Kinetics of selective catalytic reduction of NO by NH$_3$ on Fe-Mo/ZSM-5 catalyst

LI Zhe, SHEN Lin-tao, HUANG Wei*, XIE Ke-chang

Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, China. E-mail: lizhe@tyut.edu.cn

Abstract

The catalyst of Fe-Mo/ZSM-5 has been found to be more active than Fe-ZSM-5 and Mo/ZSM-5 separately for selective catalytic reduction (SCR) of nitric oxide (NO) with NH$_3$. The kinetics of the SCR reaction in the presence of O$_2$ was studied in this work. The results showed that the observed reaction orders were 0.74–0.99, 0.01–0.13, and 0 for NO, O$_2$ and NH$_3$ at 350–450°C, respectively. And the apparent activation energy of the SCR was 65 kJ/mol on the Fe-Mo/ZSM-5 catalyst. The SCR mechanism was also deduced. Adsorbed NO species can react directly with adsorbed ammonia species on the active sites to form N$_2$ and H$_2$O. Gaseous O$_2$ might serve as a reoxidizing agent for the active sites that have undergone reduction in the SCR process. It is also important to note that a certain amount of NO was decomposed directly over the Fe-Mo/ZSM-5 catalyst in the absence of NH$_3$.

Key words: selective catalytic reduction (SCR); nitric oxide (NO); Fe-Mo/ZSM-5; kinetics; activation energy

Introduction

The selective catalytic reduction (SCR) of nitrogen oxides from engine exhaust gases, especially under lean conditions such as in diesel engine exhausts, is very important in the field of catalysis research. Zeolite ZSM-5-supported iron catalysts have attracted considerable attention in recent years. The preparation of Fe/ZSM-5 with a high loading of iron, however, was proved to be a challenge. Feng and Hall (1997) reported a Fe/ZSM-5 catalyst with higher Fe/Al ratio that exhibited very high activity and encouraging stability, but the preparation used by these authors could not be reproduced (Heinrich *et al.*, 2002). Many reports have shown that Fe/ZSM-5 catalysts are active for catalytic reduction of nitrogen oxides in the presence of water vapor (Chen and Sachtler, 1998; Kucherov *et al.*, 1998). Salgado *et al.* (2003) studied the reduction of NO with ethanol over Pd-Mo/ZSM-5 catalyst, and showed that Pd-Mo/ZSM-5 was more active at a higher temperature than Pd/HZSM-5 due to the molybdenum promoter. In our previous work, Mo was found to be a good promoter for catalytic reduction of nitrogen oxides over HZSM-5 (Li *et al.*, 2005a). However, Fe-Mo/ZSM-5 has been found to be much more active than Fe/ZSM-5 and Mo/ZSM-5 catalysts separately for NO-SCR with NH$_3$ (Li *et al.*, 2005b).

The reaction mechanism of catalytic reduction of NO over zeolite-based catalysts has been studied by many researchers (Chen *et al.*, 1999; Beltramone and Anunziata, 2004; Long and Yang, 2002), but the mechanisms still represent a complex problem, especially in terms of the active sites. It has been reported that both NO$_x$ and NH$_3$ molecules could be adsorbed onto molecular sieve-type catalysts (Chen and Sachtler, 1998). The reaction orders with respect to NO and NH$_3$ varied with the reaction conditions and catalysts. On Fe-ZSM-5, Huang *et al.* (2002) concluded that the decrease in reaction order for O$_2$ with temperature might be due to the formation of NO from NH$_3$ oxidation, and catalytic oxidation of NO to NO$_2$ by O$_2$ was proposed as the rate-determining step. Eng and Bartholomew (1997) reported that the reaction orders over H-ZSM-5 were 0.73, –0.61, and 1.06 for NO, NH$_3$, and O$_2$, respectively. They concluded that adsorbed NH$_3$ was necessary for NO reduction and that gaseous NH$_3$ inhibited the SCR reaction, and the apparent activation energy for N$_2$ formation was estimated to be 61 kJ/mol. In comparison, Stevenson *et al.* (2000) observed that the reaction orders with respect to NO and O$_2$ were first-order, while that with respect to NH$_3$ changed from –0.55 to –0.35 at the temperature range 350–450°C.

It is important to understand the reaction kinetics of NO-SCR over Fe-Mo/ZSM-5 catalysts. In the present work, we investigated the kinetics of NO-SCR with ammonia in the presence of oxygen over the Fe-Mo/ZSM-5 catalyst. Kinetic experiments were performed to determine the SCR rate. A kinetic model was thus developed that satisfactorily predicts the experimental results. Clarification of the reac-

tion mechanism is essential for future improvement of this catalytic process.

1 Materials and methods

Fe-Mo/ZSM-5 catalyst with an Fe/Mo molar ratio of 1:1 was prepared by the wet impregnation method. HZSM-5 powder (Si/Al=60) was impregnated with aqueous solutions of ammonia heptamolybdate and Fe(III) nitrate, then dried at 60 and 100°C for 8 and 12 h, respectively. After calcination at 550°C for 5 h, the catalysts were crushed and sieved to yield 40–60 mesh granules. Fe-Mo/ZSM-5 was based on 5 wt% Mo content.

Steady-state kinetics experiments and the activity of SCR reaction over Fe-Mo/ZSM-5 catalysts were carried out in a conventional fixed-bed quartz reactor (i.d. 8 mm, length 350 mm). The compositions of the feed and effluent of the reactor were continuously analyzed by an online combustion gas analyzer (KM9106, Kane International Ltd., UK) capable of monitoring NO, NO$_2$, and O$_2$ simultaneously. The concentration of NH$_3$ was detected using a DX2500 Ion chromatograph with a CS12A column and an electrical conductive detector to analyze NH$_4^+$ in 0.02 mol/L CH$_3$SO$_3$H solution.

The rate of NO conversion was measured at 350, 400 and 450°C for various compositions of the feed: 100–1200 ppmv NO, 0.2 vol%–12 vol% O$_2$, and 200–1000 ppmv NH$_3$, with nitrogen as the balance gas. The total flow rate was 300 ml/min and the weight of the catalyst used was 0.2 g.

2 Results and discussion

2.1 Effect of O$_2$ concentration on NO conversion

The effect of O$_2$ concentrations on NO conversion is shown in Fig.1. NO conversion was obviously higher when the reaction temperature was lower than 580°C with 2 vol% O$_2$. This demonstrates that O$_2$ enhances NO conversion in the temperature range 250–580°C. However, no conversion in the presence of oxygen significantly decreased when temperature was higher than 580°C. The reason for this "decrease" in the presence of O$_2$ is probably
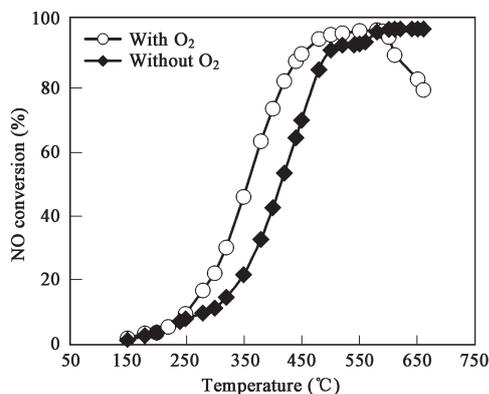

Fig. 1 Change of NO conversion with temperature with 2 vol% O$_2$ and without O$_2$.

due to the competitive adsorption between NO and O$_2$ at reaction temperatures higher than 580°C.

2.2 Effect of NH$_3$ concentration on rate of NO conversion

The rate of NO conversion as a function of NH$_3$ concentration at 300 and 450°C is shown in Fig.2. It is interesting to note that the SCR rate slightly decreased when the NH$_3$ concentration increased from 215 to 1000 ppmv at 300°C. However, this "inhibition" by the NH$_3$ concentration was slight for the higher reaction temperature of 450°C, and the rate of NO consumption was nearly constant at this temperature.
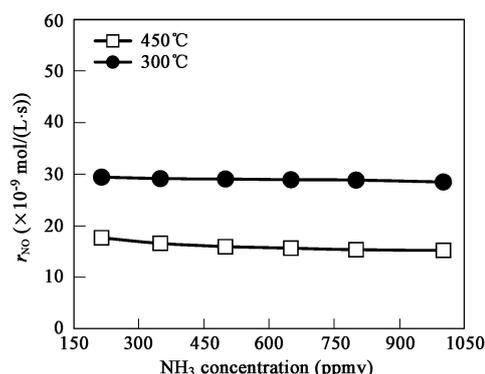

Fig. 2 Effect of NH$_3$ concentration on the rate of NO conversion at 300 and 450°C. Conditions: catalyst 0.2 g; NO 500 ppmv; O$_2$ 6 vol%; total flow rate 300 ml/min.

2.3 Kinetic analysis

The rate of NO consumption as a function of reactant concentrations can be expressed simply as a power-law Eq. (1):

$$r_{NO} = k \times C_{NO}^{\alpha} \times C_{NH_3}^{\beta} \times C_{O_2}^{\gamma} \tag{1}$$

where, r_{NO} is the SCR rate, k is the apparent rate constant, and α, β, and γ are the reaction orders for NO, NH$_3$ and O$_2$, respectively. Regression analysis was carried out to fit the experimental data to a non-linear parametric Marquardt function using Excel. The computer program was based on Marquardt's minimization procedure, and the parameters of the non-linear function were determined with confidence intervals of 99% by minimization of the residual sum of squares.

Huang *et al*. (2002) reported that the reaction on Fe/ZSM-5 was zero-order with respect to NH$_3$; the same order with respect to NH$_3$ was reported on Cu/ZSM-5 and Fe-exchanged pillared clay (Komatsu *et al*., 1994; Long and Yang, 2000). We can also conclude that the reaction was nearly zero-order with respect to NH$_3$ according to the experiment results (Fig.2), and suggest that the catalyst is completely covered by ammonia under the reaction conditions. The reaction order was further analyzed by introducing the Arrhenius expression to optimize the kinetic parameters of Eq. (1), which can thus be transformed into the following equation:

$$r_{NO} = A \exp(-E_a/RT) C_{NO}^x \times C_{O_2}^y \tag{2}$$

To determine the reaction order with respect to NO, the concentration of NH$_3$ was kept at 500 ppmv, while the concentration of NO was varied from 100 to 1200 ppmv. The reaction order was determined as a function of reaction temperature (350–450°C) and O$_2$ concentration (2 vol%–10 vol%). The regression parameters from Eq. (2) at different temperatures are listed in Table 1.

Table 1 Regression results for x, y, A and E_a at different temperatures

Temperature (°C)	x	y	A	E_a (kJ/mol)	Average E_a (kJ/mol)
350	0.74	0.13	62.98	65.78	65.16
400	0.83	0.07	72.57	65.66	
450	0.99	0.014	143.2	64.04	

The calculation results from Eq. (2) indicate that the kinetic expression fits the experimental data reasonably well. Fig.3a shows the rate of NO conversion as a function of NO concentration at 350, 400, 450°C, respectively under the condition of 0.2 g catalyst, 500 ppmv NH$_3$, 2 vol% O$_2$ and 300 ml/min of total flow rate. The rate of NO consumption increased linearly with NO concentration at each experimental temperature; it also increased with increasing temperature. Fig.3b shows the rate of NO conversion as a function of O$_2$ concentration at 350, 400, 450°C under the conditions of 500 ppmv NO and 500 ppmv NH$_3$. It is interesting to note that NO consumption significantly increased when the O$_2$ concentration was increased from 0 to 1%, then increased slightly with an increase O$_2$ concentration from 2% to 12% at 350 and 400°C. More importantly, the rate of NO conversion was higher and almost unaffected by the O$_2$ concentration at 450°C.

2.4 Variance analysis and F-test

Variance analysis and an F-test were used to determine which model is statistically good in explaining the rate of NO conversion. Significance levels of α =0.05 and α =0.01 were chosen. The results of variance analysis and F-test at different temperature are given in Table 2, from which a intrinsic rate model of the power type has been developed. And it can satisfactorily predict the observed

Table 2 Statistical data at different temperatures for inspection of their suitability

Temperature (°C)	Confidence	$F\alpha$	p^2	F
350	0.05	3.18	0.9945	586.3
	0.01	5.21	0.9945	586.3
400	0.05	3.18	0.9933	483.2
	0.01	5.21	0.9933	483.2
450	0.05	3.26	0.9996	6855.2
	0.01	5.41	0.9996	6855.2

kinetics according to the correlation coefficients $p^2 > 0.95$ and F-test $F \gg 10F\alpha$.

2.5 Reaction mechanisms

Fe-Mo/ZSM-5 was found to be highly active for ammonia SCR in our previous work (Li, 2005b). Kinetic data for the SCR reaction in this study showed that the rate of NO conversion was nearly zero-order with respect to NH$_3$, which is similar to other reports in the literature (Huang *et al.*, 2002; Komatsu *et al.*, 1994; Long and Yang, 2000). The reaction orders, however, were 0.74–0.99 and 0.01–0.13 for NO and O$_2$, respectively, at 350–450°C. The apparent activation energy was 65 kJ/mol on the Fe-Mo/ZSM-5 catalyst. The kinetic results indicate that the rate of NO conversion has a positive dependence on NO concentration. From our experiments results, it showed that the oxidation of NH$_3$ to NO by gas O$_2$ was not detected at 400°C and it was hardly oxidized at 600°C on the Fe-Mo/ZSM-5 catalyst. Therefore, we conclude that the SCR rate is independent on NH$_3$ concentration under the reaction conditions, which implies that NH$_3$ adsorbs more quickly on Fe-Mo/ZSM-5 and it is not the rate-determining step of the SCR reaction. The rate-determining step is probably related to the adsorption of NO and the formation of its active transition species. The arguments on this issue will be presented elsewhere (Li *et al.*, 2007).

To understand the oxidation of NO on the surface of Fe-Mo/ZSM-5 catalyst in the presence of O$_2$ and absence of NH$_3$, the dependence of NO and NO$_2$ concentrations on the reaction temperature is shown in Fig.4. The concentration of NO began to decrease slightly with increasing reaction temperature from 240°C and reached a minimum at 520°C, then gradually increased towards its initial
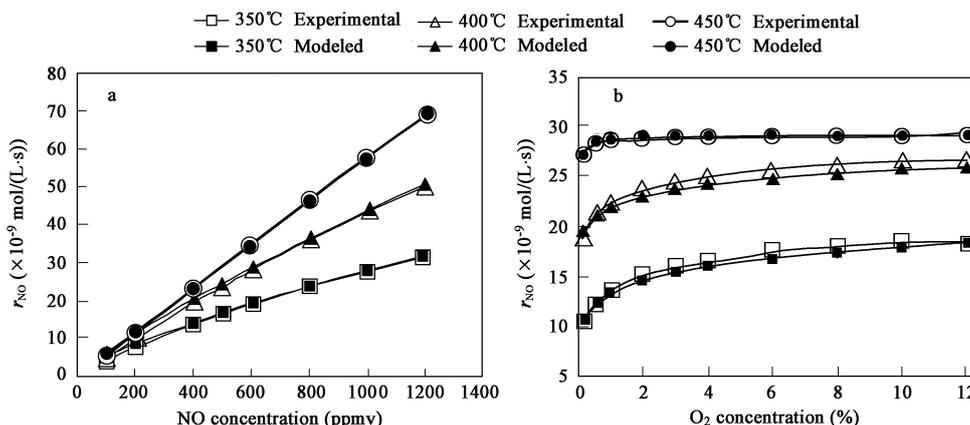

Fig. 3 Dependence of NO conversion rate on NO (a) and O$_2$ (b) concentration at 350, 400, 450°C.
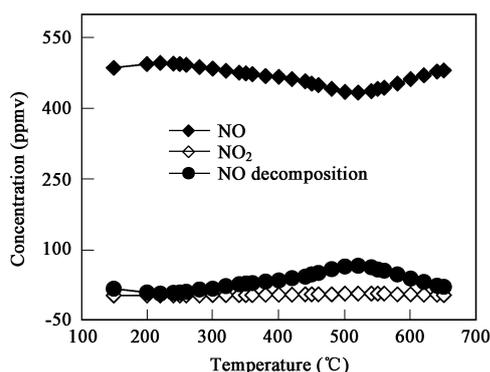
Fig. 4 Effect of temperature on the concentration of NO, NO$_2$ and the decomposition of NO over Fe-Mo/ZSM-5 catalyst. Conditions: NO 502 ppmv; NO$_2$ 4 ppmv; O$_2$ 2 vol%; gas flue rate 300 ml/min.

concentration with further increases in temperature. It should be noted that the NO$_2$ concentration detected was only 3 ppmv at most under the reaction conditions, while the consumption of NO was approximately 69 ppmv at 520°C. This means that most of the NO may be directly decomposed in the absence of NH$_3$ over the Fe-Mo/ZSM-5 catalyst. It is also important to note that in a previous study (Li et al., 2005c) we did not detect NO$_2$ during SCR reaction in the presence of NH$_3$ or during XPS measurements over Fe-Mo/ZSM-5 catalysts.

It can be deduced that the oxidation of NO by gaseous O$_2$ could not occur on the Fe-Mo/ZSM-5 catalyst, and that there was no NO$_2$ desorption from the surface either. Adsorbed NO species could directly react with adsorbed ammonia species on the active sites to form N$_2$ and H$_2$O. The role of O$_2$ in SCR over Fe-Mo/ZSM-5 catalyst is probably similar to that occurring on V$_2$O$_5$ (Topsoe et al., 1995), with gaseous O$_2$ serving as a reoxidizing agent for sites that have undergone reduction in the SCR process.

3 Conclusions

Results of the kinetics study show that the reaction orders were 0.74–0.99, 0.01–0.13 and nearly zero for NO, O$_2$ and NH$_3$, respectively, at 350–450°C. The apparent activation energy was approximately 65 kJ/mol for SCR reaction over an Fe-Mo/ZSM-5 catalyst. The calculation results indicate that the experimental data fit an intrinsic rate model of the power type reasonably well.

It can be also deduced that the rate of NO conversion has a positive dependence on the NO concentration and is independent of the NH$_3$ concentration under the reaction conditions used. This means that NH$_3$ can adsorb more quickly on Fe-Mo/ZSM-5, and it is thus not the rate-determining step of the SCR reaction. Surface reaction between adsorbed NO and oxygen species is probably the rate-determining step. Adsorbed NO species could directly

react with adsorbed ammonia species on the active sites to form N$_2$ and H$_2$O. Gaseous O$_2$ in SCR might serve as a reoxidizing agent for the active sites that have undergone reduction in the SCR process.

References

Beltramone A R, Anunziata O A, 2004. Nature and reactivity of the active species formed after NO adsorption and NO + O$_2$ coadsorption on an Fe-containing zeolite[J]. Catal Lett, 92: 131–140.

Chen H Y, Sachtler W M H, 1998. Promoted Fe/ZSM-5 catalysts prepared by sublimation: de-NO$_x$ activity and durability in H$_2$O-rich streams[J]. Catal Lett, 50: 125–130.

Chen H Y, Voskoboinikov T, Sachtler W M H, 1999. Reaction intermediates in the selective catalytic reduction of NO$_x$ over Fe/ZSM-5[J]. J Catal, 186: 91–99.

Eng J, Bartholomew C H, 1997. Kinetic and mechanistic study of NO$_x$ reduction by NH$_3$ over H-form zeolites[J]. J Catal, 171: 14–26.

Feng X, Hall W K, 1997. FeZSM-5: A durable SCR catalyst for NO$_x$ removal from combustion streams[J]. J Catal, 166: 368–376.

Heinrich F, Schmidt C, Löffler E et al., 2002. Fe-ZSM-5 catalysts for the selective reduction of NO by isobutane: The problem of the active sites[J]. J Catal, 212: 157–172.

Huang H Y, Long R Q, Yang R T, 2002. Kinetics of selective catalytic reduction of NO with NH$_3$ on Fe-ZSM-5 catalyst[J]. Appl Catal A, 235: 241–251.

Komatsu T, Nunokawa M, Moon I S et al., 1994. Kinetic studies of reduction of nitric oxide with ammonia on Cu^{2+}-exchanged zeolites[J]. J Catal, 148: 427–437.

Kucherov A V, Montreuil C N and Shelef M, 1998. In situ high-temperature ESR characterization of FeZSM-5 and FeSAPO-34 catalysts in flowing mixtures of NO, C$_3$H$_6$ and O$_2$[J]. Catal Lett, 56: 173–181.

Li Z, Xie K C, Huang W et al., 2005a. Molybdenum loaded on HZSM-5: A catalyst for selective catalytic reduction of nitrogen oxides[J]. Studies in Surface Science and Catalysis, B158: 1741–1748.

Li Z, Xie K C, Huang W et al., 2005b. Selective catalytic reduction of NO$_x$ with ammonia over Fe-Mo/ZSM-5 catalysts[J]. Chemical Engineering and Technology, 28(7): 797–801.

Li Z, Huang W, Xie K C, 2005c. Effect of Mo contents on properties of Mo/ZSM-5 zeolite catalyst for NO$_x$ reduction[J]. Journal of Environmental Sciences, 17(1): 103–105.

Li Z, Shen L T, Huang W et al., 2007. The properties of NO adsorption on the surface of Fe-Mo/ZSM-5 catalyst[J]. Chem J Chinese Universities. (in press).

Long R Q, Yang R T, 2000. Characterization of Fe-ZSM-5 catalyst for selective catalytic reduction of nitric oxide by ammonia[J]. J Catal, 194: 80–90.

Long R Q, Yang R T, 2002. Reaction mechanism of selective catalytic reduction of NO with NH$_3$ over Fe-ZSM-5 catalyst[J]. J Catal, 207: 224–231.

Salgado A L S M, Passos F B, Schmal M, 2003. NO reduction by ethanol on Pd and Mo catalysts supported on HZSM-5[J]. Catal Today, 85: 23–29.

Stevenson S A, Vartuli J C, Brooks C F, 2000. Kinetics of the selective catalytic reduction of NO over HZSM-5[J]. J Catal, 190: 228–239.

Topsoe N Y, Dumestic J A, Topsoe H, 1995. Vanadia-titania catalysts for selective catalytic reduction of nitric-oxide by ammonia: II. Studies of active sites and formulation of catalytic cycles[J]. J Catal, 151: 241–252.