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Relationship between SO_2 poisoning effects and reaction temperature for selective catalytic reduction of NO over Mn–Ce/TiO_2 catalyst

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ABSTRACT

In this paper, Mn–Ce/TiO_2 was prepared by sol–gel method and used for low-temperature selective catalytic reduction (SCR) of NO with NH_3 in the presence of SO_2 at different temperatures (100–200 °C). SO_2 had a poisoning effect on NO conversion of the Mn–Ce/TiO_2 catalyst and this effect was directly related with reaction temperature. The higher the reaction temperature, the more rapidly the catalyst activity decreased. The results of in situ diffuse reflectance infrared Fourier transform (in situ DRIFT) spectroscopy and temperature programmed desorption (TPD) profiles indicated that the active sites of the Mn–Ce/TiO_2 catalyst were seriously sulfated at 200 °C which led to an irreversible deactivation of the sample. While the formation and deposition of $(NH_4)_2SO_3$ and NH_4HSO_4 were the main causes of catalyst deactivation when the SCR reaction was carried out at 100 °C. This kind of deactivation could be almost completely recovered after water-washing treatment.

1. Introduction

Selective catalytic reduction (SCR) of NO_x with NH_3 is an effective process to remove NO_x from stationary sources and recently there have been strong interests to develop superior SCR catalyst with high activity at low temperature, which could be placed in SCR reactor and located downstream of the particle controller and the desulfurizer device [1]. Among these catalysts, Mn-based and Ce-based catalysts exhibited superior SCR activity, since manganese oxides (MnO_x) contain various kinds of labile oxygen [2], which are important to complete the catalytic cycle and ceria own high oxygen storage and redox capacity [3].

There is still low concentration of residual SO_2 in the flue gas after desulfurization. Many researchers concluded that SO_2 had a serious poisoning effect on the activity of catalyst at low temperature [4–6]. SCR reaction in the presence of SO_2 over Mn/TiO_2 and Mn–Ce/TiO_2 catalysts was also investigated in our previous study [7]. It was found that the activity of Mn/TiO_2 was strongly suppressed in the presence of SO_2 and Ce doping could greatly improve the SO_2 resistance of catalyst. The deactivation of the catalyst caused by SO_2 reflects on two aspects according to our results [7] and Xu et al.'s report [8]. Firstly, SO_2 could react with NH_3 to form $(NH_4)_2SO_3$ and NH_4HSO_4, which did not decompose at low temperature and finally deposited on the catalyst surface, blocking the active sites of catalyst. Secondly, active phase such as MnO_x on the catalyst was sulfated by SO_2 and formed stable sulfate species, which was inactive in SCR reaction.

Formation and decomposition of sulfate species on the catalyst surface are directly related to the reaction temperature. Therefore, it is believed that reaction temperature might have great effects on SO_2 deactivation of SCR catalyst. Zhu et al. [9] investigated the decomposition and reactivity of sulfate species formed on the V_2O_5/AC and V_2O_5/TiO_2 catalysts using temperature programmed method. They found the decomposition rate of the formed sulfate species sharply increased with temperature rising in the range of 260–350 °C. Xu et al. [8] dealt with Ce/TiO_2 catalyst and found that SO_2 had a significant inhibiting effect on the reduction of NO and it led to a more obvious decrease in SCR activity at 300 °C than at 350 °C.

Inspired by the above findings, we think that SO_2 may have different effects on Mn–Ce/TiO_2 catalyst at different temperatures. The formation and deposition of NH_4HSO_4 on Mn–Ce/TiO_2 catalyst surface, as well as the sulfation on catalyst active sites might be greatly influenced by the reaction temperature. However, no information is available in the literature on this aspect. Therefore, in this paper, for better understanding of these effects, Mn–Ce/TiO_2 catalyst was prepared by sol–gel method and used for low-temperature SCR of NO with NH_3 in the presence of SO_2 at different temperatures within the range of 100–200 °C, which was proved to be the most active temperature region for Mn–Ce/TiO_2 catalyst in SCR reaction in our previous study [10]. The above questions would be investigated and discussed in detail. Our results can offer useful information to understand the relationship between reaction temperature and SO_2 effects on catalyst activity, which could thereby provide some guidelines for the real application of low-temperature SCR catalysts.

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2. Experimental

2.1. Catalyst preparation

The catalyst was prepared by sol–gel method as we reported [10,11]. Tetrabutyl titanate (0.1 mol), manganese nitrate (0.04 mol), cerium nitrate (0.007 mol), ethanol (0.8 mol), water (0.6 mol) and acetic acid (0.3 mol) were mixed under vigorous stirring at room temperature to form transparent sol. The sol transformed to gel after stabilized at room temperature for two weeks. The gel was dried at 110 °C to remove organic solution. Then the solid was crushed and sieved to 40–60 mesh and calcined at 500 °C in air for 6 h in a tubular furnace.

2.2. Catalytic activity measurement

SCR activity measurements were carried out in a fixed-bed containing 3 mL catalyst with a gas hourly space velocity (GHSV) of 40,000 h^{-1}. The reactant gas typically consisted of 800 ppm NO, 800 ppm NH_3, 3% O_2, 100 ppm SO_2, 3 vol.% water and balance N_2. The reactants were pre-heated in a gas mixer, and then the mixed gas was sent to the reactor. Water vapor was generated by passing N_2 through a heated gas-wash bottle (80 °C) containing deionized water. The SCR experiment was stopped when the NO conversion of catalyst was decreased below 60%. The concentrations of NO and NO_2 were monitored by a NO–NO_2–NO_x analyzer (Thermo Fisher Scientific, Model 42i-HL), and the concentration of SO_2 was monitored by a SO_2 analyzer (Thermo Fisher Scientific, Model 43i-HL).

2.3. Catalyst characterization

The textural structures of the prepared samples were measured by N_2 adsorption at 77 K in a Micromeritics ASAP 2020 system, and specific surface areas of samples were measured using Brunauer–Emmett–Teller (BET) method. The pore size distributions were measured from the N_2 desorption isotherm using the cylindrical pore model (BJH method). X-ray photoelectron spectroscopy (XPS) was used to analyze the surface atomic state of catalyst with Al Kα X-rays (Thermo ESCALAB 250). The surface atomic concentrations were calculated from the peak area ratios of the samples.

Temperature programmed desorption (TPD) experiments were carried out on a custom-made TCD setup using 50 mg catalysts. Sample was firstly pretreated in He at 500 °C for 1 h, and then was saturated with anhydrous NH_3 or NO (4% in He) at a flow rate of 30 mL/min for about 30 min. Desorption was carried out by heating the sample in He (30 mL/min) from 100 to 800 °C with a heating rate of 5 °C/min.

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was obtained to investigate the effects of SO_2 on NH_3 and NO adsorption on Mn–Ce/TiO_2 surface at different temperatures. The DRIFT measurements were performed with ZnSe windows coupled to Nicolet 6700 FTIR spectrometers. In the DRIFT cell, the catalyst was pretreated at 500 °C in He environment for 2 h, followed by exposed to 100 ppm SO_2 at required temperature in the presence of O_2 for 30 min. Then the sample was purged by He and scanned as background. Finally, NH_3 or NO was introduced to the gas flow and the IR spectra were recorded as a function of time with subtracting from the background spectrum.

3. Results and discussion

3.1. Relationship between reaction temperature and SO_2 poisoning effect on catalyst

3.1.1. SCR performance

Fig. 1 illustrates the effects of SO_2 on NO conversion of Mn–Ce/TiO_2 catalyst at different temperatures. It clearly indicated that the poisoning effect of SO_2 was directly related with the reaction temperature. The higher the reaction temperature, the more rapidly the catalyst activity decreased. When the reaction temperature was above 180 °C, NO conversion of the sample decreased significantly to 60% in 200 min, while the Mn–Ce/TiO_2 could still provide more than 70% of NO conversion after 500 min when the reaction took place at 100 °C. When the NO conversion of catalyst was lower than 60%, the SCR reaction was stopped and these used samples were expressed as SU(*T*), where *T* stood for the SCR reaction temperature.

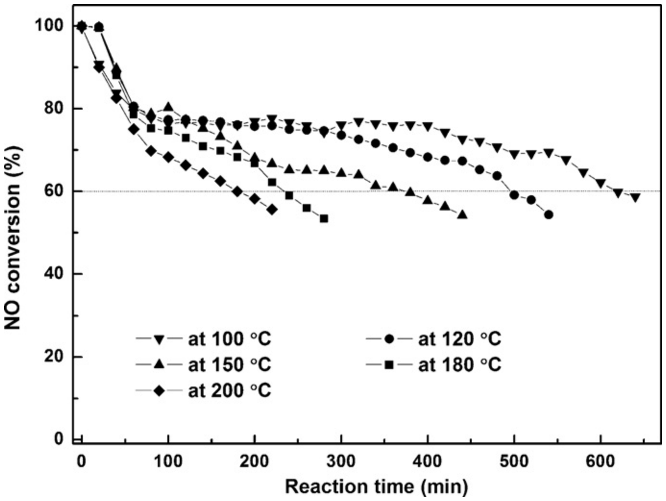


Fig. 1. NO conversions of Mn–Ce/TiO_2 in the presence of SO_2 at various temperatures ($[NH_3]$ = [NO] = 800 ppm, $[O_2]$ = 3%, $[SO_2]$ = 100 ppm, $[H_2O]$ = 3 vol.%, N_2 balance, GHSV = 40,000 h^{-1}).

These used catalysts were regenerated by deionized-water-washing and followed by dying at 105 °C for 12 h. The regenerated sample was denoted as SR(*T*), where *T* stood for the SCR reaction temperature. Fig. 2 shows the SCR activity of these regenerated samples in the absence of SO_2 at 150 °C. The NO conversion of SR(100 °C) could be almost completely recovered to original level after regeneration. When the reaction temperature was below 150 °C, above 90% activity of the samples (SR(100 °C), SR(120 °C) and SR(150 °C)) could be restored after water-washing. However, when the SCR reaction was carried out at above 150 °C, there was

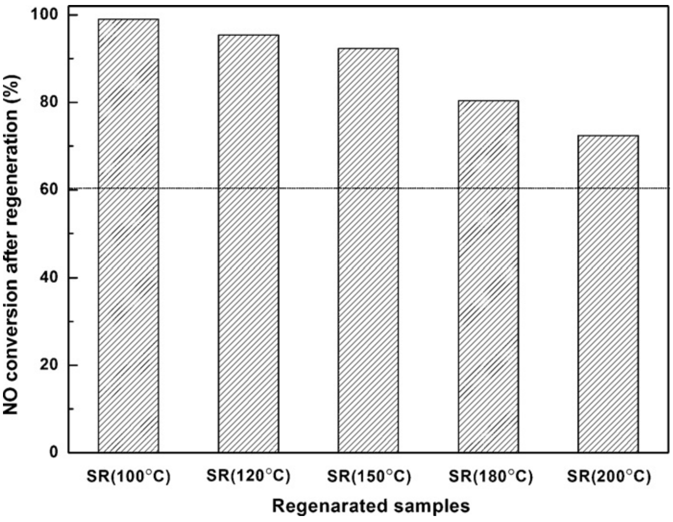


Fig. 2. NO conversions of various regenerated Mn–Ce/TiO_2 samples (reaction temperature = 150 °C, $[NH_3]$ = [NO] = 800 ppm, $[O_2]$ = 3%, $[H_2O]$ = 3 vol.%, N_2 balance, GHSV = 40,000 h^{-1}).

Table 1
Physi-chemical properties of fresh and used Mn–Ce/TiO_2 catalysts.

Catalyst	BET surface area (m^2/g)	BJH pore volume ($\times 10^{-2}$ cm^3/g)	Surface concentration of sulfur (%)
Fresh sample	157	33	–
SU(100 °C) sample	101	20	4.8
SU(200 °C) sample	65	14	4.2
SR(100 °C) sample	139	28	0.3
SR(200 °C) sample	89	18	2.8

more un-recoverable SO_2 deactivation taking place on Mn–Ce/TiO_2 catalysts. SR(200 °C) could provide only about 73% of NO conversion after regeneration.

3.1.2. BET and XPS analysis

Physical properties of fresh and used Mn–Ce/TiO_2 catalysts are listed in Table 1. It clearly showed that the surface area and pore volume of Mn–Ce/TiO_2 drastically decreased after reaction and the higher the reaction temperature, the more the loss of catalyst surface area and pore volume. The surface area of SR(100 °C) returned to 139 m^2/g after regeneration while that of SR(200 °C) could only be recovered to 89 m^2/g after washing treatment. It implied that the effects of SO_2 on catalyst microstructure were obviously related to the reaction temperature and higher reaction temperature led to more un-recoverable loss of catalyst surface area and pore volume. Furthermore, surface concentration of sulfur on various samples was measured by XPS analysis and listed in Table 1. S 2p binding energies of these samples were all in the range of 168.2–169.8 eV (not shown in this paper), which were due to SO_3^{2-} (168.5 eV) and SO_4^{2-} species (169.7 eV) [12]. Sulfur concentration on SU(100 °C) catalyst surface was a little higher than that on SU(200 °C). And only 0.3% of surface sulfur could be observed on SR(100 °C) sample, while still 2.8% of sulfur existed on SR(200 °C) surface. It indicated that most of sulfur existed in the form of washable sulfite and sulfate species for SU(100 °C), while more un-washable sulfite and sulfate species would be formed on Mn–Ce/TiO_2 surface with reaction temperature arising.

3.2. Effect of deposited $(NH_4)_2SO_3$ and NH_4HSO_4 on the NO conversion of Mn–Ce/TiO_2

In this section, fresh Mn–Ce/TiO_2 samples were firstly dipped in $(NH_4)_2SO_3$ and NH_4HSO_4 solutions followed by drying process and then SCR activity tests were carried out to analyze the effect of the deposited ammonium sulfate on NO conversion of Mn–Ce/TiO_2.

Fig. 3 displays that both of the deposited $(NH_4)_2SO_3$ and NH_4HSO_4 lowered the NO conversion of Mn–Ce/TiO_2 and the activity of these pretreated catalysts could be recovered to nearly 100% after water-washing. It suggested that the deposited $(NH_4)_2SO_3$ and NH_4HSO_4 had a poisoning effect on SCR activity of Mn–Ce/TiO_2 below 200 °C. However, the un-recoverable SO_2 deactivation as shown in Fig. 2 was not caused by ammonium sulfite or sulfate deposition but rather probably due to active sites sulfation, since $(NH_4)_2SO_3$ and NH_4HSO_4 could be washed away easily.

3.3. Effect of temperature on the catalyst active sites sulfation

In this section, Mn–Ce/TiO_2 catalyst was first exposed to 100 ppm SO_2 and 3% O_2 in the absence of NH_3 for 30 min at 100 and 200 °C, respectively, and followed by He purging for 30 min, being denoted as ST(100 °C) and ST(200 °C) correspondingly. Then activity tests, TPD and DRIFT analyses were performed to investigate the effects of reaction temperature on catalyst active sites sulfation.

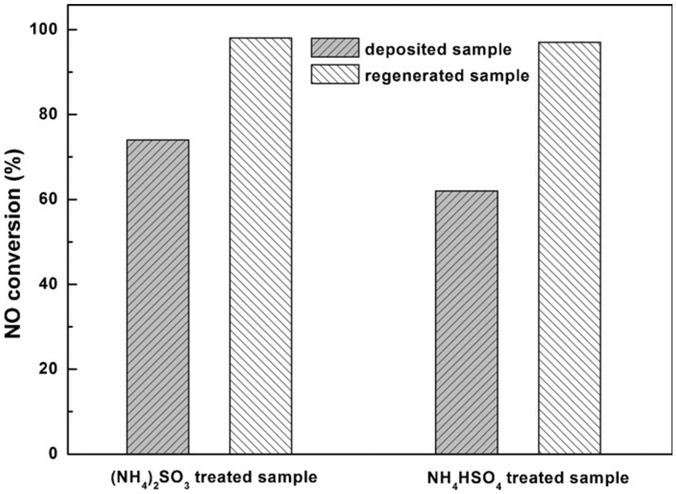


Fig. 3. NO conversions of $(NH_4)_2SO_3$ and NH_4HSO_4 deposited Mn–Ce/TiO_2 samples in the absence of SO_2 (reaction temperature = 150 °C, $[NH_3]$ = [NO] = 800 ppm, $[O_2]$ = 3%, $[H_2O]$ = 3 vol.%, N_2 balance, GHSV = 40,000 h^{-1}).

3.3.1. SCR activity tests

Fig. 4 shows that the NO conversion of ST(200 °C) catalyst sharply decreased to about 50%, while the ST(100 °C) sample could supply much higher NO conversion, which was about 82%. It suggests that much more active sites on catalysts surface would react with SO_2 and were sulfated with temperature rising. It is worth notice that when Mn–Ce/TiO_2 catalyst was exposed to only SO_2 without NH_3, its SCR catalytic activity decreased much more rapidly than exposed to SO_2 and NH_3 as shown in Fig. 1. It might be because that the presence of NH_3 occupied lots of active sites and prevented SO_2 from sulfating these catalyst active sites. These sulfated species on Mn–Ce/TiO_2 surface were inactive and could not be washed away. Therefore, unlike in Fig. 2, the SCR activity of these used samples could revert a little after regeneration as illustrated in Fig. 4.

3.3.2. Effects of catalyst active sites sulfation on the NH_3 and NO adsorption

Fig. 5 illustrates the NH_3-TPD curves for different samples. One broad and weak desorption peak spanned in the temperature range of 100–300 °C is present for all of the three samples which is attributed to NH_3 desorbed by weak and medium acid sites [13].

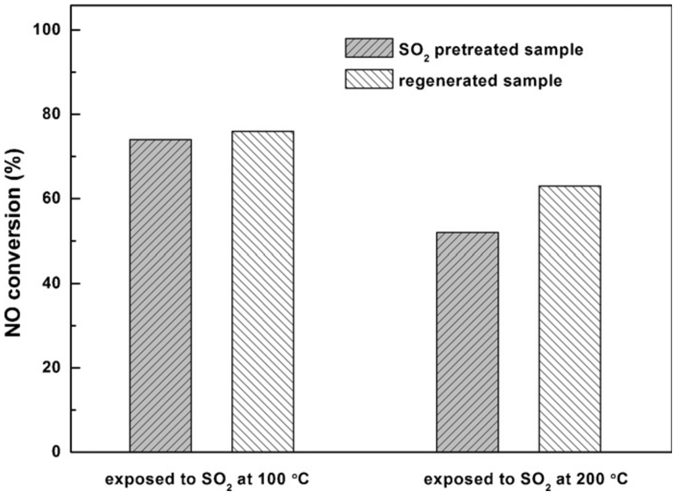


Fig. 4. NO conversions of various SO_2 pretreated Mn–Ce/TiO_2 samples (reaction temperature = 150 °C, $[NH_3]$ = [NO] = 800 ppm, $[O_2]$ = 3%, $[H_2O]$ = 3 vol.%, N_2 balance, GHSV = 40,000 h^{-1}).

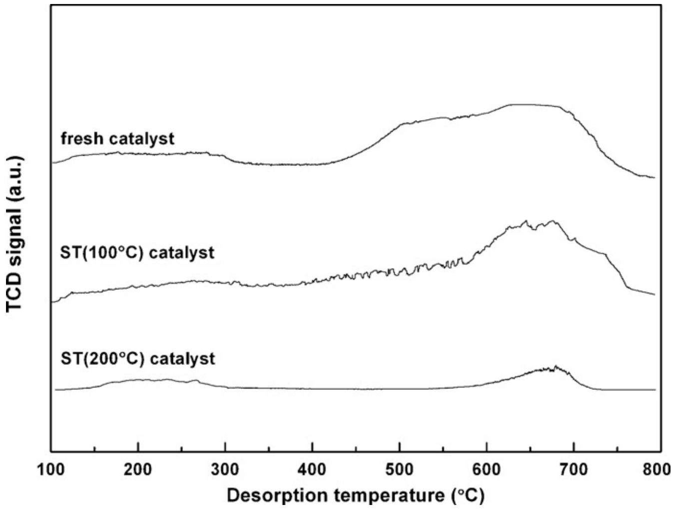


Fig. 5. NH_3-TPD profiles for various Mn–Ce/TiO_2 samples.

For fresh Mn–Ce/TiO_2 catalyst, with desorption temperature increasing, one strong and broad peak in the region of 430–770 °C is observed. It is attributed to quantity of chemisorbed NH_3 molecules adsorbed by strong acid sites [14].

The intensity of the peak located at 430–770 °C significantly decreased on the NH_3-TPD curve of ST(100 °C) sample and became very weak in the case of ST(200 °C) catalyst. It implied that the presence of SO_2 had a great influence on catalyst acid sites and this effect was directly related to the SCR reaction temperature. Higher reaction temperature led to the loss of catalyst acidity much more easily and rapidly.

In order to identify the change of acid sites before and after exposed to SO_2 at different temperatures, NH_3 was adsorbed on various catalysts and DRIFT measurements were performed as shown in Fig. 6. The introduction of NH_3 led to the formation of peaks at 940, 966, 1165, 1229, 1455, 1598 and 1687 cm^{-1} in the low wavenumber region for fresh Mn–Ce/TiO_2. The strong bands at 1598 and 1165 cm^{-1} with a shoulder at 1229 cm^{-1} are results of the NH_3 coordinatively bound to Lewis acid sites [10,14–16]. Two weak bands at 1455 and 1687 cm^{-1} are attributed to NH_4^+ bound to Brønsted acid sites, respectively [14–16]. The bands at 930 and 966 cm^{-1} were assigned to weakly-adsorb NH_3 or gas-phase NH_3 as discussed in our previous work [10]. In the high wavenumber region, peaks are observed at 3143, 3256 and 3350 cm^{-1}, which were due to stretching of NH_3 coordinated to Lewis acid sites [14,17,18].

Fig. 6B illustrates that on the DRIFT spectra of ST(100 °C) catalyst, the initial peak at 1165 cm^{-1} due to NH_3 bound to Lewis acid sites disappeared while the bands at 1455 and 1682 cm^{-1} assigned to NH_4^+ species bound to Brønsted acid sites were significantly strengthened. Therefore, the loss of catalyst acidity after SO_2 pretreatment as discussed in NH_3-TPD experiment (see Fig. 5) was most probably caused by the decrease of Lewis acid sites on catalyst surface. In the case of ST(200 °C) sample, another peak centered at 1229 cm^{-1} corresponding to NH_3 bound to Lewis acid sites totally vanished as shown in Fig. 6C. As a result, the catalyst acidity further reduced as discussed in Fig. 5.

NO-TPD experiment was also carried out on the prepared samples and the results are shown in Fig. 7. The NO-TPD profile of

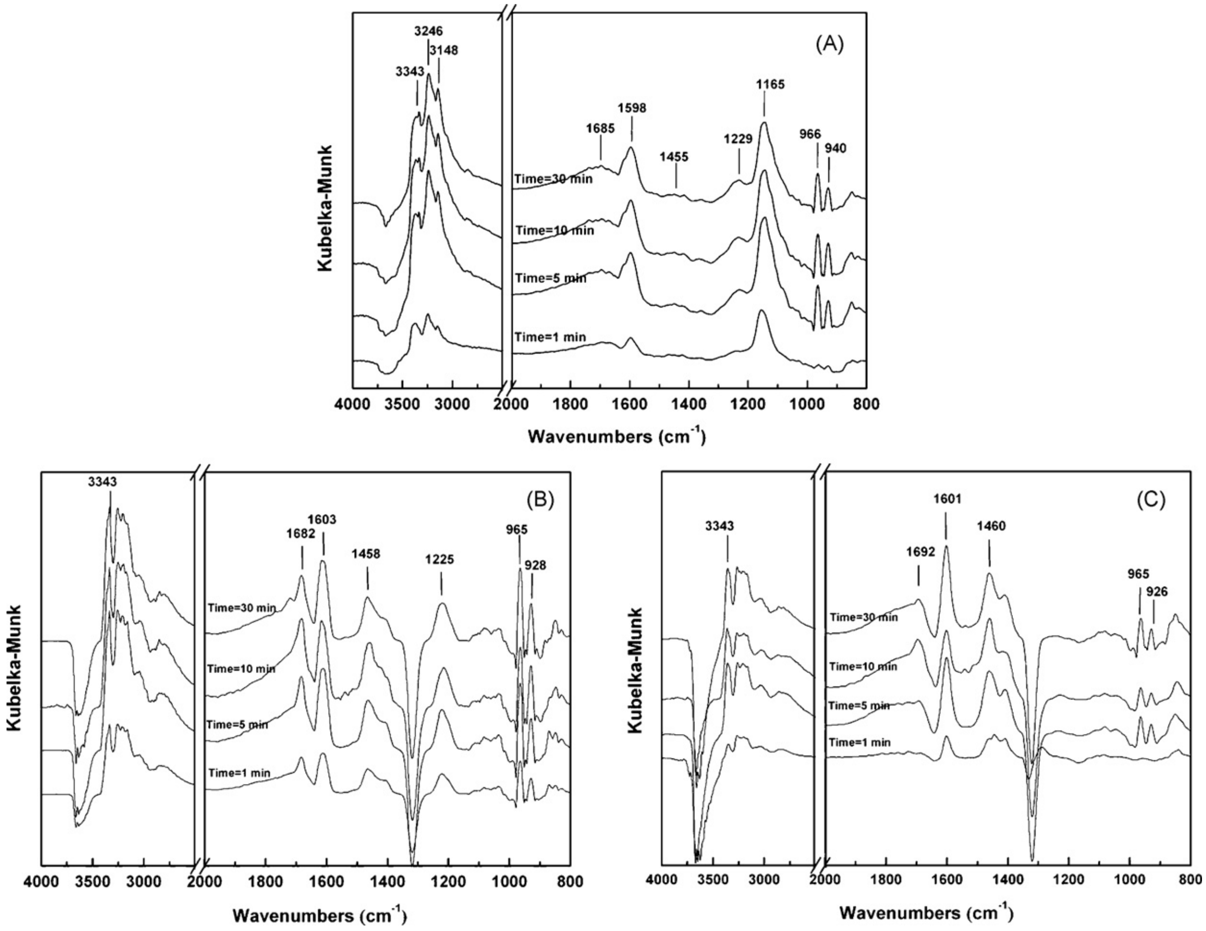


Fig. 6. DRIFT spectra of fresh and used Mn–Ce/TiO_2 exposed to 800 ppm NH_3 for various time at 150 °C. (A) Fresh catalyst; (B) ST(100 °C) catalyst; (C) ST(200 °C) catalyst.

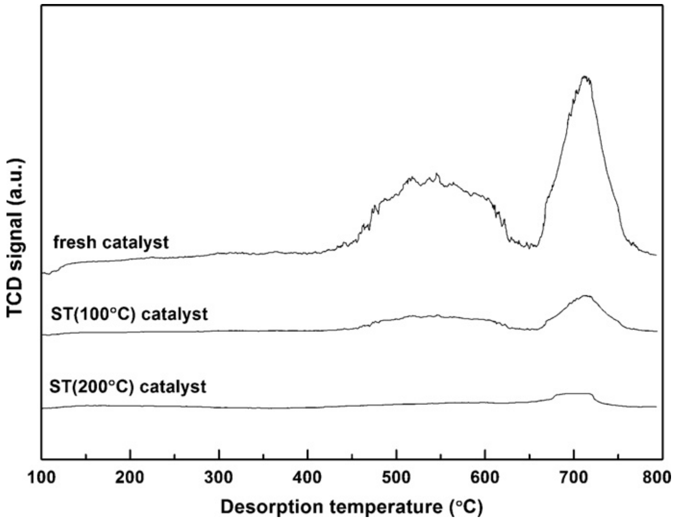


Fig. 7. NO-TPD profiles for various Mn–Ce/TiO_2 samples.

fresh Mn–Ce/TiO_2 catalyst illustrates two distinct peaks. The first broad peak appeared in the range of 450–620 °C might be related to the desorption of variously coordinated nitrite or nitrate species [19,20]. The second strong one centered at 700 °C was due to N_2 desorption. It was caused by the oxygen vacancy on Ti-based catalyst surface, which could attract O atom and lead to the mutual combination of N atoms in NO to form N_2 [21]. In the case of ST(100 °C) catalyst, both of the NO desorption peaks were significantly weakened. It implied that SO_2 seriously inhibited the adsorption of NO on Mn–Ce/TiO_2. When SO_2 pretreatment temperature was up to 200 °C, nearly no desorption peak could be obtained on ST(100 °C) sample's NO-TPD profile, suggesting that SO_2 further decreased the number of base site for NO adsorption with pretreatment temperature arising.

The corresponding DRIFT spectra of fresh and SO_2 poisoned Mn–Ce/TiO_2 samples obtained after exposure to NO + O_2 are shown in Fig. 8. Bands at 1610, 1580, 1548 and 1280 cm^{-1} appeared after NO adsorption on fresh sample (see Fig. 8A). The bands at 1280 and 1580 cm^{-1} were due to nitrate species, while the peak at 1610 cm^{-1} was attributed to adsorbed NO_2 species [22,23]. The peak at 1548 cm^{-1} could also be assigned to NO_2-containing species, like nitrito (O-bound NO_2) and nitrato (NO_3) species [24]. All of these peaks except the one at 1610 cm^{-1} were extinguished on DRIFT spectra of ST(100 °C) catalyst. And the peak at 1610 cm^{-1} became extremely weak and no other peaks due to nitrite or nitrate species could be obtained on DRIFT spectra of ST(200 °C) catalyst. The results of Figs. 7 and 8 suggest that SO_2 has an obviously inhibiting effect on NO adsorption on Mn–Ce/TiO_2 catalyst surface both at 100 and 200 °C.

3.4. Effects of the reaction temperature on SO_2 deactivation of Mn–Ce/TiO_2 catalyst

Based on the results mentioned above, it was found that the different poisoning effects of SO_2 on SCR activity of the Mn–Ce/TiO_2 catalyst at various temperatures (in the range of 100–200 °C) were not directly related to the formation and deposition of $(NH_4)_2SO_3$

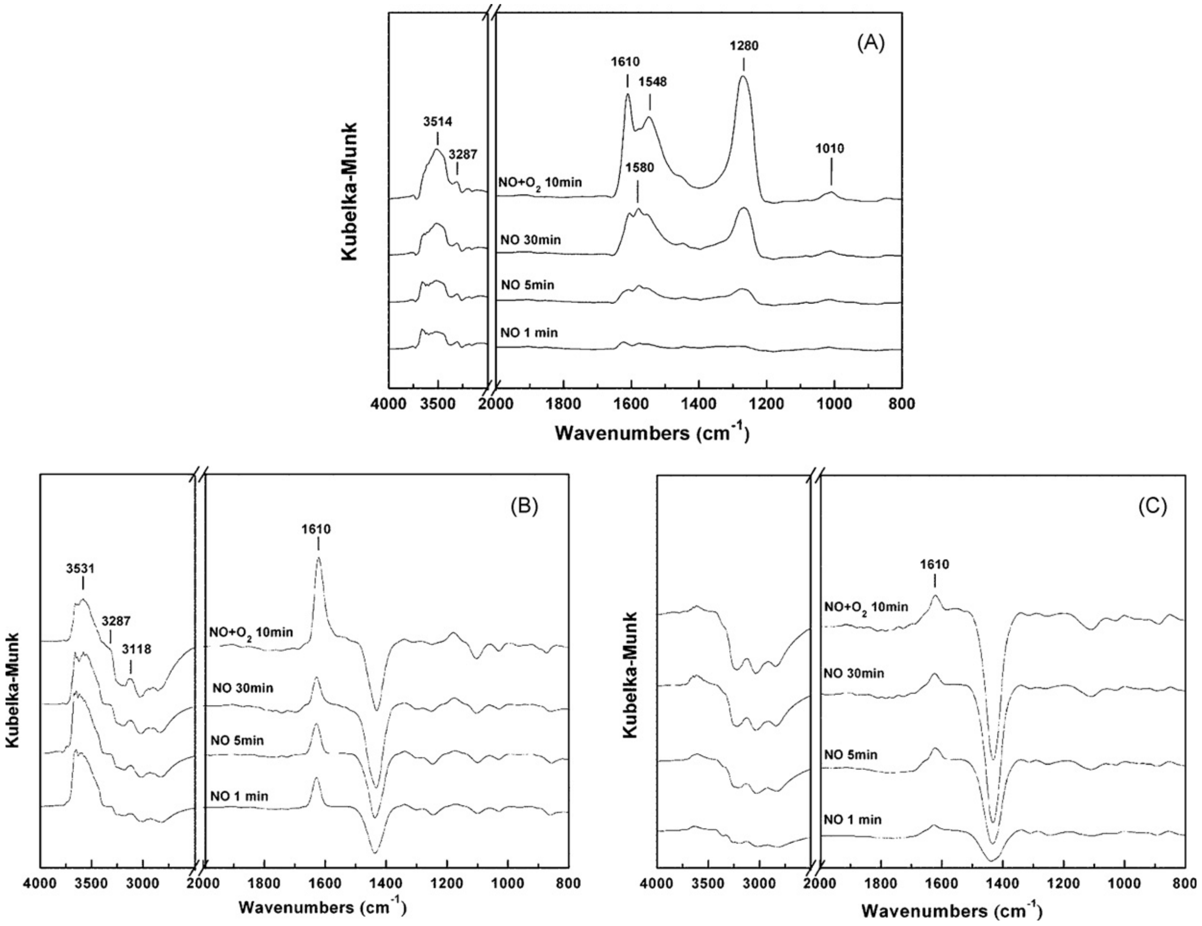
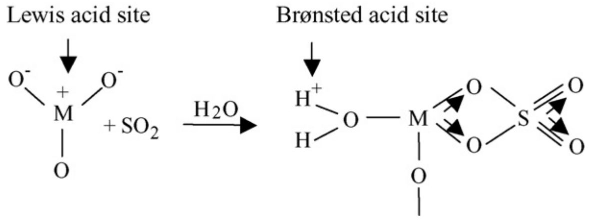


Fig. 8. DRIFT spectra of fresh and SO_2 pretreated Mn–Ce/TiO_2 catalysts exposed to 800 ppm NO in the presence of O_2 for various time at 150 °C. (A) Fresh catalyst; (B) ST(100 °C) catalyst; (C) ST(200 °C) catalyst.



Scheme 1. Poisoning effect of SO_2 on Lewis acid sites in the fresh Mn–Ce/TiO_2 catalyst at 200 °C (M stands for the metal of Mn–Ce–Ti mixed oxides).

and NH_4HSO_4 species, but were most probably caused by the sulfation on the catalyst active sites, which was more complex and directly related to reaction temperature. With the increase of reaction temperature, the sulfation of catalyst active sites plays a more important role in the SO_2 poisoning effects on the catalyst.

When the SCR reaction was carried out at 200 °C, the adsorbed SO_2 on Mn–Ce/TiO_2 surface led to the reduction of initial Lewis acid sites (1168 and 1229 cm^{-1} in Fig. 6) and the enhancement of Brønsted acid sites (1455 cm^{-1} in Fig. 6) as seen in Scheme 1, which was proposed in the literature [25]. Therefore, the adsorption and activation of ammonia on Lewis acid sites on Mn–Ce/TiO_2 surface were severely disrupted. Although the strength of Brønsted acidity of Mn–Ce/TiO_2 catalyst was greatly enhanced after exposed to SO_2 at 200 °C, it has been proved that NH_4^+ adsorbed on Brønsted acid sites was only able to react with adsorbed NO_2 species to carry out SCR reaction according to Long et al.'s reports [26,27]. However, NO adsorption and oxidation on Mn–Ce/TiO_2 were seriously restrained after SO_2 pretreatment at 200 °C according to the results of Fig. 8C. Therefore, the reaction pathway was interdicted and NO conversion of catalyst sharply decreased for SO_2 poisoned Mn–Ce/TiO_2 catalyst at 200 °C.

With the decrease of reaction temperature, the sulfation of active sites was greatly relieved (see Fig. 6B) and the SCR process could still take place to ensure high SCR activity for Mn–Ce/TiO_2 catalyst at 100 °C. However, the formation and deposition of $(NH_4)_2SO_3$ and NH_4HSO_4, which led to restorable deactivation of catalyst could not be completely avoided at 100 °C. Therefore, the NO conversion of Mn–Ce/TiO_2 also decreased gradually at 100 °C, but could be almost completely recovered after regeneration by water-washing.

4. Conclusion

SO_2 has various poisoning effects on SCR activity of the Mn–Ce/TiO_2 catalyst at different temperatures. The NO conversion of the catalyst decreased from nearly 100% to about 60% in 200 min at 200 °C, while it still was above 70% after 500 min when the SCR reaction took place at 100 °C. SO_2 reacted with NH_3 to form $(NH_4)_2SO_3$ and NH_4HSO_4, which deposited on the catalyst surface and did not decompose below 200 °C, but could be washed away easily. Serious sulfation of active sites and loss of Lewis acidity was obtained on Mn–Ce/TiO_2 catalyst when the SCR reaction was carried out at 200 °C. It was the main reason of the irreversible deactivation of catalyst in SCR reaction. The results of this paper give suggestions that the un-recoverable SO_2 deactivation can be greatly retarded if the low-temperature SCR process over Mn–Ce/TiO_2 is operated at about 100 °C.

Acknowledgments

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