

# Performance and kinetics study for low-temperature SCR of NO with NH<sub>3</sub> over MnO<sub>x</sub>–CeO<sub>2</sub> catalyst

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## Abstract

A series of manganese–cerium oxide catalysts were prepared by different methods and used for low-temperature selective catalytic reduction (SCR) of NO<sub>x</sub> with ammonia in the presence of excess O<sub>2</sub>. The Mn–Ce–O<sub>x</sub> catalysts showed high activities. The experimental results showed that the best Mn–Ce mixed-oxide catalyst yielded nearly 100% NO conversion at 120 °C at a high space velocity of 42,000 h<sup>-1</sup>. As the manganese content was increased from zero to 30% (i.e., the molar ratio of Mn/(Mn + Ce)), NO conversion increased significantly, but decreased at higher manganese contents. The most active catalyst was obtained with a molar Mn/(Mn + Ce) ratio of 0.3. The effect of the calcination temperature was also investigated and the optimum calcination temperature was 650 °C. These catalysts are substantially more active than all other catalysts reported in the literature. SO<sub>2</sub> and H<sub>2</sub>O (at high concentrations) have slight effects on the SCR activity. From a steady-state kinetics study, it was found that the low-temperature SCR reaction was zero order with respect to NH<sub>3</sub> and first order with respect to NO. Compared with the other catalysts reported for low-temperature SCR of NO with ammonia, based on the first-order rate constants, the MnO<sub>x</sub>–CeO<sub>2</sub> catalyst was several times more active than other catalysts reported in the literature. Only N<sub>2</sub> rather than N<sub>2</sub>O was found in the product when the temperature was below 150 °C. At higher temperatures, trace amounts of N<sub>2</sub>O were detected.  
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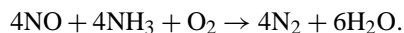
*Keywords:* Selective catalytic reduction of NO; Low-temperature SCR by NH<sub>3</sub>; Mn–Ce mixed oxide; Kinetics of NO reduction

## 1. Introduction

Nitrogen oxides (NO, NO<sub>2</sub>, and N<sub>2</sub>O) remain a major source of air pollution. They contribute to photochemical smog, acid rain, ozone depletion, and greenhouse effects [1]. Nearly all NO<sub>x</sub> (95%) derives from transportation (49%) and power plants (46%) [2]. In recent years, many methods have been used to reduce the emission of nitrogen oxide. Catalytic technologies are attractive because of their low cost and high efficiency [1]. In the case of automotive catalytic converters, CO acts as the main reducing agent for NO [3,4]. Hydrocarbons such as methane, propane, or propylene can also be used as reductants [5–9]. However, highly active and stable catalysts have not been found for hydrocarbon SCR.

The major technology for reducing nitrogen oxide emissions from stationary sources is selective catalytic reduction (SCR) of NO<sub>x</sub> ( $x = 1, 2$ ) by ammonia. The general reaction

is as follows:



Many catalysts have been reported to be active for the above reaction [1]. The commercial catalysts for this process are V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (anatase) mixed with WO<sub>3</sub> or MoO<sub>3</sub> [10–17]. Although the vanadium-based catalysts are highly active and resistant to SO<sub>2</sub>, there are also some disadvantages. This catalyst is active within a narrow temperature window of 300–400 °C, while this temperature range also helps to avoid pore plugging from the deposition of ammonium sulfate salts such as NH<sub>4</sub>HSO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>7</sub> on the catalyst surface. Consequently, it is necessary to locate the SCR unit upstream of the desulfurizer and electrostatic precipitator in order to avoid reheating of the flue gas as well as deposition of dust on the catalyst [1].

For the above reasons, there has been strong interest in developing highly active catalysts for low-temperature SCR. Such a catalyst would be placed downstream of the desulfurizer and electrostatic precipitator, and the temperature at this point is 150–160 °C. Success in developing such a catalyst

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would significantly improve the economics of SCR. Moreover, there is still residual SO<sub>2</sub> remaining after the desulfurizer. Thus, SO<sub>2</sub> resistance needs to be considered. The main disadvantage of low-temperature SCR is its susceptibility to ammonium bisulfate precipitation and formation of solid ammonium salts with NO<sub>2</sub> (especially ammonium nitrate). The effect could be minimized by increasing catalyst volume to provide spare surface area for deposition and by periodic operation at higher temperatures to evaporate the deposited ammonium bisulfate.

Some transition-metal-containing catalysts have been investigated for the low-temperature SCR reaction, such as chromia [2], NiSO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> [18], MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> [19], V<sub>2</sub>O<sub>5</sub>/activated carbon [20], iron–silica aerogels [21], MnO<sub>x</sub>/NaY [22], and other oxides [23]. They showed various SCR activities at below 200 °C under different conditions. Recently, we found that Fe–Mn-based transition-metal oxides [24] were highly active for low-temperature SCR of NO with NH<sub>3</sub> with 100% selectivity to N<sub>2</sub> at a high space velocity.

Ceria (CeO<sub>2</sub>) has been studied extensively for its oxygen storage and redox properties. For example, CeO<sub>2</sub> has been used as an important component of three-way catalysts (TWCs) [25–27]. The most important property of CeO<sub>2</sub> is as an oxygen reservoir, which stores and releases oxygen via the redox shift between Ce<sup>4+</sup> and Ce<sup>3+</sup> under oxidizing and reducing conditions, respectively. Ceria should enhance the oxidization of NO to NO<sub>2</sub>, thereby increasing the activity of SCR of NO by ammonia. Long and Yang [28,29] studied the promoting role of cerium oxide over Fe–Ti–PILC and Fe–ZSM-5 catalysts for SCR of NO with NH<sub>3</sub> and concluded that the doping of cerium oxide enhanced the activity resulting from an increase of NO oxidation to NO<sub>2</sub>.

This paper describes work performed in our laboratory [30,31] in developing active catalysts for the low-temperature SCR of NO with NH<sub>3</sub> (≤ 150 °C). The results show that MnO<sub>x</sub>–CeO<sub>2</sub> is a superior catalyst for NO reduction by NH<sub>3</sub> in the low-temperature window of 80–150 °C. The catalyst yielded 100% N<sub>2</sub> selectivity and complete NO conversion at temperatures as low as 120 °C and at GHSV = 42,000 h<sup>-1</sup> (GHSV was based on powder catalyst). Although much work has been performed on the catalytic performance of the manganese catalyst, no fundamental work has been performed to elucidate the kinetics over manganese–cerium oxide catalysts. Therefore, in this paper, we also report the results of activities and kinetics of the MnO<sub>x</sub>–CeO<sub>2</sub> catalyst for the low-temperature SCR of NO with NH<sub>3</sub>.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Citric acid method (CA)

Manganese nitrate, cerium nitrate, and citric acid were mixed in desired proportions. The mole ratio of citric acid

to the metal components (the total mole of manganese and cerium) was 1.0. The above mixture was stirred at room temperature for 1 h. The solution was dried at 100 °C, resulting in a porous, foam-like solid. The foam-like precursor was calcined in air at a desired temperature for 6 h. The obtained solid sample was first dried at 120 °C in air for 12 h and then calcined at 650 °C for 6 h in air in a tubular furnace. Finally, the samples were crushed and sieved to 60–100 mesh. Pure manganese oxide and ceria catalysts were prepared by the same procedure. The catalyst is denoted as MnO<sub>x</sub>(z)–CeO<sub>2</sub>(y), where *z* represents the mole ratio of Mn/(Mn + Ce) and *y* denotes the calcination temperature (°C), e.g., MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(650).

#### 2.1.2. Impregnation method (IM)

In this method we used incipient wetness impregnation. The desired amount of manganese acetate solution was added to a certain amount of cerium oxide. The obtained solid sample was first dried at 120 °C in air for 12 h and then calcined at 650 °C for 6 h in a tubular furnace. Finally, the samples were crushed and sieved to 60–100 mesh.

#### 2.1.3. Coprecipitation method (CP)

In this work, a certain amount of salts (nitrate and acetate) of Mn, Ce were dissolved in water, and excess urea was added to the solution and then the temperature was increased slowly to 90 °C with stirring. The mixtures were aged for several hours and then filtered and washed with deionized water. The obtained solid samples were first dried at 120 °C in air for 12 h and then calcined at 650 °C for 6 h in a tubular furnace. Finally, the samples were crushed and sieved to 60–100 mesh.

## 2.2. Catalyst characterization

A Micromeritics ASAP 2010 micropore-size analyzer was used to measure the N<sub>2</sub> adsorption isotherms of the samples at liquid N<sub>2</sub> temperature (–196 °C). The specific surface area was determined from the linear portion of the BET plot. The pore-size distribution was calculated from the desorption branch of the N<sub>2</sub> adsorption isotherm using the Barrett–Joyner–Halenda (BJH) formula. Prior to the surface area and pore-size distribution measurements, the samples were degassed in vacuo at 350 °C for 24 h.

The powder X-ray diffraction (XRD) measurement was carried out with a Rigaku Rotaflex D/Max-C system with Cu–K<sub>α</sub> (λ = 0.1543 nm) radiation. The samples were loaded on a sample holder with a depth of 1 mm.

## 2.3. Catalytic activity measurement

The SCR activity measurement was carried out in a fixed-bed quartz reactor. The typical reactant gas composition was as follows: 1000 ppm NO, 1000 ppm NH<sub>3</sub>, 2% O<sub>2</sub>, and balance He. A 200-mg sample was used in each run. The total flow rate was 100 ml/min (under ambient conditions). Thus,

a very high GHSV (gas hourly space velocity) referred to as powder catalyst was obtained ( $4.2 \times 10^4$  L/h). The premixed gases (1.01% NO in He, 1.00% NH<sub>3</sub> in He, and 0.99% SO<sub>2</sub> in He) were supplied by Matheson. Water vapor was generated by passing He through a heated gas-wash bottle containing deionized water. The tubing of the reactor system was heat-traced to prevent formation and deposition of ammonium sulfate/bisulfate and ammonium nitrate. The NO and NO<sub>2</sub> concentrations were continually monitored by a chemiluminescent NO/NO<sub>x</sub> analyzer (Thermo Electron Corporation, Model 10). To avoid errors caused by the oxidation of ammonia in the converter of the NO/NO<sub>x</sub> analyzer, an ammonia trap containing phosphoric acid solution was installed before the sample inlet to the chemiluminescent analyzer. The products were also analyzed by a gas chromatograph (Shimadzu, 8A) at 50 °C with 5 Å molecular sieve column for N<sub>2</sub> and Porapak Q column for N<sub>2</sub>O.

Nitrogen mass balance was made at steady state based on the inlet and outlet concentrations of NO, N<sub>2</sub>O, NO<sub>2</sub>, and N<sub>2</sub> (i.e., inlet [NO] = outlet [NO] + [N<sub>2</sub>] = [N<sub>2</sub>O]). For all the experiments in this work, the nitrogen balance exceeded 95%.

#### 2.4. Steady-state kinetic measurement

Steady-state kinetics studies were carried out in a fixed-bed, quartz flow reactor. The reaction temperature was controlled by an Omega (CN-2010) programmable temperature controller. Forty mg of catalyst was used in each run. The flue gas was simulated by blending different gaseous reactants. The typical reactant gas composition was as follows: 400–2000 ppm NO, 400–2000 ppm NH<sub>3</sub>, 2% O<sub>2</sub>, and balance He. The total flow rate was 500 ml/min (under ambient conditions). The instrumentation was the same as that used for the catalytic activity measurement described above.

#### 2.5. NO oxidation to NO<sub>2</sub>

The experiment of NO oxidation to NO<sub>2</sub> was also performed in the fixed-bed quartz reactor. A 200-mg sample was used and the conversion at each temperature was obtained after 1 h at steady state. The reactant gas composition was as follows: 1000 ppm NO, 2% O<sub>2</sub>, and balance He; the total flow rate was 100 ml/min (ambient conditions). The NO concentration was continually monitored by the chemiluminescent NO/NO<sub>x</sub> analyzer. NO conversion to NO<sub>2</sub> was obtained by using the equation:

$$\text{NO conversion to NO}_2 = \frac{[\text{NO}_x] - [\text{NO}]}{[\text{NO}_x]} \times 100\%,$$

where NO<sub>x</sub> represents NO + NO<sub>2</sub>.

Table 1  
Characterization of the catalysts

Samples <sup>a</sup>	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
MnO <sub>x</sub> (0.3)–CeO <sub>2</sub> (400)	76.75	0.148	7.76
MnO <sub>x</sub> (0.3)–CeO <sub>2</sub> (500)	68.40	0.156	9.17
MnO <sub>x</sub> (0.3)–CeO <sub>2</sub> (750)	36.31	0.088	9.70
Pure CeO <sub>2</sub> (650)	27.14	0.071	10.46
Pure MnO <sub>x</sub> (650)	27.16	0.071	10.45
MnO <sub>x</sub> (0.1)–CeO <sub>2</sub> (650)	56.37	0.118	8.01
MnO <sub>x</sub> (0.2)–CeO <sub>2</sub> (650)	46.85	0.107	8.67
MnO <sub>x</sub> (0.3)–CeO <sub>2</sub> (650)	58.62	0.163	9.44
MnO <sub>x</sub> (0.4)–CeO <sub>2</sub> (650)	32.78	0.076	8.47
MnO <sub>x</sub> (0.5)–CeO <sub>2</sub> (650)	30.59	0.075	7.02
MnO <sub>x</sub> (0.3)–CeO <sub>2</sub> (650) (CP) <sup>b</sup>	82.55	0.184	7.60
MnO <sub>x</sub> (0.3)–CeO <sub>2</sub> (650) (IM) <sup>c</sup>	32.89	0.118	10.44

<sup>a</sup> The number in the first parentheses denotes mole fraction (Mn/(Mn + Ce)). That in the second parentheses denotes temperature of calcinations (°C).

<sup>b</sup> Prepared by the coprecipitation method.

<sup>c</sup> Prepared by the impregnation method.

### 3. Results

#### 3.1. Characterization of catalysts

The BET surface areas, pore volumes, and pore sizes of manganese–cerium mixed-oxide catalysts are summarized in Table 1. From Table 1 we can see that the surface areas and the pore volumes of the pure manganese and cerium oxides are smaller than that of the mixed oxides. The surface area apparently decreased as the content of manganese increased, except for MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(650). The surface area also decreased at a higher calcination temperature, MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(400) > MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(500) > MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(650) > MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(750). The average pore diameters in these catalysts were 7.02–10.46 nm. From Table 1, we can see that the preparation method can affect significantly the surface area of the catalyst. The catalyst prepared by the coprecipitation method had the highest surface area. The catalyst prepared by the impregnation method had the lowest surface area.

#### 3.2. Effect of the composition of MnO<sub>x</sub>–CeO<sub>2</sub> catalyst

Results of the NO conversion as a function of temperature are shown in Fig. 1 for Ce–Mn oxide catalysts with different molar ratios of Mn/(Mn + Ce). The activity was very low on the pure CeO<sub>2</sub> (not shown). After manganese addition the activity increased sharply. Clearly, high catalytic activities were already achieved in the lower temperature region. At 80 °C, 82% NO conversion was obtained at a space velocity of 42,000 h<sup>−1</sup> on the MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(650) catalyst. At higher temperatures, NO conversion increased significantly and reached nearly 100% at above 120 °C. GC analyses showed that all of the products were N<sub>2</sub> and H<sub>2</sub>O. N<sub>2</sub>O formation was not observed when the reaction temper-

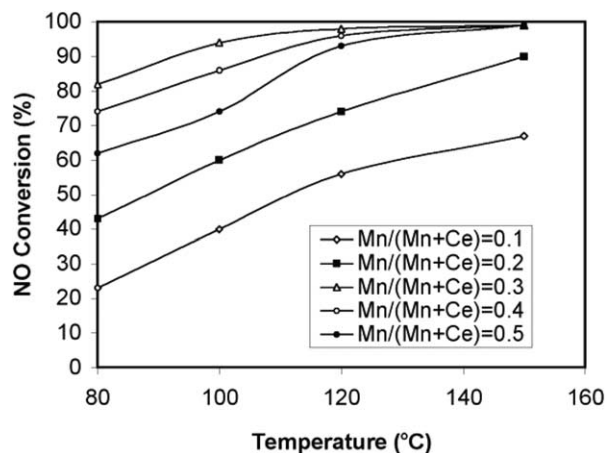


Fig. 1. NO conversion on various  $\text{MnO}_x\text{-CeO}_2$  mixed-oxide catalyst prepared by the citric acid method (all calcined at  $650^\circ\text{C}$ ) in the absence of  $\text{SO}_2$  and  $\text{H}_2\text{O}$ . Reaction conditions:  $[\text{NO}] = [\text{NH}_3] = 1000$  ppm,  $[\text{O}_2] = 2\%$ ,  $\text{GHSV} = 42,000$   $\text{h}^{-1}$ .

ature was below  $150^\circ\text{C}$ . At  $> 150^\circ\text{C}$ , very small amounts of nitrous oxide formation were observed beside  $\text{N}_2$ . Fig. 1 also shows the effect of the  $\text{Mn}/(\text{Mn} + \text{Ce})$  ratio on the activity. The SCR activity at low-temperatures decreased in the following sequence:  $\text{MnO}_x(0.3)\text{-CeO}_2(650) > \text{MnO}_x(0.4)\text{-CeO}_2(650) > \text{MnO}_x(0.5)\text{-CeO}_2(650) > \text{MnO}_x(0.2)\text{-CeO}_2(650) > \text{MnO}_x(0.1)\text{-CeO}_2(650)$ .

### 3.3. Effect of calcination temperature

Fig. 2 shows the activities of  $\text{MnO}_x\text{-CeO}_2$  mixed-oxide catalysts calcined at different temperatures. The result indicates that the calcination temperature influenced the SCR activity significantly. From Fig. 2 we can see that the catalyst calcined at  $650^\circ\text{C}$  had the highest activity. The NO conversion on the  $\text{Mn-Ce}$  mixed-oxide catalysts decreased

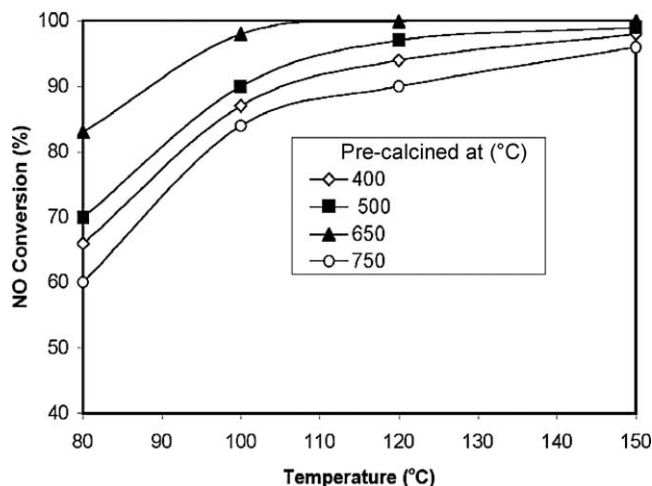


Fig. 2. SCR activity of  $\text{MnO}_x(0.3)\text{-CeO}_2$  mixed-oxide catalyst calcined at different temperatures. Reaction conditions:  $[\text{NH}_3] = [\text{NO}] = 1000$  ppm,  $[\text{O}_2] = 2\%$ ,  $\text{GHSV} = 42,000$   $\text{h}^{-1}$ . Catalysts were prepared by the citric acid method.

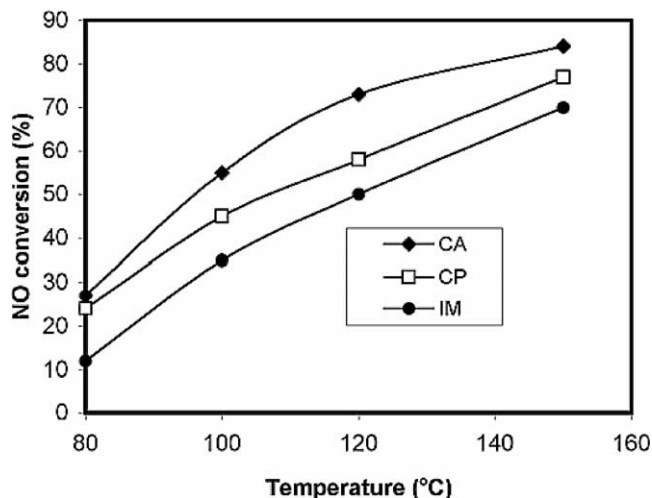


Fig. 3. SCR activity of  $\text{MnO}_x(0.3)\text{-CeO}_2(650)$  mixed-oxide catalyst prepared by different methods. Reaction conditions:  $[\text{NO}] = [\text{NH}_3] = 1000$  ppm,  $[\text{O}_2] = 2\%$ , He balance,  $0.2$  g catalyst, total flow rate =  $500$  ml/min,  $\text{GHSV} = 210,000$   $\text{h}^{-1}$ . CA, citric acid method; CP, coprecipitation method; IM, impregnation by incipient wetness.

in the order of  $\text{MnO}_x(0.3)\text{-CeO}_2(650) > \text{MnO}_x(0.3)\text{-CeO}_2(500) > \text{MnO}_x(0.3)\text{-CeO}_2(400) > \text{MnO}_x(0.3)\text{-CeO}_2(750)$ .

### 3.4. Effect of different preparation methods

The catalytic performance for SCR reaction over  $\text{MnO}_x\text{-CeO}_2$  catalysts prepared by different methods is shown in Fig. 3. Under a very high space velocity ( $\text{GHSV} = 210,000$   $\text{h}^{-1}$ ), these catalysts still show high NO conversions, especially the catalysts prepared by the citric acid method. The maximum NO conversion decreased in the sequence of  $\text{MnO}_x\text{-CeO}_2$  (CA)  $>$   $\text{MnO}_x\text{-CeO}_2$  (CP)  $>$   $\text{MnO}_x\text{-CeO}_2$  (IM). From the results of surface area for these catalysts (also shown in Table 1), the order of the surface area for these catalysts is  $\text{MnO}_x\text{-CeO}_2$  (CP)  $>$   $\text{MnO}_x\text{-CeO}_2$  (CA)  $>$   $\text{MnO}_x\text{-CeO}_2$  (IM). As noted above, the  $\text{MnO}_x\text{-CeO}_2$  (CA) catalyst showed much higher NO conversions than  $\text{MnO}_x\text{-CeO}_2$  (CP) and  $\text{MnO}_x\text{-CeO}_2$  (IM); hence, it seems that the SCR activity does not correlate with the surface area.

### 3.5. Activity of NO oxidation to $\text{NO}_2$

The oxidation activities of NO to  $\text{NO}_2$  by  $\text{O}_2$  on  $\text{MnO}_x(650)$  and  $\text{MnO}_x(0.3)\text{-CeO}_2(650)$  were also measured (Fig. 4). The oxidation activity of NO to  $\text{NO}_2$  on  $\text{MnO}_x$  was very low, especially at lower temperatures (only  $0.7\%$  conversion at  $80^\circ\text{C}$ ). After ceria addition to  $\text{MnO}_x$ , the NO oxidation activity increased significantly. This suggests that the addition of cerium oxide increased the rate of the oxidation of NO to  $\text{NO}_2$ .

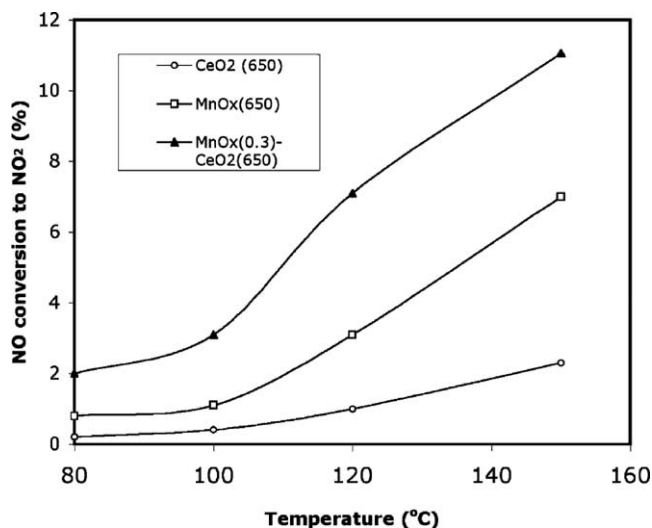


Fig. 4. Oxidation activity of NO to NO<sub>2</sub> by O<sub>2</sub> on MnO<sub>x</sub>(0.3)-CeO<sub>2</sub>(650) and MnO<sub>x</sub>(650) under the conditions of 0.2 g sample, 1000 ppm NO, 2% O<sub>2</sub>, and 100 ml/min total flow rate. Catalysts were prepared by the CA method.

### 3.6. Effect of O<sub>2</sub>

Previous studies of SCR catalysts have shown the importance of oxygen in SCR of NO with NH<sub>3</sub> [1]. The effect of oxygen on catalytic activity was also studied in this work. As shown in Fig. 5, MnO<sub>x</sub>(0.3)-CeO<sub>2</sub>(650) showed low activity for the reduction of NO by NH<sub>3</sub> at 120 °C in the absence of oxygen. However, when a small concentration of O<sub>2</sub> was introduced to the reactants, the NO conversion increased sharply. When the O<sub>2</sub> concentration was more than 0.5%, the NO conversion showed nearly no change. This indicated that O<sub>2</sub> played a significant promoting role in the SCR reaction. The importance of O<sub>2</sub> was also verified by another

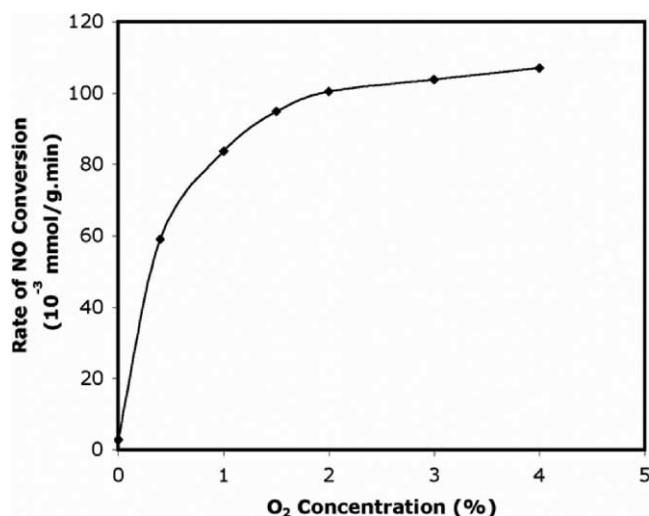


Fig. 5. Effect of O<sub>2</sub> concentration on catalytic performance on MnO<sub>x</sub>(0.3)-CeO<sub>2</sub>(650) catalyst at 120 °C. Reaction conditions: 200 mg catalyst, [NO] = [NH<sub>3</sub>] = 1000 ppm, [O<sub>2</sub>] = 0–4%, He balance, total flow 100 ml/min, GHSV = 42,000 h<sup>-1</sup>. Catalysts were prepared by the CA method.

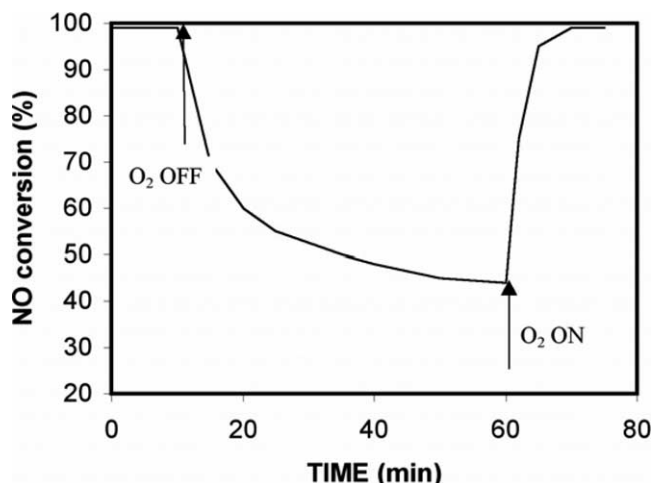


Fig. 6. Transient response on MnO<sub>x</sub>(0.3)-CeO<sub>2</sub>(650) upon switching off and on O<sub>2</sub> at 120 °C. Reaction conditions: 200 mg catalyst, [NO] = [NH<sub>3</sub>] = 1000 ppm, [O<sub>2</sub>] = 0–4%, He balance, total flow 100 ml/min, GHSV = 42,000 h<sup>-1</sup>. Catalysts were prepared by the CA method.

experiment. Transient behavior of the catalyst was tested by turning the oxygen off and on in the gas phase. The transient NO conversion is shown in Fig. 6. The NO conversion declined quickly after O<sub>2</sub> was turned off, followed by a slow decline. Switching O<sub>2</sub> back on resulted in an immediate increase in NO conversion, and the original conversion was restored quickly. Similar transient behaviors were observed for V<sub>2</sub>O<sub>5</sub>- and Cr<sub>2</sub>O<sub>3</sub>-based catalysts [32–35], indicating that the lattice oxygen was participating in the NO reduction reaction when O<sub>2</sub> was shut off.

### 3.7. Effect of H<sub>2</sub>O and SO<sub>2</sub>

Water vapor is one of the main components in flue gases and often leads to catalyst deactivation. Therefore, resistance of DeNO<sub>x</sub> catalysts to deactivation by water vapor is very important for industrial application. We further studied the effect of H<sub>2</sub>O on the SCR activities of the Ce–Mn mixed-oxide catalyst. Before adding water the SCR reaction had been stabilized for 1 h at 120 °C. When 2.5% H<sub>2</sub>O was added to the reactants, the NO conversion showed only a barely detectable decrease. Upon switching off the water vapor, the activity was rapidly restored to 100% of its original level. The inhibition by water vapor became appreciable at high water vapor concentrations, as shown in Fig. 7. When 19% H<sub>2</sub>O was added, the NO conversion decreased to about 98%. Upon removal of the water vapor supply, however, the activity was rapidly restored to its original value again.

Effect of SO<sub>2</sub> on the SCR activity is also important for the low-temperature SCR catalyst though the feed gas has passed through the desulfurizer. The effect of SO<sub>2</sub> + H<sub>2</sub>O on SCR activity of the Ce–Mn catalysts is also illustrated in Fig. 7. Our results indicated that when 100 ppm SO<sub>2</sub> and 2.5% H<sub>2</sub>O were added to the reaction gas and the reaction temperature and space velocity were kept at 120 °C and 42,000 h<sup>-1</sup>, respectively, the NO conversion on Ce–Mn

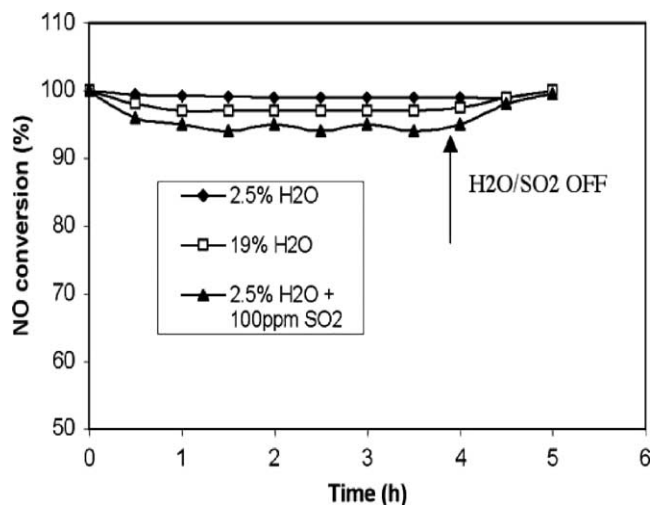


Fig. 7. Effects of on-stream time on SCR activity with H<sub>2</sub>O + SO<sub>2</sub> and without H<sub>2</sub>O + SO<sub>2</sub>. Reaction conditions: 120 °C, [NH<sub>3</sub>] = [NO] = 1000 ppm, [O<sub>2</sub>] = 2%, GHSV = 42,000 h<sup>-1</sup>. Catalyst: MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(650) prepared by the CA method.

oxides was decreased to 95% at 120 °C in 4 h. This was still a very high level of activity. Moreover, the activity was restored after SO<sub>2</sub> + H<sub>2</sub>O was stopped.

### 3.8. Steady-state kinetics studies

For determining the order of reaction with respect to NO, the concentration of NH<sub>3</sub> was kept constant at 1000 ppm, while the concentration of NO was varied from 200 to 1000 ppm. Similarly, in determining the order with respect to NH<sub>3</sub>, the concentration of NO was kept at 1000 ppm, while the concentration of NH<sub>3</sub> was varied between 400 and 1000 ppm. Since the flow rate was 500 ml/min and only 40 mg of catalyst was used, less than 15% NO conversion was obtained at 120 °C in these experiments. Therefore, the reactor may be treated as a differential reactor. The experimental results on the rate of NO conversion as a function of nitric oxide and ammonia concentrations are presented in Figs. 8 and 9, respectively. The rate of NO conversion increased with NO concentration, but it was almost unchanged with an increase in the NH<sub>3</sub> concentration. Assuming the reaction was free of diffusion limitation, the intrinsic rate of NO conversion as a function of reactant concentrations can be expressed as

$$\text{rate of NO conversion} = k[\text{NO}]^x[\text{NH}_3]^y[\text{O}_2]^z. \quad (1)$$

The reaction order  $x$  with respect to NO was calculated to be nearly 1, while the reaction order  $y$  with respect to NH<sub>3</sub> was nearly zero at 120 °C.

As shown in Fig. 5, MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(650) showed a low activity for the reduction of NO by NH<sub>3</sub> at 120 °C in the absence of oxygen. However, when a small concentration of O<sub>2</sub> was introduced to the reactants, NO<sub>x</sub> conversion increased sharply. When O<sub>2</sub> concentration was more than 2%, the NO<sub>x</sub> conversion showed nearly no change. This indicated that O<sub>2</sub>

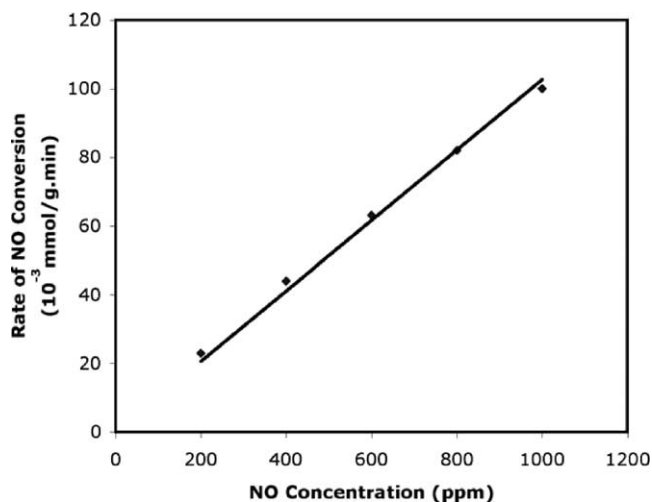


Fig. 8. Dependence of NO conversion rate on NO concentration on MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(650) at 120 °C. Catalysts were prepared by the CA method. Reaction condition: 40 mg catalyst, [NH<sub>3</sub>] = 1000 ppm, [O<sub>2</sub>] = 2%, He balance, total flow 500 ml/min, GHSV = 1.05 × 10<sup>6</sup> h<sup>-1</sup>.

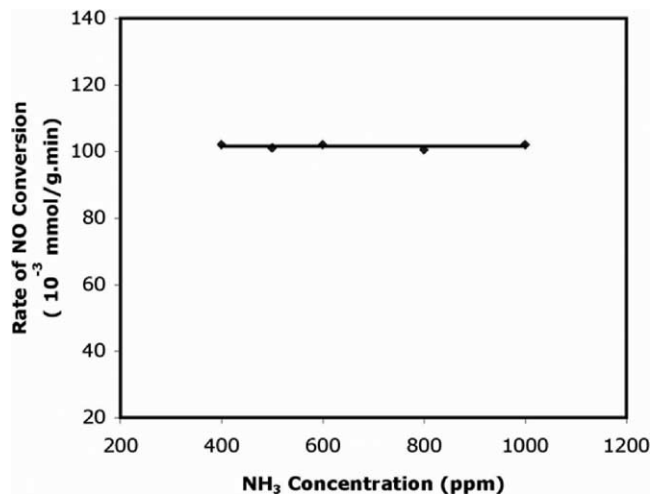


Fig. 9. Dependence of NO conversion rate on NH<sub>3</sub> concentration on MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(650) at 120 °C. Reaction conditions: 40 mg catalyst, [NO] = 1000 ppm, [O<sub>2</sub>] = 2%, He balance, total flow 500 ml/min, GHSV = 1.05 × 10<sup>6</sup> h<sup>-1</sup>. Catalysts were prepared by the CA method.

played a significant promoting role in the SCR reaction. According to Eq. (1) and the above data, the reaction order ( $z$ ) with respect to O<sub>2</sub> was calculated to be 0.56 at 120 °C when the oxygen concentration is below 1%, thus it is approximately one-half order with respect to O<sub>2</sub>. By comparison, previous results showed that the reaction order with respect to O<sub>2</sub> was one-half order for the Mn<sub>2</sub>O<sub>3</sub>–WO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst [36].

## 4. Discussion

The present work has shown that the MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(650) catalyst is more active than all known catalysts for low-temperature SCR reactions of NO with NH<sub>3</sub>. Nearly

Table 2  
Catalytic performance of MnO<sub>x</sub>–CeO<sub>2</sub> catalysts prepared by different methods in the absence of H<sub>2</sub>O and SO<sub>2</sub><sup>a</sup>

Catalyst	Preparation method	Temperature (°C)	NO <sub>x</sub> conversion (%)	k <sup>b</sup> (cm <sup>3</sup> /(g s))
MnO <sub>x</sub> (0.3)–CeO <sub>2</sub> (650)	CA	80	21	11.63
		100	54	40.49
		120	75	76.17
		150	87	120.66
MnO <sub>x</sub> (0.3)–CeO <sub>2</sub> (650)	CP	80	20	11.01
		100	43	29.31
		120	56	45.11
		150	74	79.66
MnO <sub>x</sub> (0.3)–CeO <sub>2</sub> (650)	IM	80	13	6.86
		100	34	21.66
		120	46	33.86
		150	63	58.80

<sup>a</sup> Reaction conditions: 0.2 g catalyst, [NO] = [NH<sub>3</sub>] = 1000 ppm, [O<sub>2</sub>] = 2%, He = balance, total flow rate = 500 ml/min, and GHSV = 210,000 L/h.

<sup>b</sup> First-order rate constant, as defined in the text.

100% NO conversion was obtained under a high space velocity (GHSV = 42,000 h<sup>-1</sup>) (Fig. 1 and Table 2). NO conversions on MnO<sub>x</sub>–CeO<sub>2</sub> catalysts were much higher than that on pure CeO<sub>2</sub> and MnO<sub>x</sub> (not shown). This indicated that there existed strong interaction between the manganese and the cerium oxide which resulted in the high activity. The SCR activity at low temperatures decreased in the following sequence: MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(650) > MnO<sub>x</sub>(0.4)–CeO<sub>2</sub>(650) > MnO<sub>x</sub>(0.5)–CeO<sub>2</sub>(650) > MnO<sub>x</sub>(0.2)–CeO<sub>2</sub>(650) > MnO<sub>x</sub>(0.1)–CeO<sub>2</sub>(650). Kapteijn et al. [19] investigated the manganese oxide supported on alumina extensively and found that the alumina-supported manganese oxides exhibited a high selectivity for N<sub>2</sub> formation below 425 K, although some N<sub>2</sub>O formation was also observed. This amount increased with temperature and with manganese loading. It has been suggested that the N<sub>2</sub>O formation occurs especially on well-ordered manganese oxide crystalline planes due to the presence of highly reactive oxygen. A similar conclusion has been drawn for crystalline chromia [32] and crystalline [33] and polymeric vanadia species [34]. In our work, we also found that the more manganese oxide, the more N<sub>2</sub>O was produced, especially when the ratio of Mn/(Mn + Ce) was higher than 0.5.

The above result also indicates that the calcination temperature influenced the SCR activity significantly. From Fig. 2 we can see that the catalyst calcined at 650 °C has the highest activity. The NO conversion on the Mn–Ce mixed-oxide catalysts decreased in the order of MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(650) > MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(500) > MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(400) > MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(750). Based on the results of surface area and the XRD study (not shown), we see that after the catalyst was calcined at 750 °C, the surface area decreased sharply and the CeO<sub>2</sub> phase was detected from XRD. The decrease of activity of the catalyst calcined at 750 °C may be attributed

to the sintering and CeO<sub>2</sub> segregation from the catalyst. The manganese oxide phase was not detected by XRD for all the catalysts studied. This further indicated that the manganese and cerium oxide have strong interactions. Kapteijn et al. [37] investigated the activity and selectivity of pure manganese oxides for SCR of NO by ammonia and found that the activity and selectivity of N<sub>2</sub> of the unsupported manganese oxide were determined by the oxidation state and the degree of crystallinity, and that Mn<sub>2</sub>O<sub>3</sub> exhibited the highest selectivity for nitrogen. It is well known that different calcination temperatures result in different oxidation states of manganese, so the calcination temperature affects the activity and selectivity of SCR of NO by NH<sub>3</sub>.

The results above also indicated that the addition of cerium oxide increased the activity of NO oxidation to NO<sub>2</sub> significantly. Koebel [38] investigated the low-temperature behavior of the SCR process with feed gases containing both NO and NO<sub>2</sub> and concluded that the partial conversion of NO into NO<sub>2</sub> may be helpful in increasing the performance of SCR system, especially in the range of lower temperatures. Long and Yang [39] also reported that an increase in NO oxidation to NO<sub>2</sub> on Fe-ZSM-5 would result in a significant improvement in the SCR activity, and the reaction rate of NH<sub>3</sub> with NO<sub>2</sub> + NO was much higher than that with NO alone. Therefore, it is expected that a high activity for NO conversion to NO<sub>2</sub> at low temperature may contribute to high SCR activity. The addition of cerium oxide enhanced the activity of NO to NO<sub>2</sub>, thereby increasing the SCR activity.

According to the foregoing results, the SCR reaction can be considered to be approximately first order with respect to NO, zero order with respect to NH<sub>3</sub>, and one-half order with respect to O<sub>2</sub> in the low concentration (< 1%). The reaction rate of NO consumption is expressed as

$$r_{\text{NO}} = k[\text{NO}][\text{O}_2]^{0.5}. \quad (2)$$

The above rate equation is valid only when the oxygen partial pressure is below approximately 1% atm. In experiments listed in Table 2, the partial pressures were all 2% atm. Under such conditions, the following rate equation applies:

$$r_{\text{NO}} = k[\text{NO}]. \quad (3)$$

Since the amount of oxygen is excessive, if the reaction is free of diffusion limitation, the apparent rate constant ( $k$ ) and NO conversion ( $X$ ) are related as follows:

$$k = -\frac{F_0}{[\text{NO}]_0 W} \ln(1 - X), \quad (4)$$

where  $F_0$  is the molar NO feed rate,  $[\text{NO}]_0$  is the molar NO concentration at the inlet (at the reaction temperature), and  $W$  is the catalysts amount (g).

A comparison has been made for the MnO<sub>x</sub>–CeO<sub>2</sub> catalysts prepared by different methods, given in Table 2. In order for a fair comparison, the first-order rate constants,  $k$ , were calculated by Eq. (4), assuming diffusion-limitation free. The rate constants at 150 °C are 120.66, 79.66, and

Table 3  
Performance of various catalysts for low-temperature SCR of NO with NH<sub>3</sub>

Catalyst	Feed composition			<i>t</i> (°C)	<i>X</i> <sub>NO</sub> <sup>c</sup> (%)	SV (h <sup>-1</sup> )	<i>k</i> <sup>a</sup> (cm <sup>3</sup> /(g s))	Ref.
	NO (ppm)	NH <sub>3</sub> (ppm)	O <sub>2</sub> (%)					
5% V <sub>2</sub> O <sub>5</sub> /AC	500	560	3.3	250	79.7	90,000	69.96	[20]
Fe–Mn	1000	1000	2	100	97	15,000	14.63	[24]
MnO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	500	550	2	150	63	24,000	9.40	[19]
Mn <sub>2</sub> O <sub>3</sub> –WO <sub>3</sub> /γ–Al <sub>2</sub> O <sub>3</sub>	500	550	10	150	45	91,400	21.54	[36]
15MnNaY775 <sup>b</sup>	1000	1000	5	170	82	48,000	33.98	[22]
MnO <sub>x</sub> (0.3)–CeO <sub>2</sub> (650) <sup>d</sup>	1000	1000	2	100	54	210,000	40.49	This work
				120	75		76.17	
				150	87		120.6	

<sup>a</sup> First-order rate constant.

<sup>b</sup> The feed contained 7% H<sub>2</sub>O.

<sup>c</sup> NO conversion.

<sup>d</sup> Prepared by citric acid method.

58.80 cm<sup>3</sup>/(g s) for MnO<sub>x</sub>–CeO<sub>2</sub> catalyst prepared by CA, CP, and IM methods, respectively. Obviously, the catalyst prepared by the citric acid method had the highest activity.

A summary comparison has been made for the Ce–Mn catalyst with other high-activity catalysts that were reported in the literature, given in Table 3. The vanadia/carbon system had a high activity [20], but it was at a higher temperature (250 °C) and clearly some carbon combustion was involved. The results show that the Ce–Mn catalyst is substantially more active than all other catalysts.

## 5. Conclusions

The manganese cerium mixed-oxides prepared from the citric acid method were highly active for the low-temperature SCR of NO with NH<sub>3</sub> in the presence of excess oxygen. More than 99% of NO conversion was obtained on the MnO<sub>x</sub>(0.3)–CeO<sub>2</sub>(650) catalyst at 120 °C under the condition of GHSV = 42,000 h<sup>-1</sup>.

Steady-state kinetics experiments showed that the reaction order for NO was near one and that for NH<sub>3</sub> was zero. In conclusion, a new highly active, H<sub>2</sub>O- and SO<sub>2</sub>-resistant catalyst has been developed for low-temperature SCR of NO with NH<sub>3</sub> in excess O<sub>2</sub>. Further studies are in progress for an understanding of the mechanism of the catalytic system.

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