An Investigation on the Promoting Effect of Pr Modification on SO₂ Resistance Over MnO_x Catalysts for Selective Reduction of NO with NH₃

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Abstract

Manganese oxides (MnO_x) exhibit excellent low-temperature activities in SCR reaction of NO with NH_3 , and they are considered as a promising catalyst for future application. However, MnO_x still suffer from poor resistance to SO_2 and H_2O . In this work, Pr was used to modify MnO_x catalysts via co-precipitation process, and MnPrO_x catalyst exhibited superior SO_2 resistance over pure MnO_x catalyst. A series of characterization techniques, such as XRD, BET, H_2 -TPR, XPS, TG and in-situ DRIFTS, were adopted to explore the promoting effect of Pr modification on SO_2 resistance over MnO_x catalyst in detail. The results indicated that, in the presence of SO_2 in feed gas, it seemed that PrO_x rather than MnO_x were apt to react with SO_2 , which was favorable to protect Mn active sites on the catalyst surface to some extent. It was known that there was strong competitive adsorption between SO_2 and NH_3/NO species on SCR catalyst surface. In-situ DRIFTS results revealed that the adsorption of NH_3 and NO on MnO_x catalyst had been severely suppressed after the introduction of SO_2 , resulting in the relevant SCR reactions following either L-H or E-R mechanisms would be inhibited obviously. But for Pr-modified MnO_x catalyst, the introduction of SO_2 almost had no effect on the adsorption of NH_3 on catalyst surface, while it exerted a relatively noticeable impact on the adsorption of NO. As a result, SCR reactions occurred on Pr-modified MnO_x catalyst surface could still proceed in a near-normal way through E-R rather than L-H mechanisms. Therefore, Pr modification on MnO_x catalyst exhibited a distinctively promoting effect on SO_2 resistance performance in SCR process.

Highlights

- Pr-modified MnO_x catalyst exhibited superior SO_2 resistance over MnO_x catalyst.
- Pr modification could inhibit the sulfation of Mn active sites on the surface of MnO_x catalyst.
- For Pr-modified MnO_x catalyst, the adsorption of NH_3 on Lewis acid sites was almost not affected by SO_2 , and the inhibition degree of SO_2 for NO adsorption was lower than that of MnO_x catalyst.
- The SCR reaction on Pr-modified MnO_x catalyst might follow E-R mechanism in the presence of SO_2 .

1. Introduction

Nitrogen oxides (NO_x) emitted from high-temperature combustion processes in diesel engines, power stations and industrial heaters are important atmospheric pollutants, which can lead to several environmental problems, for example, acid rain, ozone depletion, photochemical smog and greenhouse effects (Du et al. 2020; Wang et al. 2019; Zhu et al. 2020; Kim et al. 2020). Over the past few decades, selective catalytic reduction (SCR) with NH_3 has become the most effective technology for abating NO_x emissions from mobile and stationary sources (Gong et al. 2020; Ma et al. 2020). Catalysts play a crucial role in controlling the construction cost and creating efficient reactions in SCR systems (Fan et al. 2017). $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ catalysts are often used in power plants due to their excellent catalytic performance in the temperature range of 300-400 °C. However, for some plants with lower temperature flue

gas, flue gas should be reheated by spare heater unit to meet the working temperature of commercial V-based catalysts. Undoubtedly, such heating process would cost more energy for industrial application. Therefore, it is of great significance to develop non-toxic low-temperature SCR catalysts at desired working temperatures. So far, numerous low-temperature catalysts have been developed, including zeolites, transitional metal oxides, and rare-earth metal oxides. Among of them, MnO_x catalysts have attracted increasing attention due to their low-temperature catalytic activities and low cost (Yang et al. 2020; Xie et al. 2020; Lee et al. 2019; Zhang et al. 2019; Liu et al. 2020). Nevertheless, MnO_x catalysts still suffer from some challenging problems, such as narrow operation window, low N_2 selectivity, and poor resistance to H_2O and SO_2 , which restricts their commercial application. Especially, the poor SO_2 and H_2O tolerance of MnO_x catalysts pose the greatest challenge for practical applications (Khan et al. 2020; Kang et al. 2020).

It is well known that there are mainly two causes for the deactivation of MnO_x catalysts at low temperature when SO_2 existed in flue gas. On one hand, NH_3 reductant would react with SO_2 to form ammonium sulfate, further covering the catalyst active sites. On the other hand, Mn active sites would also react with SO_2 to form metal sulfates (Chang et al. 2013; Jin et al. 2014; Gao et al. 2017; Shao et al. 2020; Chen et al. 2021). Some previous works reported that the doping of rare-earth element could improve the SO_2 resistance of Mn-based catalysts. It was found that Gd modification could inhibit the transformation of MnO_2 to Mn_2O_3 and the generation of MnSO_4 , hinder the decrease of Lewis acid sites and the increase of Brønsted acid sites, and alleviate the competitive adsorption between NO and SO_2 (Fan et al. 2018). Similarly, Eu was used to restrain the formation of sulfate species over Mn/ TiO_2 catalyst under SCR conditions (Liu et al. 2018). Zhang et al. reported that Ho modification was beneficial to suppress the competitive adsorption of SO_2 with NH_3 and/or NO on the surface of Mn/ TiO_2 catalyst, thus improving the SO_2 resistance (Zhang et al. 2020). The previous studies demonstrated that the introduction of rare-earth elements is a promising option to enhance the SO_2 resistance of Mn-based catalysts.

Due to incompletely occupied 4f and empty 5d orbitals, rare-earth element praseodymium (Pr) has been widely applied as an additive in various fields (Li et al. 2021; Qi et al. 2020; Yan et al. 2020; Mamidi et al. 2018). As a promoter, Pr has also been used to enhance the catalytic activity, resistance to SO_2 and H_2O of Mn-based catalysts. The introduction of Ce/Pr to $\text{MnO}_x/\text{SAPO-34}$ catalysts had enhanced the SCR performance and SO_2 resistance (Yu et al. 2017). It was reported that the SCR performance and resistance to SO_2 poisoning of Fe-Mn/ TiO_2 catalysts could be improved with the addition of a suitable amount of Pr (Hou et al. 2020). It was reported that $\text{MnO}_x@\text{PrO}_x$ catalysts with a hollow urchin-like core-shell structure exhibited excellent SCR activity and resistance to SO_2 and H_2O (Cheng et al. 2020). Though some researchers have reported that the introduction of Pr could improve SO_2 resistance of Mn-based catalysts, few studies have investigated systematically the promoting effect and reaction mechanism of Pr on SO_2 tolerance over MnO_x catalysts.

In this work, pure MnO_x catalyst and Pr-modified MnO_x catalyst with Pr/Mn molar ratio of 0.1 were synthesized via co-precipitation method, and the SCR test results showed that Pr modification on MnO_x

catalyst had obviously improved the catalytic performance and resistance to SO₂ and H₂O. Based on the prepared catalysts, the promoting effect and reaction mechanism of Pr modification on SO₂ resistance was explored in detail with various characterization techniques, such as XRD, BET, H₂-TRP, XPS, TG and in-situ DRIFTS. And a possible mechanism was also proposed for the excellent SO₂ tolerance of Pr-modified MnO_x catalysts.

2. Experimental

2.1. Catalyst preparation

All reagents were analytical grade and used without further purification. Pr-modified MnO_x catalyst with Pr/Mn molar ratio of 0.1 was prepared using co-precipitation method with Mn(NO₃)₂·4H₂O and Pr(NO₃)₃·6H₂O as precursors. Firstly, 9.036 g Mn(NO₃)₂·4H₂O and 1.566 g Pr(NO₃)₃·6H₂O were dissolved in 50 mL deionized water successively, and stirred at room temperature for 30 min. Then ammonia solution (25 wt.%) was added dropwise to the resultant solution to initiate the co-precipitation reaction until the solution pH reached 10. Next, the solution was continuously stirred for 2 h, followed by aging at room temperature for 3h. Finally, the precipitates were separated by filtrate, dried at 120 °C overnight, and calcined at 450 °C for 3 h in air. For comparison, MnO_x catalyst without Pr modification was also prepared by using the same method without the addition of Pr element. In this work, Pr-modified MnO_x catalyst with Pr/Mn molar ratio 0.1 was designated as MnPrO_x. The MnO_x and MnPrO_x catalysts after SO₂ resistance tests were denoted as MnO_x-S and MnPrO_x-S, respectively.

2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns of the prepared catalysts were obtained by an X-ray diffractometer (Empyrean, PANalytical) with Cu Kα as radiation source in a 2θ range of 5-70° at a scanning step size of 0.02°.

N₂ adsorption-desorption isotherms of the prepared catalysts were tested by a physisorption meter (ASAP 2020 PLUS, Micromeritics). The catalyst samples were degased under vacuum at 200 °C for 3 h before each test. The N₂ adsorption-desorption data were obtained at liquid nitrogen temperature (-196 °C).

H₂-temperature programmed reduction (H₂-TPR) tests were carried out on a chemisorption analyzer (Autochem II 2920, Micromeritics). Before each test, the catalyst samples were pretreated in He stream (50 mL/min) at 200 °C for 1 h, and then cooled down to 50 °C. Finally, the catalyst samples were heated from 50 to 800 °C at a heating rate of 10 °C/min in 10 vol% H₂/Ar stream.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a surface analysis photoelectron spectrometer (AXIS-ULTRA DLD-600W, Shimadzu) using Al Kα as radiation source at 300 W. Binding energy was referred to the C 1s peak at 284.6 eV as standard.

Thermogravimetric (TG) analysis tests were carried out on a thermogravimetric analyzer (TGA-50, Shimadzu) with the heating rate of 10 °C/min from 20 to 1000 °C under N₂ atmosphere.

In-situ DRIFTS measurements were carried out on a FTIR spectrometer (Nicolet iS50, Thermo Fisher Scientific). The DRIFT spectra were recorded by accumulating 64 scans and 4 cm⁻¹ resolution. Before each test, the catalyst samples were pretreated at 350 °C for 30 min under N₂ flow, and then cooled down to target reaction temperature to collect the background.

2.3. Catalyst activity

NH₃-SCR catalytic performance measurements were performed three times for each kind of catalysts, and the averaged values were used to plot the curves. For a typical test, the catalyst sample (1 mL) was filled into a fixed-bed quartz reactor of 6 mm internal diameter. Firstly, the catalyst sample was pretreated at 200 °C for 1 h in N₂ stream, and then cooled down to 60 °C. Then a reactant gas mixture including 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, 100 ppm SO₂ (when used), 10 vol% H₂O (when used) and N₂ as balance gas passed the catalyst sample. The total flow rate of the reaction mixture gas was 500 mL/min, and the gas hourly space velocity (GHSV) was 30,000 h⁻¹. The reaction temperature increased from 60 to 300 °C. The concentrations of mixture gases (NO, NO₂, N₂O, SO₂, NH₃ and H₂O) were recorded continuously by a FTIR spectrometer (Antaris IGS, Thermo Fisher Scientific) equipped with a MCT detector. NO conversion efficiencies of the catalysts were calculated according to the following equation:

$$\text{NO conversion (\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (1)$$

3. Results And Discussion

3.1. NH₃-SCR performance

Fig. 1a shows the activities of MnO_x and MnPrO_x catalysts for NH₃-SCR reaction in the temperature range of 60-300 °C. NO conversion efficiency of pure MnO_x catalyst increased gradually from 60 to 180 °C with the increase of reaction temperature, and it reached ~ 100% at 180 °C. When further increasing reaction temperature from 180 to 300 °C, NO conversion efficiency decreased slowly. The addition of Pr element to MnO_x catalyst led to an obvious enhancement on NO conversion performance. For MnPrO_x catalyst, NO conversion efficiency was ~ 100 % in the temperature window of 120-220 °C. It indicated that Pr modification could greatly improve low-temperature activity and widen operation temperature window of pure MnO_x catalyst.

In practical circumstance, there are a small amount of H₂O and SO₂ in feed gas, which can lead to the deactivation of the catalysts (Lee et al. 2013). Therefore, the tests of H₂O and SO₂ resistance were performed at 200 °C over MnO_x and MnPrO_x catalysts, respectively.

Fig. 1b shows the influence of H₂O on NO conversion performance of MnO_x and MnPrO_x catalysts. After 5 vol% H₂O was introduced into feed gas, NO conversion efficiency of pure MnO_x catalyst decreased quickly down to ~ 60 %, and it remained at ~ 60 % with the increase of reaction time. NO conversion efficiency recovered to ~ 97 % within half an hour after stopping H₂O injection. It suggested that the deactivation of MnO_x catalyst by H₂O poisoning was reversible. However, NO conversion efficiency of MnPrO_x catalyst could be hardly influenced by H₂O during the whole reaction process, showing excellent resistance to H₂O poisoning.

Fig. 1c shows the influence of SO₂ on NO conversion performance of MnO_x and MnPrO_x catalysts. After 100 ppm SO₂ was introduced into feed gas, NO conversion efficiency of pure MnO_x catalyst decreased quickly down to 17.8 % within 1 h, then further decreasing slowly to 2.7 % after 4 h. After shutting off SO₂ gas, there was no sign of recovery in NO conversion efficiency, suggesting that irreversible deactivation occurred over pure MnO_x catalyst. Normally, SO₂ resistance performance of pure MnO_x catalysts was poor, and this result was consistent with some previous studies (Fan et al. 2018, 2020). Compared with pure MnO_x catalyst, MnPrO_x catalyst displayed much better SO₂ resistance performance. A high NO conversion efficiency of 96.2 % was maintained over MnPrO_x catalyst after feeding SO₂ for 2 h. Then it decreased quickly down to 20.5 % after introduction of SO₂ for 4 h, which was still much higher than that of pure MnO_x catalyst. The results indicated that the introduction of Pr element could greatly enhance the SO₂ resistance of pure MnO_x catalyst.

Fig. 1d shows the influence of H₂O and SO₂ simultaneous on NO conversion performance of MnO_x and MnPrO_x catalysts. For pure MnO_x catalyst, the introduction of H₂O accelerated the poisoning effect of SO₂. However, the introduction of H₂O alleviated the poisoning effect of SO₂ over MnPrO_x catalyst. NO conversion efficiency of MnPrO_x catalyst was still 87.6 % after introducing SO₂ for 4h. In addition, after H₂O and SO₂ were shut off, NO conversion efficiency was not changed over pure MnO_x catalyst. However, NO conversion efficiency was recovered to 95.2 % over MnPrO_x catalyst. It was concluded that Pr modification could obviously improve the resistance to SO₂ and H₂O of pure MnO_x catalyst.

The results showed that the introduction of Pr element could greatly improve SO₂ resistance of pure MnO_x catalyst. Therefore, the promoting effect for Pr modification on SO₂ resistance were further analyzed through the following characterizations techniques.

3.2. XRD

Fig. 2 displays the XRD patterns of fresh and deactivated catalysts. Several diffraction peaks attributed to Mn₃O₄ appeared in the XRD spectrum of MnO_x catalyst, indicating the main crystal phase of MnO_x catalyst was Mn₃O₄. After doping Pr element in MnO_x catalyst, there was no obvious diffraction peaks appeared in MnPrO_x catalyst. It suggested that Pr modification promoted the transformation of MnO_x from crystalline to highly dispersed amorphous state, and PrO_x was highly dispersed on the catalyst surface. Compared to fresh catalysts, there was no new peaks appeared in the XRD spectra of deactivated

catalysts. But the intensities of observed peaks decreased, which possibly due to the coverage of sulfate species formed on the catalyst surface, as confirmed by the TG analysis results.

3.3. N₂ adsorption/desorption

Fig. 3 shows N₂ adsorption-desorption isotherms of fresh and deactivated catalysts. The adsorption-desorption isotherms of these catalysts were type IV, implying that the mesoporous structures of the catalysts were not changed after SO₂ resistance tests (Gao et al. 2018). The specific surface areas, pore diameters, and pore volumes of these catalysts were summarized in Table.1. The results showed that the pore diameters of deactivated catalysts became larger, which might be caused by the generated sulfate species partially blocking the pore of the catalysts (Zhang et al. 2020). In addition, the specific surface area of MnO_x catalyst decreased from 14.03 to 11.88 m²/g, and that of MnPrO_x catalyst decreased from 64.76 to 40.76 m²/g after SO₂ resistance tests. Noticeably, MnPrO_x-S catalyst still exhibited a much larger specific surface area than MnO_x-S catalyst. Hence, higher specific surface area might be one reason for superior SO₂ resistance of Pr-modified MnO_x catalyst.

Table. 1. Specific surface areas, pore volumes and pore sizes of fresh and deactivated catalysts.

Catalysts	S _{BET} (m ² /g)	Pore Diameter (nm)	Pore Volume (cm ³ /g)
MnO _x	14.03	27.86	0.10
MnO _x -S	11.88	36.29	0.11
MnPrO _x	64.76	11.30	0.22
MnPrO _x -S	40.76	18.67	0.21

3.4. H₂-TPR

The reduction properties of fresh and deactivated catalysts were researched via H₂-TPR, and the results were shown in Fig. 4. H₂ consumption values and the reduction peak temperatures were listed in Table. 2. There were two reduction peaks in the curves of fresh catalysts. The low-temperature reduction peak could be assigned to the reduction of MnO₂ to Mn₂O₃ and then to Mn₃O₄ (Sun et al. 2017; Liu et al. 2020), while the high-temperature reduction peak could be assigned to the reduction of Mn₃O₄ to MnO (Shu et al. 2019; Niu et al. 2021). The curves of deactivated catalysts displayed similar reduction peaks as that of fresh catalysts. However, the reduction peak temperatures of deactivated catalysts shifted to higher temperature range, suggesting that redox properties of the catalysts decreased after SO₂ resistance tests. It's worth noting that there was a relatively lower temperature of low-temperature reduction peak and higher H₂ consumption value for MnPrO_x-S catalyst compared to MnO_x-S catalyst. It indicated that Pr modification was conducive to keep the redox ability of MnO_x catalyst when SO₂ existed in feed gas. Therefore, higher redox property might be one reason for better SO₂ resistance of Pr-modified MnO_x catalyst.

Table. 2. H₂-TPR results of fresh and deactivated catalysts.

Catalysts	Peak temperature (°C)		H ₂ consumption (cm ³ /g STP)
	Peak 1	Peak 2	
MnO _x	319	449	588.15
MnO _x -S	419	558	611.45
MnPrO _x	304	429	542.35
MnPrO _x -S	402	569	625.65

3.5. XPS

X-ray photoelectron spectra (XPS) were performed to obtain the information about the valence states of active species and atomic concentrations on the catalyst surface. The photoelectron spectra of Mn 2p, O 1s and S 2p were shown in Fig. 5 and the analysis results were shown in Table. 3.

Fig. 5a shows the Mn 2p spectra of fresh and deactivated catalysts. There were two main peaks ascribed to Mn 2p_{3/2} and Mn 2p_{1/2} for these catalysts. The Mn 2p_{3/2} peaks could be fitted into three sub-peaks. The obtained peaks could be attributed to Mn²⁺ (639.7~640.5 eV), Mn³⁺ (641.1~641.4 eV) and Mn⁴⁺ (642.8~643.6 eV), respectively (Meng et al. 2015; Guo et al. 2017). Here Mnⁿ⁺ referred to the sum of Mn²⁺, Mn³⁺ and Mn⁴⁺. As shown in Table. 3, the relative percentages of Mn⁴⁺/Mnⁿ⁺ on deactivated catalysts all decreased comparing with fresh catalysts, which was unfavorable to the low-temperature SCR reaction. In addition, Mn atomic concentration on the surface of MnO_x catalyst decreased by 4.28 %, while that of MnPrO_x catalyst decreased by 3.48 % after SO₂ resistance tests. It demonstrated that Pr modification could obviously inhibit the sulfation of Mn active sites on the catalyst surface, thus improving the SO₂ resistance of MnO_x catalyst.

Fig. 5b shows the O 1s spectra of fresh and deactivated catalysts, which could be split into two peaks. One peak at 528.2~528.6 eV could be assigned to the lattice oxygen species O²⁻ (denoted as O_β) at low binding energy. The other peak at 530.1~530.2 eV could be attributed to the chemisorbed oxygen species at high binding energy (denoted as O_α), including O⁻ (defect-oxide) and OH⁻ (hydroxyl-like group) (Wu et al. 2020; Boningari et al. 2015). As shown in Table. 3, the relative percentages of O_α/(O_α+O_β) on deactivated catalysts were higher than that of fresh catalysts, which might be reason of the existence of hydroxyl-like groups offered by S=O (Tang et al. 2018). The hydroxyl-like groups were favorable to form more acid sites on the catalyst surface and further affecting the SCR reaction process (Tang et al. 2018).

Fig. 5c shows the S 2p spectra of MnO_x-S and MnPrO_x-S catalysts, which could be split into two peaks. The two peaks could be assigned to S⁶⁺ in the form of SO₄²⁻ (168.8 eV) and S⁴⁺ in the form of SO₃²⁻ (167.3 eV), respectively (Sheng et al. 2018; Arfaoui et al. 2018). It suggested that sulfate and sulfite formed on the

catalyst surface after SO₂ resistance tests. As shown in Table. 3, the S content of on the surface of MnPrO_x-S catalyst was 3.48 %, which was slightly more than that of MnO_x-S catalyst (2.58 %), indicating that there was more sulfate species on the surface of MnPrO_x catalyst.

Table. 3. XPS results of fresh and deactivated catalysts.

Catalysts	O	Mn	Pr	S	Area ratio			
					Mn ⁴⁺ /Mn ⁿ⁺	Mn ³⁺ /Mn ⁿ⁺	Mn ²⁺ /Mn ⁿ⁺	O _α /(O _α +O _β)
MnO _x	49.05	28.39	–	–	21.0	33.2	45.8	27.8
MnO _x -S	50.18	21.50	–	2.58	18.9	31.9	49.2	35.6
MnPrO _x	50.18	21.50	4.31	–	24.2	29.8	46.0	35.1
MnPrO _x -S	49.34	18.02	3.80	3.48	23.8	27.9	48.3	44.5

3.6. TG

In order to further distinguish the sulfate species on the surface of deactivated catalysts poisoned by SO₂, thermogravimetric (TG) analysis of MnO_x-S and MnPrO_x-S catalysts were performed, and the TG curves were shown in Fig. 6. In the temperature range from room temperature to 200 °C (stage 1), the weight loss could be attributed to the evaporation of physically absorbed water. In the temperature range of 200-400 °C (stage 2), the weight loss could be ascribed to the decomposition of (NH₄)₂SO₄ or NH₄HSO₄. The weight loss above 400 °C (stage 3) could be assigned to the decomposition of metal sulfates (Tang et al. 2018; Sun et al. 2018). For MnO_x-S catalyst, there was no obvious weight loss in the temperature range of 200-400 °C (stage 2), indicating that no (NH₄)₂SO₄ or NH₄HSO₄ was formed on the surface of MnO_x catalyst. The sharp declines in weight loss at 550 °C and 760 °C were due to the thermal transformation of MnO₂ to Mn₂O₃ and the decomposition of MnSO₄, respectively (Fan et al. 2018). It indicated that the rapid deactivation of pure MnO_x catalyst was due to the formation of MnSO₄, as illustrated in Fig. 1c. For MnPrO_x-S catalyst, the distinct weight loss could be observed in the temperature range of 200-400 °C (stage 2), suggesting that Pr modification could promote the formation of (NH₄)₂SO₄ or NH₄HSO₄ on the catalyst surface. At higher temperature range (above 400°C), compared with MnPrO_x-S catalyst, MnO_x-S catalyst showed more obvious thermal transformation of MnO₂ to Mn₂O₃ and decomposition of MnSO₄. It indicated that Pr modification could inhibit the thermal transformation of MnO₂ to Mn₂O₃ and the generation of MnSO₄ to some extent, thus enhancing the SO₂ resistance of MnO_x catalyst.

3.7. In-situ DRIFTS

In order to further investigate the adsorption behavior and the SCR reaction mechanism in the presence of SO₂ at low temperature, in-situ DRIFTS tests were performed at relatively low temperature (200 °C).

3.7.1. SO₂ + O₂ adsorption on the catalysts

Fig. 7 shows in-situ DRIFT spectra of SO₂ + O₂ adsorption over MnO_x and MnPrO_x catalysts. For a typical test, the catalyst sample was pretreated for 30 min, then 100 ppm SO₂ and 5 vol% O₂ (100 mL/min) were introduced for 30 min, IR spectra were recorded continuously. As shown in Fig. 7a, several bands at 1617, 1550, 1423, 1336, 1273, 1251, 1148 and 1052 cm⁻¹ were observed over MnO_x catalyst. The band at 1617 cm⁻¹ was attributed to adsorbed HSO₄⁻. The band at 1423 cm⁻¹ was assigned to the symmetrical stretching vibration of gaseous SO₂. The bands at 1336, 1273 and 1251 cm⁻¹ were ascribed to the asymmetric stretching vibration of O=S=O (Tang et al. 2020). The band at 1148 cm⁻¹ was correspond to bulk metal sulfate, and the band at 1052 cm⁻¹ was assigned to the S–O stretching vibrations of bidentate sulfates located on the catalyst surface (Gao et al. 2019). As shown in Fig. 7b, several bands at 1641, 1535, 1146 and 1043 cm⁻¹ were observed over MnPrO_x catalyst. The band at 1636 cm⁻¹ was assigned to adsorbed H₂O (Wang et al. 2019). The band at 1146 cm⁻¹ was attributed to bulk metal sulfate, and the band at 1043 cm⁻¹ was ascribed to the S–O stretching vibrations of bidentate sulfates located on the catalyst surface (Gao et al. 2019). Comparing the adsorption spectra of these two catalysts, it could be found that the absorbance intensities of the bands increased with the increase of reaction time. However, fewer sulfate species were observed over MnPrO_x catalyst, indicating that the adsorption capacity of SO₂ on the surface of MnPrO_x catalyst was weaker than that of MnO_x catalyst. Therefore, Pr modification could improve the SO₂ resistance of MnO_x catalyst.

3.7.2. Effect of SO₂ on NH₃ adsorption on the catalysts

Aiming to insight into the effect of SO₂ on NH₃ adsorption on the surface of MnO_x and MnPrO_x catalysts, in-situ DRIFTS measurement of the adsorption of NH₃ + SO₂ at 200 °C were performed. After pretreatment, the catalysts were exposed to 500 ppm NH₃ (100 mL/min) for 30 min, following by the addition of SO₂ for 30 min, and the IR spectra were recorded with the increase of reaction time.

As shown in Fig. 8a, several bands were observed in the spectra of MnO_x catalyst after the adsorption of NH₃ for 30 min. The bands at 1192 and 1603 cm⁻¹ could be assigned to coordinated NH₃ on Lewis acid sites, and the band at 1427 cm⁻¹ could be ascribed to NH₄⁺ species on Brønsted acid sites (Fan et al. 2018). The absorbance intensity of the band (1427 cm⁻¹) attributed to NH₄⁺ species on Brønsted acid sites was enhanced gradually with the introduction of SO₂. In addition, a new band (1678 cm⁻¹) ascribed to NH₄⁺ species on Brønsted acid sites appeared in the spectra of MnO_x catalyst. Zhang et al. also found that SO₂ could facilitate the generation of NH₄⁺ species on Brønsted acid sites (Zhang et al. 2020). However, the band (1192 cm⁻¹) assigned to coordinated NH₃ species on Lewis acid sites disappeared within 1 min after the introduction of SO₂. In the meantime, the bands (1268, 1144 and 1029 cm⁻¹) assigned to sulfate species appeared, and the intensities of these bands also enhanced gradually with the increase of SO₂ injection duration. It suggested that the adsorption of NH₃ on Lewis acid sites was restrained by the

introduction of SO_2 , thus reducing the SCR activity at low temperature. As shown in Fig. 8b, the change in absorbed bands of MnPrO_x catalyst was similar to that of MnO_x catalyst. However, the absorbance intensity of the band (1181 cm^{-1}) assigned to coordinated NH_3 species on Lewis acid sites increased gradually after the introduction of SO_2 . According to the previous study, the adsorbed NH_3 species on Lewis acid sites played a key role in the process of SCR reaction at low temperature (Zuo et al. 2014). The results showed that Pr modification could inhibit the competitive adsorption of SO_2 and NH_3 on Lewis acid sites, which might be an important factor for high SO_2 tolerance of MnPrO_x catalyst.

3.7.3. Effect of SO_2 on $\text{NO} + \text{O}_2$ adsorption on the catalysts

In order to investigate the effect of SO_2 on NO adsorption on the surface of MnO_x and MnPrO_x catalysts. After pretreatment, the catalysts were pre-adsorbed with 500 ppm NO and 5% O_2 for 30 min, then 100 ppm SO_2 was introduced. As shown in Fig. 9a, several bands of adsorbed NO species appeared at 1627, 1545, 1345, and 1266 cm^{-1} in the spectra of MnO_x catalyst after the introduction of $\text{NO} + \text{O}_2$ for 30 min, which could be assigned to adsorbed NO_2 species (1627 cm^{-1}), bidentate nitrate (1545 cm^{-1}), free NO_3^- (1345 cm^{-1}), monodentate nitrate (1266 cm^{-1}), respectively (Fan et al. 2018; Gao et al. 2017). With the introduction of SO_2 , the absorbance intensities of these bands in the spectra of MnO_x catalyst decreased clearly. In addition, several new bands ($1616, 1337, 1274, 1152$ and 1057 cm^{-1}) assigned to sulfate species appeared with the injection of SO_2 , and the absorbance intensities of these bands increased gradually. It indicated that there was obvious competitive adsorption between SO_2 and NO on the surface of MnO_x catalyst. In other words, SO_2 could restrain the adsorption of NO on the catalyst surface, which obviously inhibited the SCR reaction following L-H mechanism on MnO_x catalyst. This might be one important reason for the decline of NO conversion efficiency in the presence of SO_2 (Jin et al. 2014). For MnPrO_x catalyst, the inhibiting effect of SO_2 on NO adsorption on the catalyst surface was similar to that of MnO_x catalyst. It's worth noting that the band (1557 cm^{-1}) attributed to bidentate nitrate was still present after the introduction of SO_2 for 30 min, while this band (1545 cm^{-1}) of MnO_x catalyst disappeared within 5 min. It indicated that the adsorption capacity of MnPrO_x catalyst for NO was slightly stronger than that of MnO_x catalyst in the presence of SO_2 . This might be one reason for better SO_2 resistance of Pr-modified MnO_x catalyst.

3.8. Discussion

In this paper, Pr-modified MnO_x catalyst exhibited superior SO_2 resistance at low temperature over pure MnO_x catalyst. The previous study reported that the deactivation of Mn-based catalysts at low temperature was mainly due to the sulfation of the Mn active sites (Yu et al. 2017). The characterization analysis results demonstrated that PrO_x rather than MnO_x were apt to react with SO_2 , which was favorable to protect Mn active sites on the catalyst surface to some extent, and Pr modification promoted the formation of $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 on the catalyst surface. In-situ DRIFTS results showed that there was strong competitive adsorption between SO_2 and NH_3/NO on the surface of MnO_x catalyst. The adsorption of NH_3

and NO on MnO_x catalyst had been severely suppressed after the introduction of SO_2 , resulting in that the relevant SCR reactions following either L-H or E-R mechanisms would be inhibited obviously. However, for Pr-modified MnO_x catalyst, the introduction of SO_2 almost had no effect on the adsorption of NH_3 on catalyst surface. The competitive adsorption between SO_2 and NO was also observed on the surface of Pr-modified MnO_x catalyst, while the degree of inhibition for NO adsorption was lower than that of MnO_x catalyst. Therefore, only the SCR reaction through L-H mechanism was suppressed. As a result, SCR reaction could still proceed in a near-normal way through E-R mechanism on Pr-modified MnO_x catalyst. In the end, the promoting effect and reaction mechanism of Pr modification on SO_2 resistance for NH_3 -SCR reaction over MnO_x catalyst were proposed, which was shown in Fig. 10.

4. Conclusions

In this work, the promoting effect and reaction mechanism of Pr modification on SO_2 resistance over MnO_x catalyst were investigated systematically. The results showed that Pr modification on MnO_x catalyst could effectively improve SO_2 tolerance at low temperature. After 100 ppm SO_2 was introduced into feed gas, NO conversion efficiency of pure MnO_x catalyst decreased quickly down to $\sim 20\%$ within 1 h. However, NO conversion efficiency of MnPrO_x catalyst decreased down to $\sim 20\%$ after the introduction of SO_2 for 4 h. The characterization analysis results showed that the deactivation of pure MnO_x catalyst was mainly due to the sulfation of the Mn active sites. After Pr modification on MnO_x catalyst, it seemed that PrO_x rather than MnO_x were apt to react with SO_2 , which was favorable to protect the Mn active sites on catalyst surface to some extent. In-situ DRIFTS results revealed that there was strong competitive adsorption between SO_2 and NH_3/NO on the surface of MnO_x catalyst. Therefore, the SCR reactions following E-R or L-H mechanisms were both inhibited obviously. However, for Pr-modified MnO_x catalyst, the adsorption of NH_3 was almost not affected by SO_2 , and the inhibition degree of SO_2 for NO adsorption was lower than that of MnO_x catalyst. The SCR reaction on Pr-modified MnO_x catalyst might still proceed in a near-normal way E-R mechanism in the presence of SO_2 . Therefore, Pr-modified MnO_x catalyst exhibited superior SO_2 resistance over MnO_x catalyst.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Authors' contributions

ZTH and GPZ designed the experiment, GPZ performed the experiment, analyzed and processed the data. HD and YG also assisted in the experiment. The first draft of the manuscript was written by GPZ. ZTH and XXP reviewed and revised the manuscript. All authors read and approved the final manuscript.

Availability of data and materials

Not applicable

Competing interests

The authors declare that they have no competing interest.

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Figures

Figure 1

NH₃-SCR performance of MnO_x and MnPrO_x catalysts: (a) NO Conversion, (b) H₂O resistance, (c) SO₂ resistance, and (d) SO₂ and H₂O resistance tests (Reaction condition: 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, 100 ppm SO₂ (when used), and 10 vol% H₂O (when used), balanced with N₂, GHSV = 30,000 h⁻¹).

Figure 2

XRD patterns of (a) MnOx, (b) MnOx-S, (c) MnPrOx and (d) MnPrOx-S catalysts.

Figure 3

Nitrogen adsorption and desorption isotherms of fresh and deactivated catalysts.

Figure 4

H₂-TPR curves of fresh and deactivated catalysts.

Figure 5

(a) Mn 2p, (b) O 1s and (c) S 2p spectra of fresh and deactivated catalysts.

Figure 6

TG curves of $\text{MnO}_x\text{-S}$ and $\text{MnPrO}_x\text{-S}$ catalysts.

Figure 7

In-situ DRIFT spectra of (a) MnO_x and (b) MnPrO_x catalysts exposed to 100 ppm SO₂ + 5 vol% O₂ at 200 °C.

Figure 8

In-situ DRIFT spectra of (a) MnOx and (b) MnPrOx catalysts exposed to 500 ppm NH₃ followed by the addition of 100 ppm SO₂ at 200 °C.

Figure 9

In-situ DRIFT spectra of (a) MnOx and (b) MnPrOx catalysts exposed to 500 ppm NO + 5 vol% O₂ followed by the addition of 100 ppm SO₂ at 200 °C.

Figure 10

The promoting effect and reaction mechanism of Pr modification on SO₂ resistance over MnO_x catalyst.