

# Experimental study on a low-temperature SCR catalyst based on $\text{MnO}_x/\text{TiO}_2$ prepared by sol–gel method

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## Abstract

A catalyst based on  $\text{MnO}_x/\text{TiO}_2$  was prepared by sol–gel method for low-temperature selective catalytic reduction (SCR) of NO with  $\text{NH}_3$ . Focusing on the effects of the operating parameters, the SCR reaction was investigated at temperatures from 353 to 523 K under steady and transient states. Under the optimal conditions, the efficiency of NO removal could exceed 90% at temperature of 423 K. Furthermore, within the range investigated, the reaction order of NO,  $\text{NH}_3$ ,  $\text{O}_2$  was determined to be 1, 0, and 0.5, respectively. Apparent activation energy was also calculated to be 38 kJ/mol, lower than that for most of the catalysts reported by previous investigations.

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*Keywords:* NO;  $\text{MnO}_x/\text{TiO}_2$ ; SCR; Operating parameters; Apparent activation energy

## 1. Introduction

Selective catalytic reduction (SCR) of nitrogen oxides ( $\text{NO}_x$ ) with ammonia is one of the prospective processes for cleaning the flue gas from stationary sources [1,2]. It is a well established commercial technology, which employing  $\text{V}_2\text{O}_5\text{--}\text{WO}_3$  (or  $\text{MoO}_3$ )/ $\text{TiO}_2$  as catalyst [3,4]. However, the narrow temperature window (573–673 K) of the reactivity is the main obstacle for its real application, since high concentrations of sulfur dioxide and dust would deactivate the catalyst. Therefore, there is a rising interest in developing the low-temperature (353–523 K) SCR catalyst. The SCR reactor with this type of catalyst can be moved to downstream of the desulfurization scrubber and/or particulate control device, where most of sulfur dioxide and dust is removed and then its deactivation is weakened.

Manganese oxides attract interest as low-temperature SCR catalysts since they contain various types of labile oxygen, which are necessary to complete the catalytic cycle. The activity and selectivity of pure manganese oxides in SCR have been intensively investigated by Kapteijn et al. [5], and 90% of NO conversion was obtained at 450 K. Furthermore, to prolong the useful life and catalytic activity of catalyst, manganese oxides

were always based on titania [6]. Among the different types of manganese oxide catalysts, it was reported [7,8] that amorphous manganese oxide had good performance in SCR reaction, while crystalline manganese oxide contributed little to the activity.

However, almost all of the catalysts studied [9–11] were prepared by solution impregnation method, the dispersion would decline with high manganese loading, and amorphous manganese oxide would transform to crystalline one. Thus, the limit of the dispersion would lead to a reduction of NO conversion. It was concluded by Qi and Yang [12] that when the manganese loading was higher than 10%, the increase of manganese loading did not increase the activity due to its limited dispersion on the catalyst support. To solve this problem, the sol–gel method may be a better way to obtain SCR catalysts with good dispersion on the surface and nanoscaled oxides in the structure. Thus, in this paper, the catalyst was prepared by sol–gel method to achieve higher NO conversion and an experimental scale SCR process was carried out by using this catalyst.

Due to their great effects on the SCR system performances, the operating parameters including catalyst composition, reaction temperature, and oxygen and ammonia concentration were experimentally studied. Furthermore, apparent activation energy is an important parameter to evaluate the catalytic activity. In previous studies, apparent activation energy was calculated to describe the activity of catalysts [13,14]. In our study, we also carried out experiments to obtain the apparent activation energy,

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which could be used to compare the performance of  $\text{MnO}_x/\text{TiO}_2$  with that of other catalysts in low-temperature window.

## 2. Experiment set up

### 2.1. 2.1 Catalyst preparation

The catalyst was prepared by sol–gel method. All chemicals used were of analytical grade. Butyl titanate (0.1 mol), ethanol (0.8 mol), water (0.6 mol), acetic acid (0.3 mol) and manganese nitrate (0.04 mol) were mixed under vigorous stirring at room temperature, and formed transparent yellow sol. After being stable at room temperature for several days, the sol transformed to gel. The gel was dried at 378 K and transform to a porous solid. Then the solid was crushed and sieved to 50–90 mesh. After that the solid were calcined at 773 K for 6 h in air in a tubular furnace. The catalyst was denoted as  $\text{MnO}_x(z)/\text{TiO}_2$ , where  $z$  represents the mole ratio of Mn/Ti, e.g.  $\text{MnO}_x(0.4)/\text{TiO}_2$ .

### 2.2. Catalytic activity measurement

The SCR activity measurement was carried out in a fixed-bed, stainless steel flow reactor. The experiments were performed in both an integral reactor and a differential reactor under atmospheric pressure at 353–523 K. The integral reactor (i.d. 1 cm) consisted of a steel tube in which 4 ml of catalyst was placed, while in the differential reactor 0.4 ml (0.5 g) catalyst was placed. The typical reactant gas composition was: NO of 200–1500 ppm,  $\text{NH}_3$  of 200–1000 ppm,  $\text{O}_2$  of 0–5%, and balanced  $\text{N}_2$ . And the total flow rate was 1600–3200 ml/min. The tubing of the reactor system was heat traced to prevent formation and deposition of ammonium nitrate and the reaction temperature was controlled by an OMRON programmable temperature controller. NO,  $\text{NO}_2$ , and  $\text{O}_2$  concentration were monitored by a flue gas analyzer (KM9006 Quintox Kane International Limited). For the reaction was carried out at low temperature, it should be confirmed that the decrease of NO was not the result of the adsorption of NO in the catalysts. Thus, at the beginning of each experiment, we purged the catalyst with reaction gas until the NO concentration of out gas reached the inlet gas concentration.

### 2.3. Characterization of the samples

Adsorbed-1 Quantachrom was used to calculate the surface area, pore volume and average pore size of the samples. X-ray diffraction (XRD) measurements were carried out with a XD-2 X-ray diffractometer using Cu K $\alpha$  radiation.

## 3. Results and discussion

### 3.1. Influence of operating parameters

#### 3.1.1. Catalyst composition

It could be known from the literature [12] that SCR activity was relative to the dispersion of manganese oxides. Thus, the composition of catalysts would have effects on the SCR

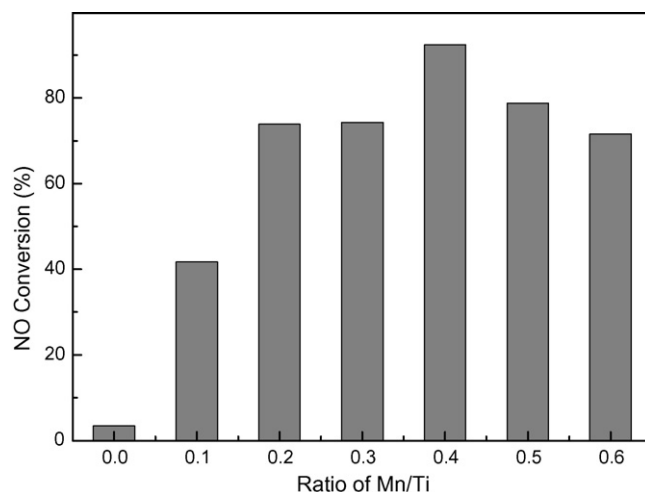


Fig. 1. The variation of NO conversion with  $\text{MnO}_x/\text{TiO}_2$  catalysts with different ratio of Mn/Ti at 423 K. Reaction conditions:  $[\text{NO}] = [\text{NH}_3] = 1000$  ppm,  $[\text{O}_2] = 3\%$ , balance  $\text{N}_2$ , total flow rate 2000 ml/min, catalyst 4 ml.

efficiency. Fig. 1 shows the NO conversion for  $\text{MnO}_x/\text{TiO}_2$  catalysts with different molar ratios of Mn/Ti at 423 K. There was neglected efficiency on the pure  $\text{TiO}_2$ . After manganese addition, the activity increased quickly. Higher manganese loading would improve NO conversion until the mole ratio of Mn/Ti reached 0.4. Beyond this value, a further increase of manganese loading did not improve the activity. From the previous studies [15,16], when manganese loading was beyond a certain value, there would be a sintering in the catalyst, and well-ordered manganese oxide crystalline planes were formed, which would lead to the decreasing of NO conversion. In this study, the value of Mn/Ti was 0.4, which was much higher than that of the catalysts prepared by solution impregnation method [12].

Fig. 2 shows the XRD patterns of the  $\text{MnO}_x/\text{TiO}_2$  catalysts with different Mn loading. From the X-ray diffraction, it could be seen that the intensity of the peaks due to  $\text{TiO}_2$  decreased with the increasing of manganese loading. It indicated that Mn would interact with  $\text{TiO}_2$  in the catalysts. At low manganese loadings, none of the XRD spectra gave intense peaks for manganese oxides, indicating that manganese oxides were well dispersed and kept as amorphous phase on the titania support. With the

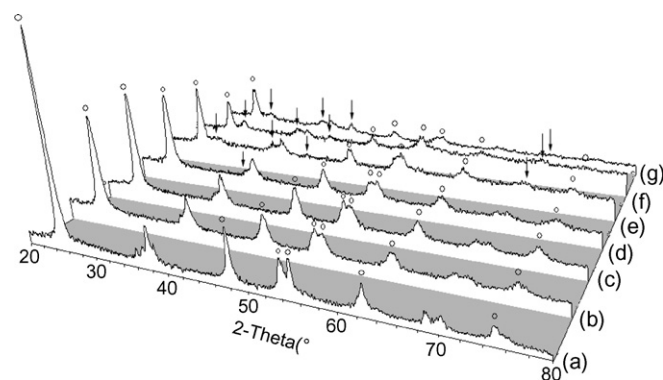


Fig. 2. XRD spectra of: (a)  $\text{TiO}_2$ , (b)  $\text{MnO}_x(0.1)/\text{TiO}_2$ , (c)  $\text{MnO}_x(0.2)/\text{TiO}_2$ , (d)  $\text{MnO}_x(0.3)/\text{TiO}_2$ , (e)  $\text{MnO}_x(0.4)/\text{TiO}_2$ , (f)  $\text{MnO}_x(0.4)/\text{TiO}_2$ , and (g)  $\text{MnO}_x(0.6)/\text{TiO}_2$  (○, anatase; ↓,  $\text{MnO}_2$ ).

Table 1  
The physical characteristics of the catalysts

Samples	BET surface area (m <sup>2</sup> /g)	Pore volume (×10 <sup>-2</sup> cm <sup>3</sup> /g)	Average pore size (nm)
TiO <sub>2</sub>	55.6	2.9	5.71
MnO <sub>x</sub> (0.1)/TiO <sub>2</sub>	59.4	3.1	5.69
MnO <sub>x</sub> (0.2)/TiO <sub>2</sub>	64.5	3.4	5.71
MnO <sub>x</sub> (0.3)/TiO <sub>2</sub>	76.2	3.7	5.64
MnO <sub>x</sub> (0.4)/TiO <sub>2</sub>	75.3	3.7	5.57
MnO <sub>x</sub> (0.5)/TiO <sub>2</sub>	70.9	3.7	5.59
MnO <sub>x</sub> (0.6)/TiO <sub>2</sub>	65.4	3.4	5.61

Mn loading continued increasing, the crystalline phase of MnO<sub>2</sub> became apparent. When the ratio was more than 0.4, there were apparent peaks of MnO<sub>2</sub> formed in the catalyst. It implied that when Mn loading was larger than 0.4, the sintering took place and then led to the formation of the well-ordered crystalline MnO<sub>2</sub>, which contributed little to NO removal. Therefore, when the ratio of Mn/Ti increased from 0.4 to 0.6, the reduction of NO conversion (as shown in Fig. 1) was due to the transformation of amorphous manganese oxides to crystalline phase. The results were in good agreement with the study of Duffy et al. [17]. According to the study of Qi and Yang [12], crystalline phase of manganese oxides would be formed when the manganese loading was larger than 10%. Thus, by using sol-gel method, more manganese oxides could be well dispersed and kept as amorphous phase in the catalyst, and then higher activity was obtained.

Table 1 shows the BET surface area, pore volume and pore size of the catalysts. In previous studies [2,3,18], it was reported that when the catalysts were prepared by impregnation method, the surface area and pore volume would decrease with the increasing of the active component loading. In this study, when the catalysts were prepared by sol-gel method, the surface area and pore volume increased with the addition of Mn. Furthermore, this variation was in good agreement with the catalytic activity (as shown in Fig. 1). Therefore, with appropriate loading of Mn, the nano-structure of the catalyst would be changed and catalytic activity was improved.

### 3.1.2. Reaction temperature

The variations of NO conversion with GHSV (gas hourly space velocity) at different temperatures were shown in Fig. 3. The results indicated that temperature had significant effect on the SCR activity. The NO conversion increased for a higher temperature. And more than 90% of NO was converted at 423 K for a flow rate of 2000 ml/min. Furthermore, it could be seen that the increasing of the GHSV would lead to lower NO conversion. However, at higher temperature, the gas flow rate had less effect on the efficiency of reaction than that at lower temperature. At 353 K, when GHSV increased from 24,000 to 48,000 h<sup>-1</sup>, the value of NO conversion decreased by 6.3%, while there are only a little reduction of about 0.4% for NO conversion at 453 K.

### 3.1.3. Oxygen concentration

It was known from previous studies [19] that O<sub>2</sub> had significant effect on SCR performance. In this paper, the effects

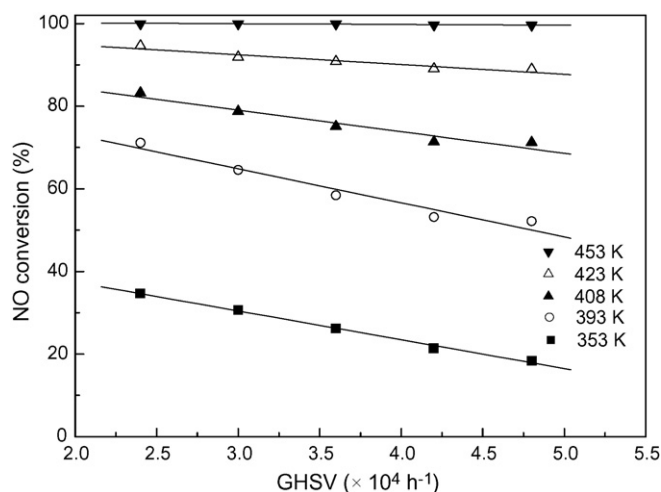


Fig. 3. The variation of NO conversion with different GHSV. Reaction conditions: [NO]=[NH<sub>3</sub>]=1000 ppm, [O<sub>2</sub>]=3%, balance N<sub>2</sub>, total flow rate 1600–3200 ml/min, catalyst 4 ml.

of oxygen concentration on NO conversion had been studied and shown in Fig. 4. At low O<sub>2</sub> concentration, MnO<sub>x</sub>(0.4)/TiO<sub>2</sub> showed a low activity for the reduction of NO by NH<sub>3</sub>. When O<sub>2</sub> concentration increased, there was a great increase of the NO conversion, and the conversion was stable when the value of O<sub>2</sub> concentration was more than 3%.

Fig. 5 shows the transient behavior of the catalyst tested by switching the oxygen supply off and on in the inlet gas. It could be seen from Fig. 5 that when the oxygen supply was switched off, the NO conversion decreased slowly. After 78 min, NO conversion decreased gradually to reach a steady-state. According to the study of Bosch [20], reoxidising the reduced surface sites of catalysts was a significant step in the SCR process, and these sites could be reoxidised by both O<sub>2</sub> and NO. In this study, when the oxygen supply was switched off, there were still some adsorbed oxygen and lattice oxygen in the system, which were available for reoxidation. Thus, the decrease of NO conversion was a slow one. After 78 min, when the catalyst was reoxidised

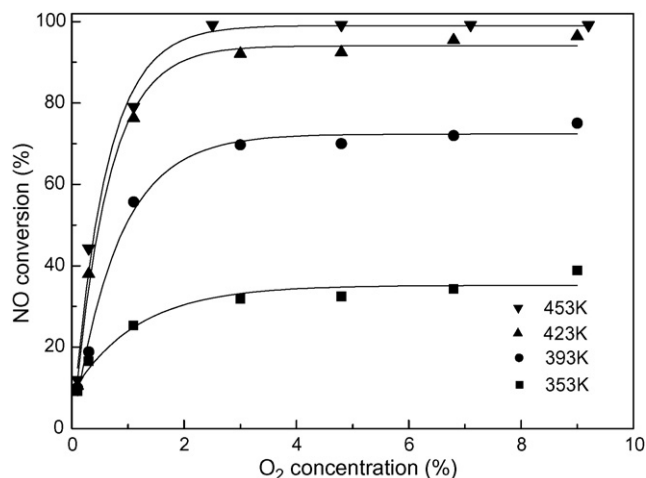


Fig. 4. The variation of NO conversion with different oxygen concentration in the feed gas. Reaction conditions: [NO]=[NH<sub>3</sub>]=1000 ppm, balance N<sub>2</sub>, total flow rate 2000 ml/min, catalyst 4 ml.

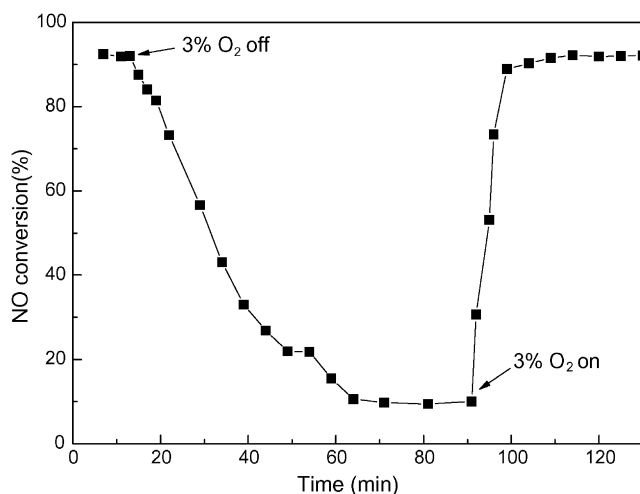
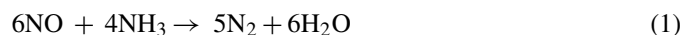


Fig. 5. Transient response on  $\text{MnO}_x(0.4)/\text{TiO}_2$  upon switching off and on  $\text{O}_2$  at 423 K. Reaction conditions:  $[\text{NO}] = [\text{NH}_3] = 1000$  ppm,  $[\text{O}_2] = 0\text{--}3\%$ , balance  $\text{N}_2$ , total flow rate 2000 ml/min, catalyst 4 ml.

by NO in absence of  $\text{O}_2$ , only less than 10% of NO was removed in the way of Eq. (1) [21]. It indicated that the reoxidising effect of NO was much less than that of  $\text{O}_2$  in this system. When oxygen was fed again, oxygen was adsorbed on the surface of the catalyst and lattice oxygen restored quickly, and the reduced surface sites of the catalyst was reoxidised by  $\text{O}_2$  again. Therefore, the NO conversion increased in several minutes, and the original efficiency of SCR reaction was restored:



Therefore, it was confirmed that oxygen had significant effect on the NO– $\text{NH}_3$  reaction. The oxygen was considered to be an important oxidation agent for the catalyst.

#### 3.1.4. $\text{NH}_3$ concentration

The effect of  $\text{NH}_3$  concentration on the reaction was shown in Fig. 6, when the ratio of  $[\text{NH}_3]/[\text{NO}]$  was low, NO conver-

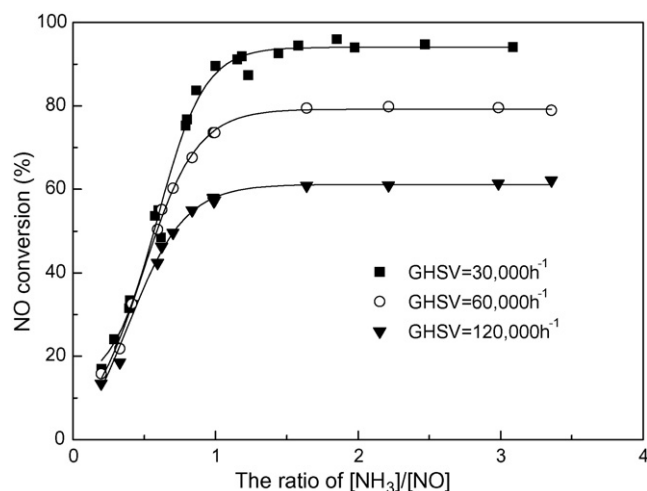


Fig. 6. The variation of NO conversion with different ammonia concentration in the feed gas. Reaction conditions:  $[\text{O}_2] = 3\%$ , balance  $\text{N}_2$ , total flow rate 2000 ml/min, catalyst 1–6 ml.

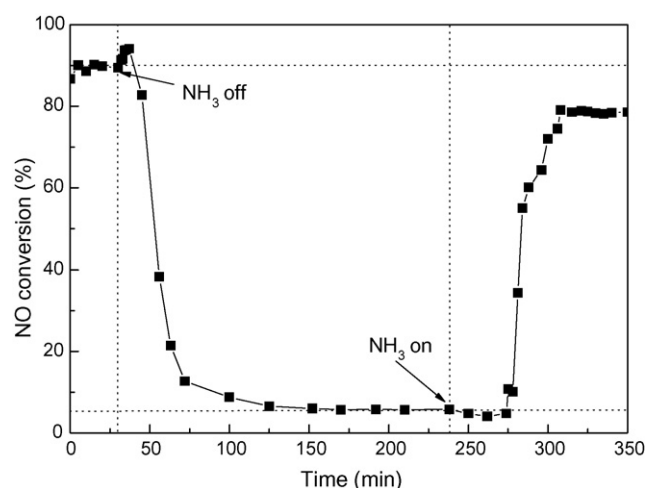


Fig. 7. Transient response on  $\text{MnO}_x(0.4)/\text{TiO}_2$  upon switching off and on  $\text{NH}_3$  at 423 K. Reaction conditions:  $[\text{NO}] = 1000$  ppm,  $[\text{NH}_3] = 0\text{--}1000$  ppm,  $[\text{O}_2] = 3\%$ , balance  $\text{N}_2$ , total flow rate 2000 ml/min, catalyst 4 ml.

sion increased quickly with an increase in  $\text{NH}_3$  concentration. Subsequently, the increase of NO became slower. When  $\text{NH}_3$  concentration was in excess, NO conversion trended to a constant value. It was mentioned in previous study [21] that  $\text{NH}_3$  and NO had little reactivity in the gas phase and gas-phase NO with adsorbed  $\text{NH}_3$ . In the reaction, ammonia was adsorbed on the surface of the catalyst and transformed to amine species, and then reacted with NO. In this investigation, the variation of NO conversion with  $\text{NH}_3$  concentration indicated that when  $\text{NH}_3$  concentration was low, with the increase of  $\text{NH}_3$  concentration, more  $\text{NH}_3$  could be adsorbed on the catalyst and react with NO. However, when the  $\text{NH}_3$  concentration was in excess (about 1000 ppm here), the adsorbed sites was limited, no more  $\text{NH}_3$  could be adsorbed to catalyst. Therefore, NO conversion was independent with  $\text{NH}_3$  concentration. This conclusion was confirmed by varied GHSV from 30,000 to 120,000  $\text{h}^{-1}$ . When the NO conversion reached a steady-state, the value of NO removal was decided by the amount of catalyst used. The reason of the above mentioned neglected effect of  $\text{NH}_3$  on NO conversion in case of a stoichiometric excess would be investigated again in Section 3.2.

Furthermore, the effect of  $\text{NH}_3$  concentration could also be described in transient state. As shown in Fig. 7, when  $\text{NH}_3$  supply was switched off, the NO conversion decreased slowly, and was apparently stable after about 85 min. However, in the first 4 min after  $\text{NH}_3$  switched off, the NO conversion slightly increased. It indicated that NO and  $\text{NH}_3$  was adsorbed competitively on at least part of the surface sites. Subsequently, NO conversion decreased and reached a steady-state value. According to previous study [22], considerable amounts of nitrites and/or nitrates would be formed on the surface of catalyst in absence of  $\text{NH}_3$ . Therefore, when NO conversion reached a steady-state, there was still some NO conversion, which was caused by the formation of nitrites and/or nitrates during the period of  $\text{NO} + \text{O}_2$  supply. When  $\text{NH}_3$  was reintroduced to the system, NO conversion did not increase immediately, since part of weakly adsorbed NO was desorbed from the surface of catalyst. This behavior was

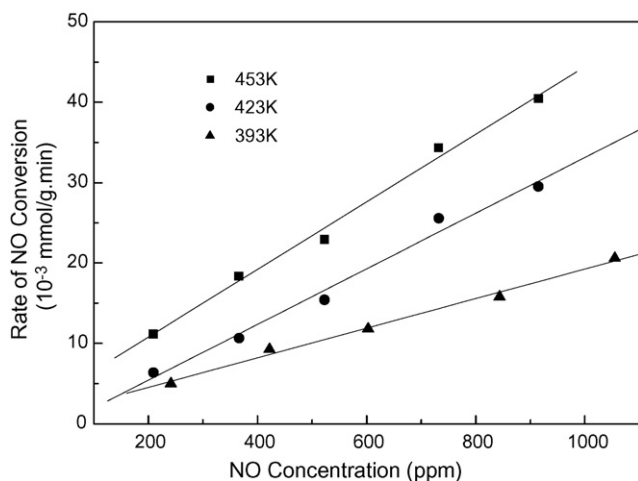


Fig. 8. The variation of NO conversion rate with NO concentration at 393–453 K. Reaction conditions: [NO] = 200–1055 ppm, [NH<sub>3</sub>] = 1000 ppm, [O<sub>2</sub>] = 3%, balance N<sub>2</sub>, total flow rate 2000 ml/min, catalyst 0.4 ml.

different from that in the transient investigation of O<sub>2</sub>. After a slight decrease, NO conversion increased quickly in several minutes. However, in the later period of the restoration, the increase of NO conversion became slower, since part of NH<sub>3</sub> would react with the monodentate and bridged nitrite [23]. When the NO conversion reached a steady-state again, it was still a little lower than that before switching off the NH<sub>3</sub> since part of the catalyst was deactivated by nitrites and/or nitrates which could not be removed.

### 3.2. Apparent activation energy

As mentioned in Section 1, apparent activation energy was a significant parameter to evaluate the performance of catalyst. To calculate the apparent activation energy, we should obtain the rate constant at different temperatures. In this investigation, about 0.5 g catalyst was used, and the conversion of NO was kept below 25%. According to previous study [24], it was reasonable to assume this reactor as a differential reactor. The reaction rate of NO conversion is a function of reactant concentration which could be expressed as follows

$$R_{\text{NO}} = -k[\text{NO}]^x[\text{NH}_3]^y[\text{O}_2]^z \quad (2)$$

where  $R_{\text{NO}}$  is the rate of NO conversion,  $k$  is the rate constant, and  $x$ ,  $y$ ,  $z$  are the reaction orders of NO, NH<sub>3</sub> and O<sub>2</sub>, respectively.

The experimental results for the variation of NO conversion rate with concentration of NO, NH<sub>3</sub>, O<sub>2</sub> were presented in Figs. 8–10, respectively. The SCR reaction was obtained to be first-order to NO, zero-order to NH<sub>3</sub> and half-order to O<sub>2</sub> with the maximum error of 13.6% within the range investigated (catalyst of 0.5 g, NO of 200–1500 ppm, NH<sub>3</sub> of 200–1000 ppm, O<sub>2</sub> of 0.6–5%). These results agreed well with those from previous studies [13,14,25],  $R_{\text{NO}} = -k[\text{NO}][\text{O}_2]^{0.5}$ . The zero-order for NH<sub>3</sub> could explain the neglected effect of NH<sub>3</sub> concentration on NO conversion when NH<sub>3</sub> was added in a stoichiometric excess (see Fig. 6).

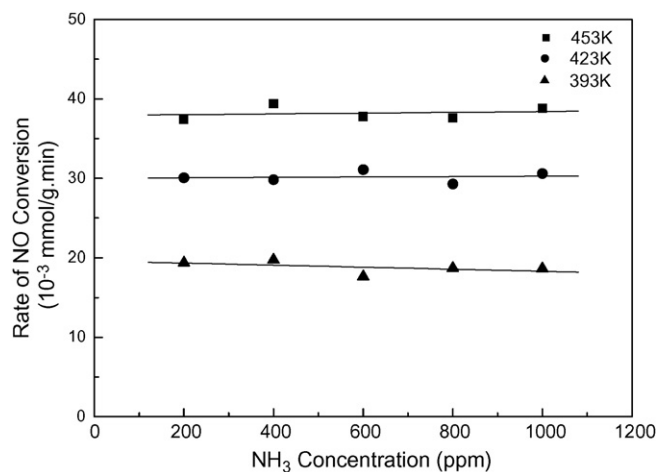


Fig. 9. The variation of NO conversion rate with NH<sub>3</sub> concentration at 393–453 K. Reaction conditions: [NO] = 1000 ppm, [NH<sub>3</sub>] = 200–1000 ppm, [O<sub>2</sub>] = 3%, balance N<sub>2</sub>, total flow rate 2000 ml/min, catalyst 0.4 ml.

Since only 0.4 ml (0.5 g) catalyst was used and NO conversion was controlled below 25%, as noted by Huang et al. [24], the reaction could be assumed free of diffusion limitation. And in this system, the amount of oxygen was excessive (the partial pressure of O<sub>2</sub> was all 0.03 atm). Under this condition, Eq. (2) could be changed as

$$R_{\text{NO}} = -k^*[\text{NO}] \quad (3)$$

where  $k^* = k[\text{O}_2]^{0.5}$ . The above equation had been integrated, and the relationship between apparent rate constant ( $k^*$ ) and NO conversion ( $\eta$ ) could be given by

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

where  $F_0$  is the molar NO feed rate (mol/min), [NO]<sub>0</sub> the molar NO concentration (mol/L), and  $W$  is the mass of catalyst (g).

The relationship between  $\ln(1 - \eta)$  and  $W[\text{NO}]_0/F_0$  at different temperatures was shown in Fig. 11. And the value of the

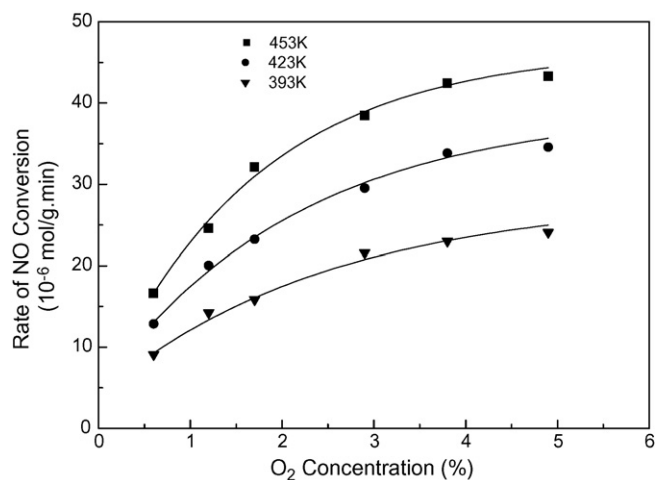


Fig. 10. The variation of NO conversion rate with O<sub>2</sub> concentration at 393–453 K. Reaction conditions: [NO] = [NH<sub>3</sub>] = 1000 ppm, [O<sub>2</sub>] = 0–5%, balance N<sub>2</sub>, total flow rate 2000 ml/min, catalyst 0.4 ml.

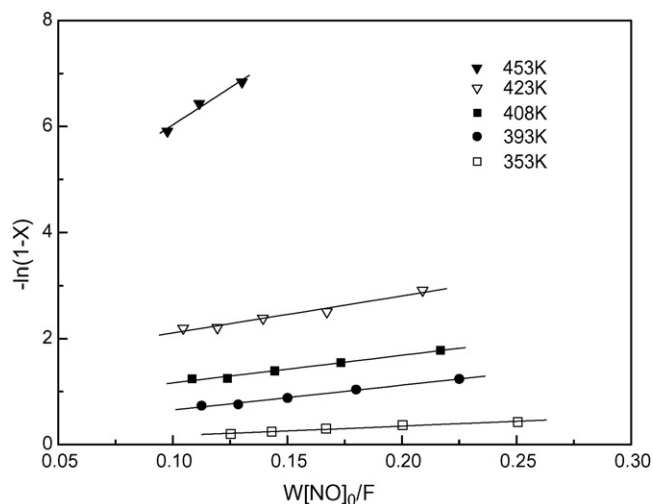


Fig. 11. First-order plots with respect to NO with different gas flow rate at 353–453 K.

apparent rate constant ( $k^*$ ) had been calculated. The rate constant for  $\text{MnO}_x/\text{TiO}_2$  prepared by sol–gel method at 423 K was  $6.97 \text{ l}/(\text{g min})$  ( $116.13 \text{ cm}^3/(\text{g s})$ ), which was much higher than that prepared by co-precipitation method ( $4.78 \text{ l}/(\text{g min})$ ) [26] and impregnation method ( $3.53 \text{ l}/(\text{g min})$ ) [26].

The apparent activation energy could be calculated by using Arrhenius equation:

$$k = k_0 e^{-E_a/RT} \quad (5)$$

where  $E_a$  is the apparent activation energy. It could be calculated from the slope of the curve  $\ln(k^*)$  versus  $1/T$ , an apparent activation energy of  $38 \text{ kJ/mol}$  was obtained for the SCR reaction on  $\text{MnO}_x/\text{TiO}_2$ , it was much lower than the values obtained on H-ZSM-5 [27] ( $55 \text{ kJ/mol}$ ), and lower than H-MOR [28] ( $58 \text{ kJ/mol}$ ). It indicated that less energy was needed for activation in the reaction. Therefore, the catalytic activity was significantly improved and NO conversion would increase.

#### 4. Conclusion

The catalyst based on  $\text{MnO}_x/\text{TiO}_2$  was prepared by sol–gel method. By using a stainless steel flow reactor, the catalyst was employed by low-temperature (393–523 K) SCR experiment. Within the reaction temperature window (423–523 K), more than 90% of NO could be removed. The main conclusions could be drawn as follows:

- (1) Higher manganese loading led to higher efficiency of NO removal, and the optimal value of the ratio of Mn/Ti was 0.4.
- (2) At low temperature, NO conversion was much higher than that using commercial catalyst. At 423 K, more than 90% of NO could be removed, while less than 10% of NO was removed by using commercial catalyst [2].
- (3) NO conversion increased with an increase in  $\text{O}_2$  concentration. However, when  $\text{O}_2$  concentration was more than 3%, the NO conversion trended to a constant value.

- (4) In the reaction,  $\text{NH}_3$  was adsorbed on the surface of catalyst and reacted with NO. Therefore, with low  $\text{NH}_3$  concentration, NO conversion increased with an increase in  $\text{NH}_3$  concentration. However, when  $\text{NH}_3$  concentration was excessive to the adsorptive capacity of catalyst, it had neglected effect on the NO removal.
- (5) Within the range investigated, the reaction order of NO,  $\text{NH}_3$ ,  $\text{O}_2$  was determined to be 1, 0, and 0.5, respectively. And the apparent active energy of the reaction was calculated to be  $38 \text{ kJ/mol}$ , which was lower than most of the low-temperature SCR catalyst reported previously.

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