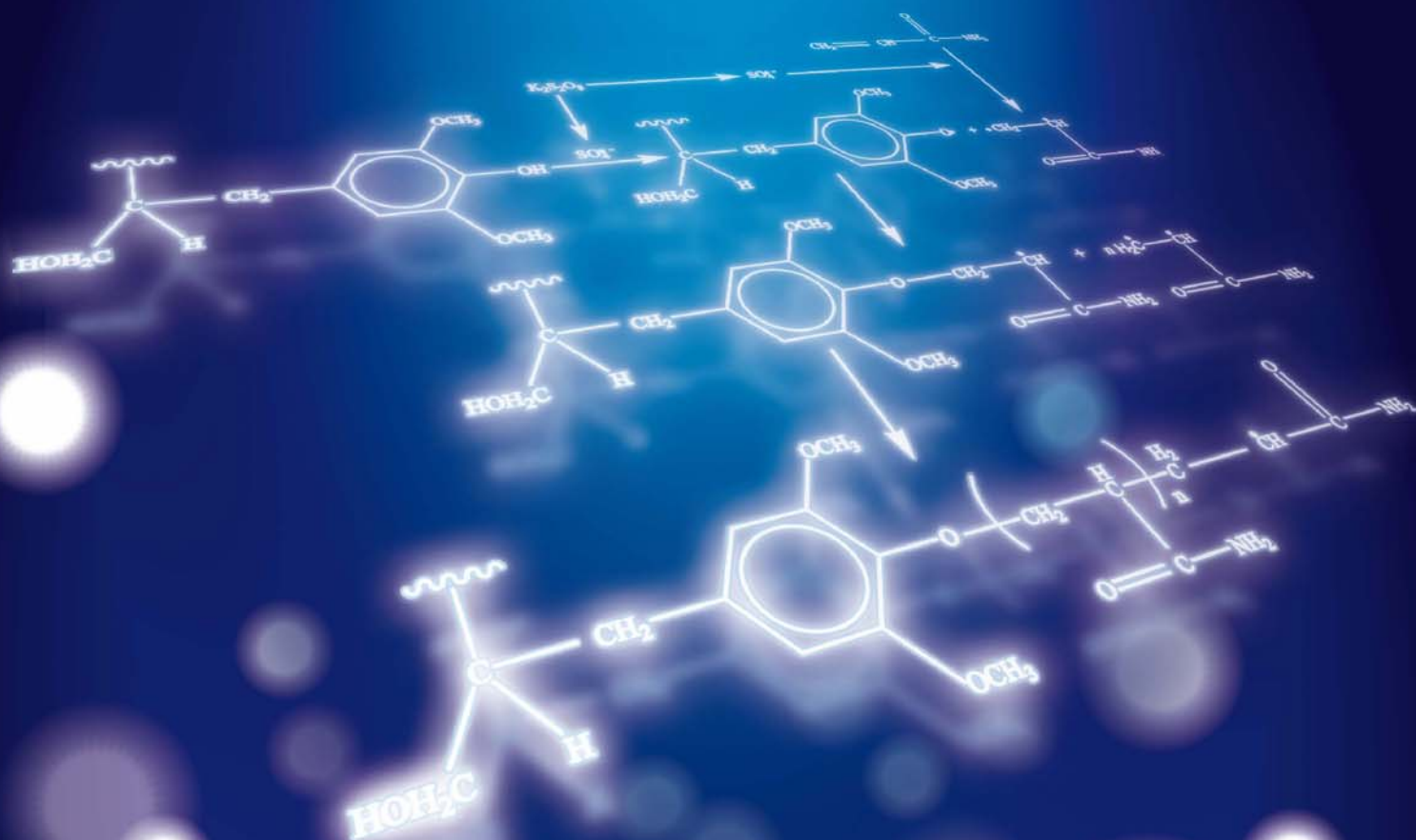


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Fe₂O₃ particles as superior catalysts for low temperature selective catalytic reduction of NO with NH₃

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Abstract

Fe₂O₃ particle catalysts were experimentally studied in the low temperature selective catalytic reduction (SCR) of NO with NH₃. The effects of reaction temperature, oxygen concentration, [NH₃]/[NO] molar ratio and residence time on SCR activity were studied. It was found that Fe₂O₃ catalysts had high activity for the SCR of NO with NH₃ in a broad temperature range of 150–270°C, and more than 95% NO conversion was obtained at 180°C when the molar ratio [NH₃]/[NO] = 1, the residence time was 0.48 seconds and O₂ volume fraction was 3%. In addition, the effect of SO₂ on SCR catalytic activity was also investigated at the temperature of 180°C. The results showed that deactivation of the Fe₂O₃ particles occurred due to the presence of SO₂ and the NO conversion decreased from 99.2% to 58% in 240 min, since SO₂ gradually decreased the catalytic activity of the catalysts. In addition, X-ray diffraction, Thermogravimetric analysis and Fourier transform infrared spectroscopy were used to characterize the fresh and deactivated Fe₂O₃ catalysts. The results showed that the deactivation caused by SO₂ was due to the formation of metal sulfates and ammonium sulfates on the catalyst surface during the de-NO reaction, which could cause pore plugging and result in suppression of the catalytic activity.

Key words: low-temperature SCR; Fe₂O₃; NO; FT-IR; SO₂

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Introduction

Nitrogen oxides originating from the combustion of stationary sources are the major source of some environmental problems such as acid deposition, photochemical smog and the greenhouse effect (Sheng et al., 2012; Qi et al., 2003). Selective catalytic reduction (SCR) of NO_x with NH₃ is a major technology for reducing NO_x emissions due to its high efficiency (Sheng et al., 2012; Qi et al., 2003; Liu et al., 2009; Xu et al., 2010; Lee et al., 2012; Huang et al., 2008; Chen et al., 2009; Shen et al., 2010). The most widely used commercial catalysts are V₂O₅–WO₃ (MoO₃)/TiO₂, which show the highest activity in the temperature range 300–400°C (Sheng et al., 2012; Qi et al., 2003; Liu et al., 2009; Lee et al., 2012; Chen et al., 2009; Tang et al., 2007). This temperature is higher than that of flue gas passing through the desulfurization unit. Therefore, many studies are focused on the catalytic activity of SCR catalysts at low temperature (< 200°C). Such a catalyst would show high catalytic activity at low temperature and thus the SCR system could be located

downstream of the desulfurizer and the particulate-removal device without gas preheating (Sheng et al., 2012; Qi et al., 2003; Liu et al., 2009; Lee et al., 2012; Huang et al., 2008; Chen et al., 2009; Shen et al., 2010; Tang et al., 2007). Success in this technology would not only avoid gas preheating but also the occurrence of pore plugging from the deposition of sulfate species.

Many catalyst systems containing Mn-based catalysts (Huang et al., 2008; Kang et al., 2006; Yu et al., 2010), V-based catalysts (Zhu et al., 1999; Huang et al., 2002; Ha et al., 2008), Fe-based catalysts (Huang et al., 2008; Yao et al., 2010a, 2010b) and other metal oxide catalysts (Xie et al., 2004; Li et al., 2012) are active for the low-temperature SCR of NO. However, there remain small concentrations of SO₂ in combustion gas even after the desulfurizer, and the catalyst is usually deactivated, mainly by sulfur compounds (Sheng et al., 2012; Qi et al., 2003; Lee et al., 2012; Huang et al., 2008; Chen et al., 2009; Shen et al., 2010; Tang et al., 2007; Xie et al., 2004). Based on previous studies (Sheng et al., 2012; Qi et al., 2003; Xie et al., 2004), the deactivation of the catalysts caused by SO₂ are attributed to the formation of sulfate species, which deposit on the catalyst surface and thus result in their

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deactivation.

In this study, particulate Fe_2O_3 catalysts prepared by the Research Institute of Nanjing Chemistry Industry Group were used in the selective catalytic reduction of NO with NH_3 at low temperature. The effects of reaction temperature, oxygen concentration, $[\text{NH}_3]/[\text{NO}]$ molar ratio, and residence time were experimentally studied in a fixed bed. Moreover, the effects of SO_2 on catalytic activity were also investigated and the deactivation mechanism of the catalysts was studied by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR).

1 Experimental

1.1 Catalyst preparation

The particulate Fe_2O_3 catalyst evaluated in this study was provided by the Research Institute of Nanjing Chemistry Industry Group and the Fe_2O_3 particles were prepared as follows: after aqueous solutions of ferric sulfate and ferrous sulfate were pre-mixed, a solution of ammonia (1:1, V/V) was continuously added to the mixture until the pH of the solution reached 8. Then the resulting precipitate was washed several times with deionized water and separated by filtration under suction, followed by extrusion molding and evaporation to dryness at 120°C . Finally, the particles were calcined at 300°C in air for 3 hr and crushed to 35–65 mesh. The bulk density of the Fe_2O_3 catalyst particles was 1.06 g/cm^3 and the BET surface area, pore volume, and pore size of the Fe_2O_3 catalysts were $90.79\text{ m}^2/\text{g}$, $0.2582\text{ cm}^3/\text{g}$ and 11.38 nm , respectively.

1.2 Catalyst characterization

X-ray diffraction (XRD) measurements were carried out to determine the crystalline structures of catalysts on a Rigaku D/MAC-III instrument with $\text{Cu } K\alpha$ radiation at room temperature.

TGA experiments were carried out to determine the sulfate species forming on the surface of Fe_2O_3 catalysts with a Perkin Elmer TGA 7 apparatus. The heating program was carried out under a nitrogen flow of 50 mL/min with a heating rate of 10°C/min from room temperature to 1000°C .

FT-IR spectra of the catalyst were recorded in the $400\text{--}4000\text{ cm}^{-1}$ range to determine sulfur-containing species on the catalyst surface using a Nicolet Nexus 470 Fourier transform infrared spectrometer.

1.3 Catalytic activity measurement

Experiments to investigate the catalytic activity of the catalysts were carried out in a fixed-bed quartz reactor, shown in Fig. 1.

The experimental setup mainly consisted of four units: a simulated flue gas system, a fixed bed reactor, an electric heating system and a flue gas analysis system. The reaction

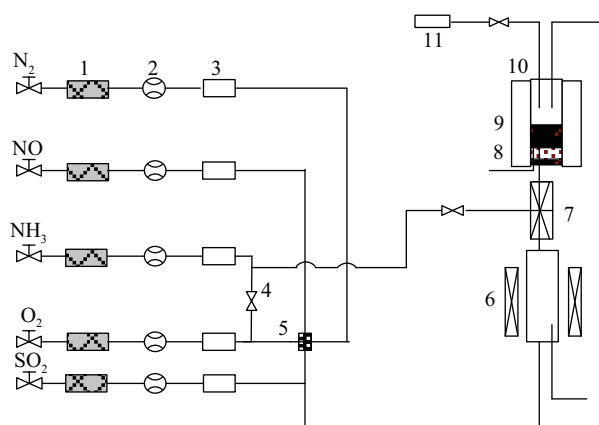


Fig. 1 Schematic diagram of experimental setup for NO removal. (1) filter; (2) mass flow rate controller (MFC); (3) buffer tank; (4) valve; (5) mixing tank; (6) primary heater; (7) secondary heater; (8) thermocouple; (9) heater; (10) reactor; (11) gas analyzer.

gas components were as follows: 500 ppm NO, 500 ppm NH_3 , 3% O_2 (V/V) in N_2 , 1000 ppm SO_2 (when used), and balance N_2 . The feed gases were premixed in a glass chamber, but the NH_3 was fed directly into the reactor to avoid possible reaction between SO_2 and NH_3 before the reactor. All data were recorded when the SCR reaction reached steady state, and the product components in the outlet gases were measured online by an online flue gas analyzer (rbr ecom-J2KN, Germany).

2 Results and discussion

2.1 Catalyst characterization

The XRD patterns of Fe_2O_3 particles before and after reaction are shown in Fig. 2. The results indicate that the main phases found in the Fe_2O_3 catalysts before and after reaction were $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) and $\alpha\text{-Fe}_2\text{O}_3$ (hematite). This also means that the Fe_2O_3 particles used in the experiments function as catalysts, and their components are not substantially changed by the SCR reaction.

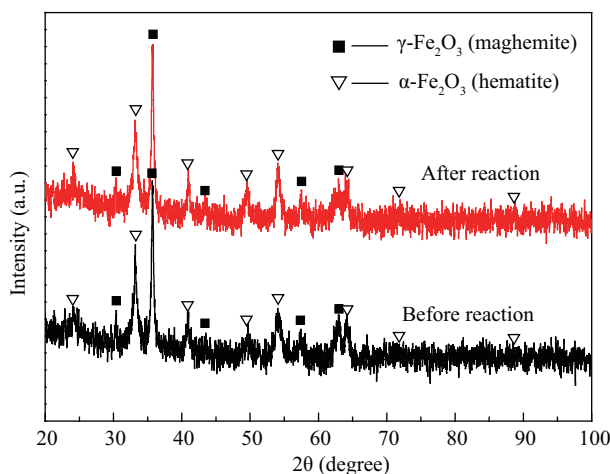


Fig. 2 XRD patterns of the Fe_2O_3 catalysts before and after reaction.

2.2 Effect of reaction temperature on SCR activity

Figure 3 shows the NO conversion measured for Fe₂O₃ catalysts with 3% O₂ and without oxygen in the reactor at temperatures ranging from 90 to 300°C. It can be clearly seen from **Fig. 3** that the NO conversion on Fe₂O₃ catalysts in the absence/presence of O₂ were very sensitive to temperature, and increased with temperature before 210°C and then decreased. The maximum efficiency of NO conversion was 98.5% in the presence of 3% O₂ at 210°C, and the efficiency of NO conversion was over 90% in the absence of O₂. Therefore, Fe₂O₃ catalysts showed high catalytic activity at low temperatures in the presence/absence of O₂.

It is well known that the function of catalysts is to change the reaction pathway of NO conversion and decrease the activation energy and reaction temperature. Selective non-catalytic reduction (SNCR) is mainly operated in the temperature range of 850–1100°C without catalysts (Gang et al., 2008), while SCR is highly effective under the effects of V-based catalysts at comparatively lower temperatures (300–400°C) (Qi et al., 2003). Although this reaction temperature is lower than that in SNCR, it is also higher than the temperature of post-desulfurization. The experimental results of this article show that the temperature for high efficiency NO conversion with Fe₂O₃ catalysts was 210°C and this catalyst could be used downstream of the desulfurizer. This is due to the fact that the new catalysts provide a new reaction pathway for NO conversion, and the activation energy for Fe₂O₃ in the SCR process was calculated to be 28.32 kJ/mol (Yao et al., 2010a), lower than values obtained by other researchers, such as for V₂O₅/TiO₂ (85 kJ/mol) (Amiridis and Solar, 1996), H-ZSM-5 (55 kJ/mol) (Stevenson et al., 2000), and MnO_x/TiO₂ (38 kJ/mol) (Wu et al., 2007). It is well known that the activation energy in the SCR reaction is an important parameter to

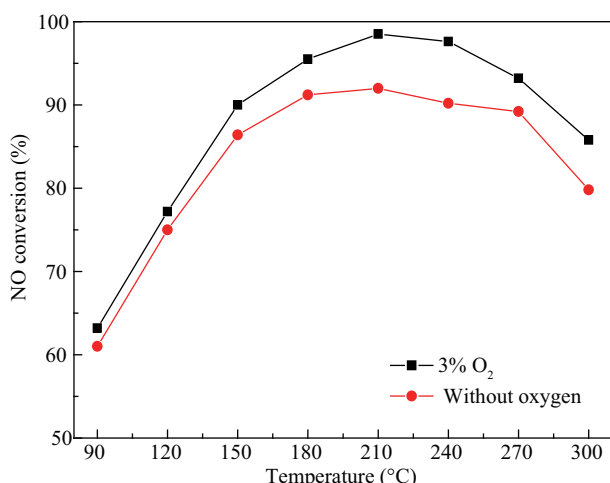


Fig. 3 Effect of reaction temperature on de-NO efficiency. Reaction conditions: [NO] = [NH₃] = 500 ppm, balance N₂, total flow rate 1500 mL/min, catalyst 12 mL.

evaluate the performance of the catalysts. The lower the activation energy is, the lower the activation temperature required for the reaction would be. Therefore, the Fe₂O₃ catalysts are superior catalysts for low temperature SCR of NO with NH₃. The second reason may be due to its large BET surface area (90.79 m²/g). The reaction rate is determined by both chemical reaction and ‘mass transfer and diffusion’ (Yao et al., 2010a). Therefore, the specific surface area of catalysts is important for a catalytic reaction. Since the BET surface area of the Fe₂O₃ particles was 90.79 m²/g and was larger than that of commercial V-based catalysts (83.76 m²/g) (Zhu et al., 2009), the adsorption of the gaseous reactants on the catalyst surface would be strengthened and promoted during the SCR reaction, and thus more free radicals would be generated on the active sites of catalysts to promote the reaction. Furthermore, it can be seen from the XRD results of the Fe₂O₃ catalysts that they consist of α-Fe₂O₃ and γ-Fe₂O₃. Cation vacancies in the lattice of γ-Fe₂O₃ can be classified as point lattice defects, which can provide more active sites for the catalytic reaction and contribute to the surface electron transfer in the reaction, and thus increase the low temperature catalytic activity.

In addition, the difference of NO conversion on Fe₂O₃ catalysts with and without oxygen indicated that the additional oxygen caused enhancement of the catalytic activity. However, compared with the results of oxygen absence, the downward trend of NO conversion declined faster in the presence of O₂ when the temperature exceeded 210°C, which might due to the oxidation of NH₃ at high temperatures.

2.3 Effect of O₂ on SCR activity

Based on previous studies, it was well known that oxygen is important for SCR of NO with NH₃ at low temperature. The effect of oxygen concentration on SCR activity was also tested in this work and shown in **Fig. 4**. It can

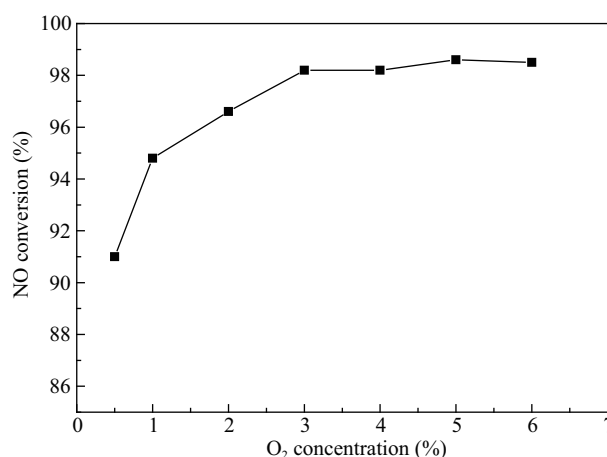


Fig. 4 Effect of O₂ on de-NO efficiency at 210°C. Reaction conditions: [NO] = [NH₃] = 500 ppm, balance N₂, total flow rate 1500 mL/min, catalyst 12 mL.

be seen that NO conversion over the catalysts increased with increasing oxygen concentration, especially when the oxygen concentration was less than 3%. At 210°C, 91% NO conversion was obtained in the presence of 0.5% O₂. When 3% O₂ was added, a conversion of NO up to 98.2% was obtained. However, there was no significant increase of the de-NO efficiency with increasing oxygen concentration further. It is indicated that O₂ enhanced the SCR activity of Fe₂O₃ catalysts at low temperature and the optimum concentration of oxygen was 3% under the conditions used. According to our previous study (Yao et al., 2010b), the oxidation of ammonia occurred on the Fe₂O₃ catalysts in the presence of O₂ and then NO was oxidized to NO₂ at low temperatures. A partial conversion of NO into NO₂ would result in a significant improvement of the catalytic activity, and the reaction rate of NH₃ with NO₂ + NO was much higher than that with NO alone (Qi and Yang, 2003; Koebel et al., 2001; Long and Yang, 2001). Therefore, the observed results may be due to the fact that the Fe₂O₃ catalysts increased the activity for NO oxidation to NO₂ in the presence of O₂ at low temperatures, and thereby increased the catalytic activity.

2.4 Effect of the [NH₃]/[NO] molar ratio on SCR activity

It is well known that the [NH₃]/[NO] molar ratio is a key parameter in SCR of NO with NH₃. To determine the effect of the [NH₃]/[NO] molar ratio on NO removal, experiments were performed at different molar ratios of NH₃ to NO at 210°C. The effect of [NH₃]/[NO] molar ratio on the SCR reaction is shown in Fig. 5. It can be seen that NO conversion increased rapidly with [NH₃]/[NO] molar ratio when it was less than one and varied more gradually when a higher molar ratio of [NH₃]/[NO] was used. Hence, considering some increment for safety, the [NH₃]/[NO] molar ratio of 1.2 is suitable and there is no necessity to increase the [NH₃]/[NO] molar ratio over 1.2.

Based on previous studies (Lázaro et al., 2006; Mochida

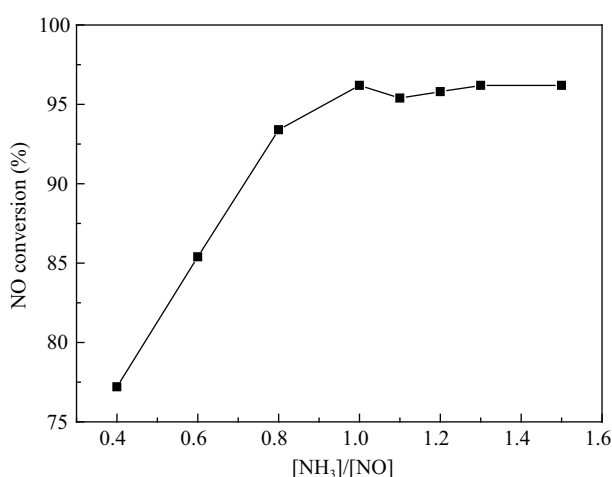


Fig. 5 Effect of [NH₃]/[NO] molar ratio on de-NO efficiency at 210°C. Reaction conditions: [NO] = 500 ppm, 3% O₂ (V/V), balance N₂, total flow rate 1500 mL/min, catalyst 12 mL.

et al., 2000; Boyano et al., 2008), the reaction between NO and NH₃ could be divided into the following two parts: one in the gas phase and the other on the surface of the catalysts. Because the reactivity between NO and NH₃ was low in the gas phase, the main part of the reaction was on the surface of the catalysts. The NH₃ was first absorbed on the surface of catalysts, and then reacted with NO on the surface. When the concentration of NH₃ was increased, more NH₃ could be adsorbed on the catalyst and react with NO. However, the adsorption sites were limited on the surface of catalyst, and thus the adsorbed NH₃ was also limited. Therefore, additional concentration of NH₃ cannot increase NO conversion.

2.5 Effect of residence time on SCR activity

The effect of residence time on NO conversion was investigated at different temperatures, by changing the residence time, which could be obtained through varying catalyst volume. Figure 6 shows the NO conversions obtained at different temperatures under different residence time values. The results clearly showed from Fig. 6 that the activity increased with increasing residence time at different temperatures. The same strong effect of residence time was widely confirmed by other authors (Wu et al., 2007; Qi and Yang, 2003; Lázaro et al., 2006; Boyano et al., 2008; Niu et al., 2011; Izquierdo et al., 2001) who previously studied the effects of residence time on de-NO_x efficiency. In addition, at higher temperature, the residence time had less effect on NO conversion than that at lower temperature. When residence time increased from 0.36 to 0.48 sec, the efficiency of NO conversion increased by 4.5% at 120°C, while the increase was only 1.9% at 210°C.

2.6 Effect of SO₂ on SCR activity

It is well known that the effect of SO₂ on NO conversion is noticeable for the low temperature SCR reaction. The

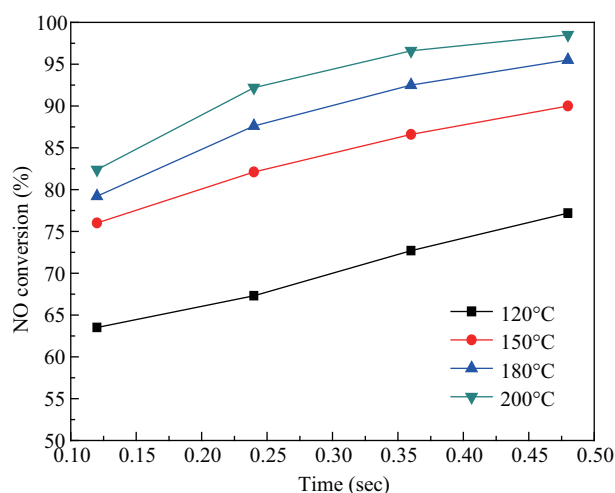


Fig. 6 Effect of residence time on de-NO efficiency at different temperatures. Reaction conditions: [NO] = [NH₃] = 500 ppm, 3% O₂ (V/V), balance N₂, total flow rate 1500 mL/min, catalyst 3–12 mL.

effect of SO₂ on the activity of catalysts has been studied by many researchers (Kang et al., 2006; Qi et al., 2003; Tang et al., 2007; Huang et al., 2008; Li et al., 2012; Ha et al., 2008; Xie et al., 2004) who found that the catalysts could be gradually deactivated by SO₂. For example, 100–200 ppm SO₂ could gradually deactivate the Cu-CNTs catalysts, and NO conversion on the catalysts decreased sharply from the original level (about 65%) to about 45% in less than 150 min (Li et al., 2012); NO conversion on the Mn/TiO₂ catalysts decreased from about 96% to 60% in less than one hr and then reached a stable level in the presence of 100 ppm SO₂ and 2.5% H₂O (Qi and Yang, 2003). Xie et al. (2004) reported that 1600 ppm SO₂ could seriously deactivate the CuO/Al₂O₃ catalyst in 120 min during the SCR process. Yang et al. (2011) studied the effect of 2000 ppm SO₂ on the NO reduction with NH₃ over sulfated CaO and found that NO conversion decreased sharply. Thus, how to improve the SO₂ resistance of catalysts is an important issue in the industrial application of catalysts; but few researchers have studied the effect of SO₂ on the SCR activity of Fe₂O₃ particles. Therefore, we studied the effect of SO₂ on the catalytic activities of the Fe₂O₃ particles.

The effect of SO₂ on SCR activity was studied through the following experiment at a temperature of 180°C. As shown in Fig. 7, when 1000 ppm SO₂ was added to the simulated flue gas after 40 min of stable reaction, the NO conversion on Fe₂O₃ catalysts showed almost no change and the NO conversion still remained more than 92% after 60 min. Finally, the NO conversion on the Fe₂O₃ catalysts decreased from 99.2% to 58% in 240 min and basically reached a stable level. Compared with the previous reports mentioned above (Li et al., 2012; Qi and Yang, 2003; Xie et al., 2004), our experimental results showed that the Fe₂O₃ catalysts were highly active for the low-temperature SCR reaction and had better resistance to SO₂ at 180°C in one hour of added SO₂. But just

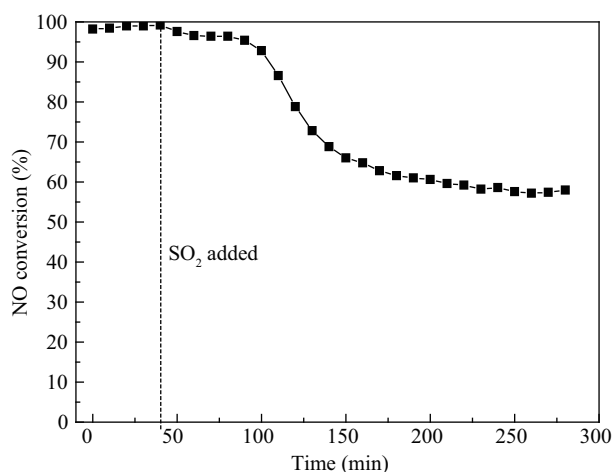


Fig. 7 Effect of SO₂ on de-NO efficiency at 180°C. Reaction conditions: [NO] = [NH₃] = 500 ppm, 3% O₂ (V/V), [SO₂] = 1000 ppm, balance N₂, total flow rate 1000 mL/min, catalyst 6 mL.

at that point, substantial deactivation occurred with time and NO conversion decreased sharply. These experimental results clearly indicate that SO₂ significantly deactivates the Fe₂O₃ catalyst for the reaction of NO-NH₃-O₂-SO₂, and sulfates may be formed on the surface of the catalysts during the SCR reaction when SO₂ is present for more than one hour.

The XRD patterns of the deactivated Fe₂O₃ catalyst are shown in Fig. 8. The results indicated that the main phases found in the deactivated Fe₂O₃ catalysts were γ-Fe₂O₃ (maghemite) and α-Fe₂O₃ (hematite). Moreover, no visible peaks of sulfur or sulfate were observed, which might be due to the fact that sulfur or sulfate species existed as surface sulfate or amorphous bulk sulfate and were poorly crystallized (Sheng et al., 2012; Liu et al., 2009; Xu et al., 2009). Since XRD is inappropriate to characterize matter in a non-crystalline state, the deactivated catalysts were examined by TGA and FT-IR and the results are shown in Figs. 9 and 10.

The curves of TG and DTG for the deactivated Fe₂O₃ catalyst at the heating rate of 10°C/min are shown in Fig. 9. It can be seen from Fig. 9 that the deactivated Fe₂O₃ catalyst has several temperature regions of weight loss. The initial loss below 200°C is due to water desorption from the catalyst surface (Huang et al., 2008). The next stage for decomposition is between 280 and 480°C, and the weight loss for this step can be attributed to the decomposition of the ammonium sulfate on the deactivated Fe₂O₃ catalyst surface, and ammonia desorption from the decomposition of the ammonium sulfate occurs during this stage (Huang et al., 2008; Xie et al., 2004; Li et al., 2012). The last stage after 590°C could be attributed to the decomposition of metallic sulfates during the heating course of the TG analysis (Huang et al., 2008; Xie et al., 2004).

To confirm the above conclusions, FT-IR analysis was performed and provided further evidence for the formation of ammonium sulfate. The FT-IR spectra of the fresh

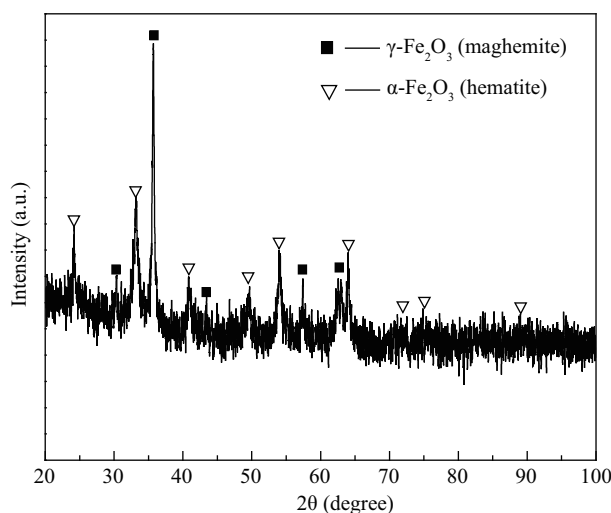


Fig. 8 XRD patterns of the deactivated Fe₂O₃ catalysts.

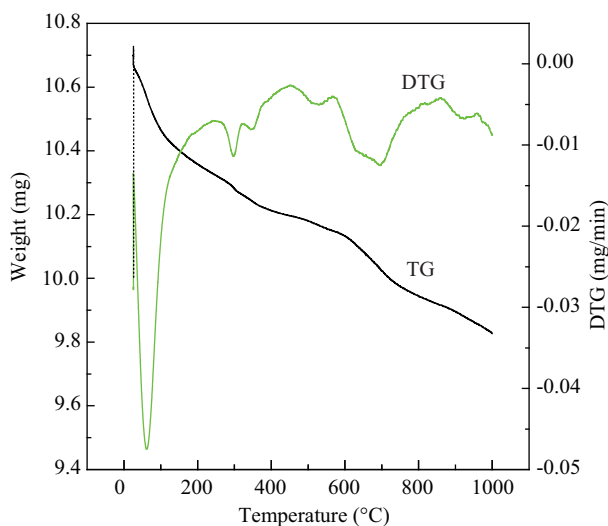


Fig. 9 TG and DTG spectra for the deactivated Fe_2O_3 catalysts at heating rate of $10^\circ\text{C}/\text{min}$.

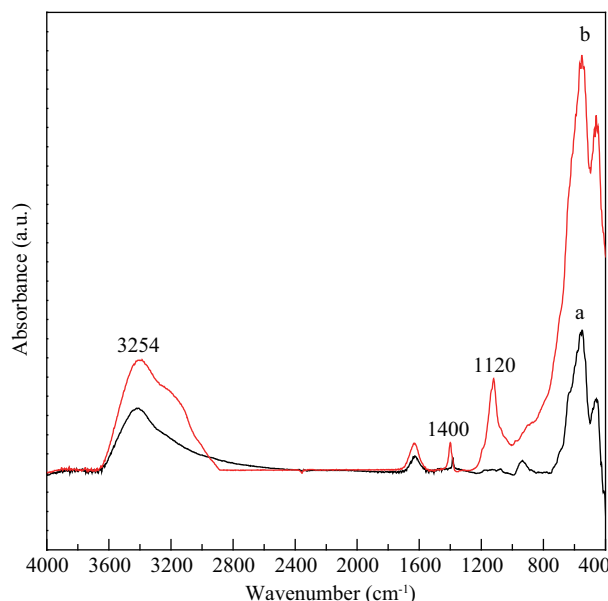


Fig. 10 FT-IR spectra of the fresh catalysts (line a) and the deactivated catalysts (line b).

catalysts and the deactivated catalysts are shown in **Fig. 10**. Compared to the fresh catalysts, the spectra of the deactivated Fe_2O_3 catalysts exhibit some new bands at 1120, 1400, and 3254 cm^{-1} . The new bands at 1120 and 1400 cm^{-1} are due to the adsorption peak of the SO_4^{2-} group (Phil et al., 2010; Pietrogiacomini et al., 2009; Labádi et al., 2006), whereas the band at 3254 cm^{-1} is attributed to the corresponding N–H stretching vibration of NH_4^+ ions (Xie et al., 2004). These results show that sulfate salts such as $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 were formed during the SCR reaction in the presence of SO_2 , which is in excellent agreement with the TGA results.

Based on the discussion above, it can be found that deactivation of the Fe_2O_3 catalysts in the presence of SO_2 is due to the formation of ammonium sulfate and metallic

sulfates on the surface of the catalyst during the SCR reaction.

3 Conclusions

Particulate Fe_2O_3 catalysts were used for the low temperature SCR of NO with NH_3 in the presence of oxygen. The effects of reaction temperature, oxygen concentration, $[\text{NH}_3]/[\text{NO}]$ molar ratio and residence time on SCR activity were experimentally studied. The experimental results showed that the Fe_2O_3 catalysts had high activity for the low temperature SCR of NO with NH_3 in a broad temperature range of $150\text{--}270^\circ\text{C}$ and more than 95% NO conversion was obtained at 180°C when the molar ratio $[\text{NH}_3]/[\text{NO}]$ was 1, the residence time was 0.48 sec and the O_2 volume fraction was 3%. Moreover, according to the results of TGA and FT-IR, the deactivation caused by SO_2 may be due to the formation of metal sulfates and ammonium sulfates on the catalyst surface.

Acknowledgments

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