal B Environ 68:21–27

Kang M, Yeon TH, Park ED, Yie JE, Kim JM (2006b) Novel MnO_x catalysts for NO reduction at low temperature with ammonia. Catal Lett 106:77–80

Koebel M, Elsener M, Madia G (2001) Reaction pathways in the selective catalytic reduction process with NO and NO_2 at low temperatures. Ind Eng Chem Res 40:52–59

Koebel M, Madia G, Raimondi F, Wokaun A (2002) Enhanced reoxidation of vanadia by NO_2 in the fast SCR reaction. J Catal 209:159–165

Kwon DW, Nam KB, Hong SC (2015) The role of ceria on the activity and SO_2 resistance of catalysts for the selective catalytic reduction of NO_x by NH_3. Appl Catal B Environ 166–167:37–44

Liu J, Li X, Zhao Q, Ke J, Xiao H, Lv X, Liu S, Tadé M, Wang S (2017) Mechanistic investigation of the enhanced NH_3-SCR on cobalt-decorated Ce-Ti mixed oxide: in situ FTIR analysis for structure-activity correlation. Appl Catal B Environ 200:297–308

Ma Z, Wu X, Feng Y, Si Z, Weng D (2015) Effects of WO_3 doping on stability and N_2O escape of MnO_x–CeO_2 mixed oxides as a low-temperature SCR catalyst. Catal Commun 69:188–192

Madia G, Koebel M, Elsener M, Wokaun A (2002) The effect of an oxidation precatalyst on the NO_x reduction by ammonia SCR. Ind Eng Chem Res 41:3512–3517

Miessnera H, Francke K-P, Rudolph R, Hammer T (2002) NO_x removal in excess oxygen by plasma-enhanced selective catalytic reduction. Catal Today 75:325–330

Niu Y, Shang T, Hui S, Zhang X, Lei Y, Lv Y, Wang S (2016) Synergistic removal of NO and N_2O in low-temperature SCR process with MnO_x/Ti based catalyst doped with Ce and V. Fuel 185:316–322

Niu J, Yang X, Zhu A, Shi L, Sun Q, Xu Y, Shi C (2006) Plasma-assisted selective catalytic reduction of NO_x by C_2H_2 over co-HZSM-5 catalyst. Catal Commun 7:297–301

Obradović BM, Sretenović GB, Kuraica MM (2011) A dual-use of DBD plasma for simultaneous NO_x and SO_2 removal from coal-combustion flue gas. J Hazard Mater 185:1280–1286

Patil BS, Cherkasov N, Lang J, Ibhadon AO, Hessel V, Wang Q (2016) Low temperature plasma-catalytic NO_x synthesis in a packed DBD reactor: effect of support materials and supported active metal oxides. Appl Catal B Environ 194:123–133

Peña DA, Uphade BS, Smirniotis PG (2004) TiO_2-supported metal oxide catalysts for low-temperature selective catalytic reduction of NO

with NH_3: I. Evaluation and characterization of first row transition metals Journal of Catalysis 221:421–431

Peng Y, Li K, Li J (2013) Identification of the active sites on CeO_2–WO_3 catalysts for SCR of NOx with NH_3: an in situ IR and Raman spectroscopy study. Appl Catal B Environ 140-141:483–492

Phil HH, Reddy MP, Kumar PA, Ju LK, Hyo JS (2008) SO_2 resistant antimony promoted V_2O_5/TiO_2 catalyst for NH_3-SCR of NO_x at low temperatures. Appl Catal B Environ 78:301–308

Putluru SSR, Schill L, Jensen AD, Siret B, Tabaries F, Fehrmann R (2015) Mn/TiO_2 and $Mn–Fe/TiO_2$ catalysts synthesized by deposition precipitation—promising for selective catalytic reduction of NO with NH_3 at low temperatures. Appl Catal B Environ 165:628–635

Shaju KM, Subba Rao GV, Chowdari BVR (2002) Performance of layered $li(Ni_1/3Co_1/3Mn_{1/3})\ O_2$ as cathode for li-ion batteries. Electrochim Acta 48:145–151

Shen B, Wang Y, Wang F, Liu T (2014) The effect of Ce–Zr on NH_3-SCR activity over $MnO_{x(0.6)}/Ce_{0.5}Zr_{0.5}O_2$ at low temperature. Chem Eng J 236:171–180

Shu Y, Aikebaier T, Quan X, Chen S, Yu H (2014) Selective catalytic reaction of NO_x with NH_3 over Ce–Fe/TiO_2-loaded wire-mesh honeycomb: resistance to SO_2 poisoning. Appl Catal B Environ 150-151:630–635

Tang X, Hao J, Xu W, Li J (2007) Low temperature selective catalytic reduction of NO_x with NH_3 over amorphous MnO_x catalysts prepared by three methods. Catal Commun 8:329–334

Thirupathi B, Smirniotis PG (2011a) Co-doping a metal (Cr, Fe, co, Ni, cu, Zn, Ce, and Zr) on Mn/TiO_2 catalyst and its effect on the selective reduction of NO with NH_3 at low-temperatures. Appl Catal B Environ 110:195–206

Thirupathi B, Smirniotis PG (2011b) Effect of nickel as dopant in Mn/TiO_2 catalysts for the low-temperature selective reduction of NO with NH_3. Catal Lett 141:1399

Tran DN, Aardahl CL, Rappe KG, Park PW, Boyer CL (2004) Reduction of NO_x by plasma-facilitated catalysis over in-doped γ-alumina. Appl Catal B Environ 48:155–164

Wan Y, Zhao W, Tang Y, Li L, Wang H, Cui Y, Gu J, Li Y, Shi J (2014) Ni-Mn bi-metal oxide catalysts for the low temperature SCR removal of NO with NH_3. Appl Catal B Environ 148-149:114–122

Wang X, Li X, Zhao Q, Sun W, Tade M, Liu S (2016) Improved activity of W-modified MnO_x-TiO_2 catalysts for the selective catalytic reduction of NO with NH_3. Chem Eng J 288:216–222

Wu Z, Jiang B, Liu Y, Zhao W, Guan B (2007) Experimental study on a low-temperature SCR catalyst based on MnO_x/TiO_2 prepared by sol–gel method. J Hazard Mater 145:488–494

Xie J, Fang D, He F, Chen J, Fu Z, Chen X (2012) Performance and mechanism about MnO_x species included in MnO_x/TiO_2 catalysts for SCR at low temperature. Catal Commun 28:77–81

Yang N-z, Guo R-t, Pan W-g, Q-l C, Wang Q-s, Lu C-z (2016) The promotion effect of Sb on the Na resistance of Mn/TiO_2 catalyst for selective catalytic reduction of NO with NH_3. Fuel 169:87–92

Yoshida K, Kuwahara T, Kuroki T, Okubo M (2012) Diesel NO_x aftertreatment by combined process using temperature swing adsorption, NO_x reduction by nonthermal plasma, and NO_x recirculation: improvement of the recirculation process. J Hazard Mater 231–232:18–25

Yu J, Guo F, Wang Y, Zhu J, Liu Y, Su F, Gao S, Xu G (2010) Sulfur poisoning resistant mesoporous Mn-base catalyst for low-temperature SCR of NO with NH_3. Appl Catal B Environ 95:160–168

Zhou A, Yu D, Yang L, Sheng Z (2016) Combined effects Na and SO_2 in flue gas on Mn-Ce/TiO_2 catalyst for low temperature selective catalytic reduction of NO by NH_3 simulated by Na_2SO_4 doping. Appl Surf Sci 378:167–173