An investigation on the promoting effect of Pr modification on SO₂ resistance over MnOₓ catalysts for selective reduction of NO with NH₃

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Abstract
Pr-modified MnOₓ catalyst was synthesized through a facile co-precipitation process, and the results showed that MnPrOₓ catalyst exhibited much better selective catalytic reduction (SCR) activity and SO₂ resistance performance than pristine MnOₓ catalyst. The addition of Pr in MnOₓ catalyst led to a complete NO conversion efficiency in 120–220 °C. Moreover, Pr-modified MnOₓ catalyst exhibited a superior resistance to H₂O and SO₂ compared with MnOₓ catalyst. After exposing to SO₂ and H₂O for 4 h, the NO conversion efficiency of MnPrOₓ catalyst could remain to 87.6%. The characterization techniques of XRD, BET, hydrogen-temperature programmed reduction (H₂-TPR), ammonia-temperature programmed desorption (NH₃-TPD), XPS, TG and in situ diffuse reflectance infrared spectroscopy (DRIFTS) were adopted to further explore the promoting effect of Pr doping in MnOₓ catalyst on SO₂ resistance performance. The results showed that MnPrOₓ catalyst had larger specific surface area, stronger reducibility, and more L acid sites compared with MnOₓ catalyst. The relative percentage of Mn⁴⁺/Mn³⁺ on the MnPrOₓ-S catalyst surface was also much higher than those of MnOₓ catalyst. Importantly, when SO₂ exists in feed gas, PrOₓ species in MnPrOₓ catalyst would preferentially react with SO₂, thus protecting the Mn active sites. In addition, the introduction of Pr might promote the reaction between SO₂ and NH₃ rather than between SO₂ and Mn active sites, which was also conducive to protect the Mn active sites to a great extent. Since the presence of SO₂ in feed gas had little effect on NH₃ adsorption on the MnPrOₓ catalyst surface, and the inhibiting effect of SO₂ on NO adsorption was alleviated, SCR reactions could still proceed in a near-normal way through the Eley-Rideal (E-R) mechanism on Pr-modified MnOₓ catalyst, while SCR reactions through the Langmuir-Hinshelwood (L-H) mechanism were suppressed slightly.

Keywords Selective catalyst reduction · MnOₓ catalysts · Pr modification · SO₂ resistance

Introduction
Nitrogen oxides (NOₓ) emitted from high-temperature combustion processes in diesel engines, power stations, and industrial heaters are one of the main atmospheric pollutants, which can cause several environmental problems, such as acid rain, ozone depletion, photochemical smog, and greenhouse effects (Du et al. 2020; Wang et al. 2019b). Over the past few decades, selective catalytic reduction (SCR) with NH₃ as reductant has become the most effective technology for abating NOₓ emission from mobile and stationary sources (Gong et al. 2020; Ma et al. 2020). Generally, catalysts play a crucial role in controlling the construction cost and creating efficient reactions in SCR systems (Fan et al. 2017). V₂O₅-WO₃(MoO₃)/TiO₂ 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 a 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.

Up to date, a great effort has been devoted to develop low-temperature catalysts. Especially, transition metal oxide catalysts exhibit outstanding catalytic activities, which are of great potential for industrial application. Among them, MnOx catalysts have attracted increasing attention due to their low-temperature catalytic activities and low cost (Lee and Bai 2019; Liu et al. 2020; Xie et al. 2020; Yang et al. 2020; Zhang et al. 2019). Nevertheless, MnOx catalysts still suffer from some challenging problems, such as narrow operation window, low N2 selectivity, and poor resistance to H2O and SO2, which restricts their commercial application to a great extent. Up to date, it still requires a great of research to improve the SO2 tolerance of Mn-based catalysts (Khan et al. 2020; Kang et al. 2020).

Generally, there are mainly two causes for the deactivation of MnOx catalysts at low temperature when SO2 exists in flue gas. On one hand, NH3 reductant would react with SO2 to form ammonium sulfate, which would cover catalyst active sites. On the other hand, Mn active sites would also directly react with SO2 to form metal sulfates (Chang et al. 2013; Chen et al. 2021; Gao et al. 2017b; Jin et al. 2014; Shao et al. 2020). Previous works reported that doping of rare-earth element could improve the SO2 resistance of Mn-based catalysts. Nd modification on Mn/TiO2 catalyst could inhibit the sulfation of Mn active species through a preferential reaction between SO2 and NdOx (Chen et al. 2018). The introduction of Ce could also inhibit the accumulation of ammonium sulfates over Mn/TiO2 catalyst in SCR reactions (Wang et al. 2020). Zhang et al. reported that Ho modification was beneficial to suppress the competitive adsorption of SO2 and NH3/NO on the surface of Mn/TiO2 catalyst, thus improving SO2 resistance (Zhang et al. 2020). The above-mentioned studies indicate that the introduction of rare-earth elements is an effective way to enhance the SO2 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; Mamidi et al. 2018; Qi and Wang 2020; Yan et al. 2020). According to the theory of ionic polarization, SO2 is more liable to react with PrOx rather than MnOx, making PrOx acting as a sacrifice additive to protect Mn active sites. In view of this, some research work has been done to introduce Pr in Mn-based catalysts for enhancing SCR activity, SO2 and H2O tolerance. The previous work demonstrated that the addition of Ce and Pr in MnOx/SAPO-34 catalysts could obviously enhance the SCR performance and SO2 resistance (Yu et al. 2017). The addition of a suitable amount of Pr in Fe–Mn/TiO2 catalysts also could improve the SCR performance and SO2 resistance (Hou et al. 2020). MnOx@PrOx catalysts with a hollow urchin-like core-shell structure had been synthesized, which exhibited excellent SCR activity and resistance to SO2 and H2O (Cheng et al. 2020). Pr-modified MnOx catalysts were also prepared through co-precipitation method, and the effect of Pr doping amount on SCR activity at low temperature was also explored in detail (Zhai et al. 2021). However, to the best of our knowledge, it still lacks some systematic research focusing on the enhancement effect and relevant reaction mechanism of Pr modification on MnOx catalysts on SO2 tolerance.

In this work, pristine MnOx catalyst and Pr-modified MnOx catalyst with Pr/Mn molar ratio of 0.1 were synthesized via co-precipitation method, and the SCR activity test results showed that the introduction of Pr in MnOx catalyst had distinctively improved the resistance to SO2 and H2O. A series of characterization techniques, including XRD, BET, H2-TPR, NH3-TPD, XPS, TG and in situ DRIFTS, had been adopted to explore the promoting effect of Pr modification on SO2 tolerance, together with the corresponding reaction mechanism in depth. A possible reaction mechanism was also proposed to explain the reaction pathways for Pr-modified MnOx catalysts with superior SO2 tolerance.

**Experimental**

**Catalyst preparation**

All reagents were analytical grade and used without further purification. Pr-modified MnOx catalyst with Pr/Mn molar ratio of 0.1 was prepared using co-precipitation method. Firstly, 9.036 g Mn(NO3)2·4H2O and 1.566 g Pr(NO3)3·6H2O were dissolved in 50 mL deionized water at 450 °C for 3 h in air. Here, the obtained Pr-modified MnOx catalyst was designated as MnPrOx. For comparison, MnOx catalyst with no Pr modification was also prepared by using the same method without the addition of Pr precursor. The MnOx and MnPrOx catalysts that suffered from SO2 resistance tests were denoted as MnOx-S and MnPrOx-S, respectively. MnPrOx catalyst subjected to SO2 and H2O resistance test was denoted as MnPrOx-SH.
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 sample was degassed 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 sample was pretreated in He stream (50 mL/min) at 200 °C for 1 h and then cooled down to 50 °C. Finally, the sample was heated from 50 to 800 °C at a heating rate of 10 °C/min in 10 vol.% H₂/Ar stream.

NH₃-temperature programmed desorption (NH₃-TPD) experiments were conducted using a chemisorption analyzer (Autochem II 2920, Micromeritics) with a U-tube quartz reactor. Prior to each test, the sample was pretreated at 200 °C for 1 h in He stream (50 mL/min), cooled down to 100 °C, and then saturated with NH₃ for 30 min. Next, the sample was flushed at 100 °C for 2 h in pure He stream (50 mL/min) to remove physically absorbed NH₃. Finally, the TPD profile was collected by heating the sample from 100 to 400 °C with a ramping rate of 10 °C/min in He stream (50 mL/min).

X-ray photoelectron spectroscopy (XPS) measurements were performed on a surface analysis photoelectron spectrometer (AXIS-ULTRA DLD-600 W, Shimadzu) using Al Kα as radiation source at 300 W. Binging 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 in N₂ atmosphere.

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

Catalyst activity

For NH₃-SCR activity test, 1 mL of catalyst sample was filled into a fixed-bed quartz reactor (ID 6 mm). Firstly, the catalyst sample was pretreated at 200 °C for 1 h in N₂ stream and then cooled down to 60 °C. Then, a gas mixture including 500 ppm NO, 500 ppm NH₃, 5 vol.% O₂, 100 ppm SO₂ (when used), 5 vol.% H₂O (when used), and N₂ as balance gas was fed into the reactor with a total flow rate of 500 mL/min. The corresponding gas hourly space velocity (GHSV) was 30,000 h⁻¹. The reaction temperature increased from 60 to 300 °C. The concentrations of NO, NO₂, N₂O, NH₃ and H₂O, were monitored continuously by a FTIR spectrometer (Antaris IGS, Thermo Fisher Scientific) equipped with a MCT detector. NO conversion efficiency was calculated according to the following equation:

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

Results and discussion

NH₃-SCR performance

Fig. 1a illustrated the NH₃-SCR activities of MnOₓ and MnPrOₓ catalysts in the temperature range of 60–300 °C. It could be observed that NO conversion efficiency of pristine MnOₓ catalyst increased gradually from 60 to 180 °C with the rising of reaction temperature, and it reached ~100% at 180 °C. But when further increasing reaction temperature from 180 to 300 °C, NO conversion efficiency decreased slowly. By contrast, the addition of Pr element in MnOₓ catalyst led to an obvious enhancement on NO conversion performance. NO conversion efficiency of MnPrOₓ catalyst could maintain at ~100% in the temperature range of 120–220 °C. This result demonstrated that Pr modification on MnOₓ catalyst was helpful to greatly improve low-temperature activity and widen operation temperature window.

In practice, a certain amount of H₂O and SO₂ always exist in flue gas, which may lead to the deactivation of SCR catalysts (Lee et al. 2013). In this regard, it was crucial to perform H₂O and SO₂ resistance tests with the prepared catalysts.

As shown in Fig. 1b, with the introduction of 5 vol.% H₂O in feed gas at 200 °C, NO conversion efficiency of pristine MnOₓ catalyst decreased quickly down to ~60% and then remained stable when further increasing the reaction duration. But when stopping H₂O injection, NO conversion rate would recover to ~97% within half an hour. It suggested that the deactivation of MnOₓ catalyst by water vapor was reversible. It was interesting that, during the whole reaction process, the injection of H₂O imposed little effect on NO conversion efficiency of MnPrOₓ catalyst, indicating that Pr modification on MnOₓ catalyst could enhance H₂O resistance significantly.

The results of SO₂ resistance tests were presented in Fig. 1c. As 100 ppm SO₂ was introduced in feed gas at
200 °C, NO conversion efficiency of pristine MnO\textsubscript{x} catalyst decreased quickly down to 17.8% within 1 h, then further decreasing slowly to 2.7% after extra 4 h. In addition, there was no sign of recovery in NO conversion efficiency after shutting off SO\textsubscript{2} gas, suggesting that the deactivation of MnO\textsubscript{x} catalyst by SO\textsubscript{2} poisoning was irreversible. Generally, SO\textsubscript{2} resistance performance of pristine MnO\textsubscript{x} catalysts is a little poor, and our result is consistent with the previous studies (Fan et al. 2018, 2020). But it could be seen that, MnPrO\textsubscript{x} catalyst displayed much better SO\textsubscript{2} resistance performance than MnO\textsubscript{x} catalyst. NO conversion efficiency of MnPrO\textsubscript{x} catalyst just decreased down to 96.2% even after exposing to SO\textsubscript{2} for 2 h. When further subjecting to SO\textsubscript{2} for another 4 h, it decreased quickly down to 20.5%. This result indicated that the introduction of Pr in MnO\textsubscript{x} catalyst was beneficial to enhance the SO\textsubscript{2} tolerance.

The influences of coexisting H\textsubscript{2}O and SO\textsubscript{2} in feed gas on NO conversion performance of MnO\textsubscript{x} and MnPrO\textsubscript{x} catalysts were investigated at 200 °C, and the results were shown in Fig. 1d. It was clear that the coexistence of H\textsubscript{2}O and SO\textsubscript{2} in feed gas would worsen the deactivation of pristine MnO\textsubscript{x} catalyst. However, Pr-modified MnO\textsubscript{x} catalyst exhibited an outstanding resistance to H\textsubscript{2}O and SO\textsubscript{2}, and the possible reason had been analyzed in the following Sect. 3.8. After exposing to H\textsubscript{2}O and SO\textsubscript{2} for 4 h, NO conversion efficiency of MnPrO\textsubscript{x} catalyst just decreased down to 87.6%. Furthermore, NO conversion efficiency of MnPrO\textsubscript{x} catalyst could recover to 95.2% when stopping the injection of H\textsubscript{2}O and SO\textsubscript{2}. The result demonstrated that Pr modification on MnO\textsubscript{x} catalyst could also improve the resistance to SO\textsubscript{2} and H\textsubscript{2}O obviously.

According to the above-mentioned results, one might conclude that Pr modification on MnO\textsubscript{x} catalyst could promote the SCR activity and SO\textsubscript{2}/H\textsubscript{2}O resistance. Considered that it was relatively difficult to reveal the promotional effect of Pr doping in MnO\textsubscript{x} catalyst on H\textsubscript{2}O resistance, the subsequent work mainly focused on the exploration of the influence of Pr modification on SO\textsubscript{2} resistance.

**XRD**

Fig. 2 displayed the XRD patterns of fresh and SO\textsubscript{2}-deactivated catalysts. It could be observed that several diffraction peaks attributed to Mn\textsubscript{3}O\textsubscript{4} clearly appeared in the XRD spectrum of fresh MnO\textsubscript{x} catalyst, indicating that Mn\textsubscript{3}O\textsubscript{4} was the main crystalline phase in MnO\textsubscript{x} catalyst. As to MnO\textsubscript{x}-S catalyst, the characteristic peaks corresponding
to the crystalline phase of Mn$_3$O$_4$ could also be observed, but the peak intensities decreased largely. On one hand, a certain amount of ammonium sulfates would be formed unavoidably due to the reactions between NH$_3$ and SO$_2$ at 200 °C, which would deposit on the surface of MnO$_x$-S catalyst. On the other hand, a portion of manganese oxides at the surface might be sulphated to MnSO$_4$ in SO$_2$ resistance test. The reason for the decrease in diffraction peak intensities could be further confirmed by the following TG analysis results.

As to MnPrO$_x$ and MnPrO$_x$-S catalysts, almost no obvious diffraction peaks appeared in the corresponding XRD patterns. It was possible that the introduction of Pr imposed a great impact on the crystalline phase species of MnO$_x$ in the preparation process and resulted in fine nanocrystalline MnO$_x$.

**N$_2$ adsorption/desorption**

Fig. 3 showed N$_2$ adsorption–desorption isotherms of fresh and SO$_2$-deactivated catalysts. It could be seen that all the adsorption–desorption isotherms of these catalysts belonged to type IV, implying that SO$_2$ resistance tests had not changed the mesoporous structures of the catalysts (Gao et al. 2018). Fig. S1 illustrated the curves of pore diameter distribution of fresh and SO$_2$-deactivated catalysts. It could be seen that the centralised pore diameter of MnO$_x$ catalyst shifted from 52.88 to 54.53 nm due to SO$_2$ resistance test. As for MnPrO$_x$ catalyst, it shifted from 21.62 to 22.92 nm.

The specific surface areas, pore diameters, and pore volumes of these catalysts were summarized in Table 1. Obviously, the averaged pore diameter of SO$_2$-deactivated catalyst was much larger than the corresponding fresh catalyst. It was ascribed to the sulfate species generated in SO$_2$ resistance test, which would partially block the fine mesopores of the catalysts (Zhang et al. 2020). The specific surface area of MnO$_x$-S catalyst decreased down to 11.88 m$^2$/g compared with MnO$_x$ catalyst (14.03 m$^2$/g). As for MnPrO$_x$ catalyst, it decreased greatly from 64.76 to 40.76 m$^2$/g before and after SO$_2$ resistance test. Since the specific surface area of MnPrO$_x$ catalyst was much higher than that for MnO$_x$ catalyst, it seemed normal that the specific surface area of MnPrO$_x$-S catalyst was still much higher than that for MnO$_x$-S catalyst. The high specific surface area was considered as a significant cause for superior SO$_2$ resistance of MnPrO$_x$ catalyst.

**H$_2$-TPR**

The redox properties of fresh and SO$_2$-deactivated catalysts were investigated via H$_2$-TPR, and the results were shown in Fig. 4. H$_2$ consumption values and the reduction peak temperatures were listed in Table 2. It could be seen that there were three reduction peaks in the curves of MnO$_x$ and MnPrO$_x$ catalysts. The first reduction peak could be ascribed to the reduction of MnO$_2$ to Mn$_2$O$_3$, the second peak ascribed to the reduction of Mn$_2$O$_3$ to Mn$_3$O$_4$, and
the third peak ascribed to the reduction of Mn₃O₄ to MnO (Guo et al. 2017). As to MnOₓ-S catalyst, only two reduction peaks were observed in the curve. The first reduction peak could be assigned to the reduction of MnO₂ to Mn₂O₃ and then to Mn₃O₄ (Liu et al. 2020a; Sun et al. 2017), while the second reduction peak could be assigned to the reduction of Mn₃O₄ to MnO (Shu et al. 2019; Niu et al. 2021). But for MnPrOₓ-S catalyst, there were still three reduction peaks in the curve, among which two reduction peak locations approached those of MnOₓ-S catalyst. But the third reduction peak appeared at ~630 °C could be assigned to the reduction of Pr₂O₃ to Pr₃O₄ (Cheng et al. 2020). Compared with the fresh catalysts, the reduction peak temperatures of corresponding SO₂-deactivated catalysts had shifted to higher temperature zone, suggesting the decrease in redox properties of SO₂-deactivated catalysts. However, compared with MnOₓ-S catalyst, MnPrOₓ-S catalyst still possessed a higher H₂ consumption value, and its low-temperature reduction peak appeared at a relatively lower temperature. It indicated that Pr modification on MnOₙ catalyst was conducive to maintain its redox ability in the presence of SO₂ in feed gas. In view of this, the high redox ability might be another reason for MnPrOₙ catalyst with excellent SO₂ resistance.

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 presented in Fig. 5, and the analysis results were shown in Table S2.

Fig. 5a showed the Mn 2p spectra of fresh and SO₂-deactivated catalysts. There were two main peaks ascribed to Mn 2p₃/2 and Mn 2p₁/2 for these catalysts. The Mn 2p₃/2 peaks could be further split into three sub-peaks, which could be attributed to Mn²⁺ (639.7 ~ 640.5 eV), Mn³⁺ (641.1 ~ 641.4 eV), and Mn⁴⁺ (642.8 ~ 643.6 eV), respectively (Guo et al. 2017; Meng et al. 2015). Here, Mnⁿ⁺ was denoted as the sum of Mn²⁺, Mn³⁺, and Mn⁴⁺. As shown in Table S2, compared with fresh catalysts, the relative percentages of Mn⁴⁺/Mnⁿ⁺+ on the surface of the corresponding SO₂-deactivated catalysts decreased slightly. Note that the relative percentage of Mn⁴⁺/Mnⁿ⁺+ on the MnPrOₓ-S catalyst surface was much higher than those of MnOₓ and MnOₓ-S catalysts. Generally, it was considered that a relatively high Mn⁴⁺ proportion played a key role in enhancing the SCR activity at low temperature. This result demonstrated that Pr modification was in favor of maintaining a high level of Mn⁴⁺ proportion in Mn-based catalysts, thus improving the SCR performance and SO₂ resistance. In addition, Mn atomic concentration on the surface of MnPrOₓ catalyst was 21.50% which was obviously lower than that of MnPrOₓ-S catalyst (28.39%). Though the introduction of Pr would result in the decrease of Mn atomic concentration on the surface of MnPrOₓ catalyst, the SCR performance had been improved greatly. It seemed that Pr modification rather than Mn atomic concentration in MnPrOₓ catalyst was the key factor for improving SCR activity.

Fig. 5b showed the O 1s spectra of fresh and SO₂-deactivated catalysts. Each O 1s spectrum 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 Oₐ) 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 Oₐ oxidation (denoted as Oₐ), including O₁⁻ (defect-oxide) and OH⁻ (hydroxyl-like group) (Boningari et al. 2015; Wu et al. 2020). As shown in Table S2, the SO₂ resistance tests resulted in an increase of Oₐ/(Oₐ + Oₐ) ratio, and the Oₐ/(Oₐ + Oₐ) ratio of MnPrOₓ-S catalysts was much higher than the other catalysts. The increase in Oₐ/(Oₐ + Oₐ) ratio might be ascribed to the existence of hydroxyl-like groups offered by S = O (Tang et al. 2018). Since the hydroxyl-like groups were in favor of forming more acid sites on the catalyst surface, it might impose a positive impact on the SCR activity of MnPrOₓ catalyst.

Table 2 H₂-TPR results of fresh and SO₂-deactivated catalysts

| Catalysts  | Peak temperature (°C) | H₂ consumption (cm³/g STP) |
|------------|------------------------|-----------------------------|
|            | Peak 1  | Peak 2  | Peak 3  | Peak 1  | Peak 2  | Peak 3  |
| MnOₓ       | 319    | 449    | 520    | 588.15  |
| MnOₓ-S     | 419    | 558    | –      | 611.45  |
| MnPrOₓ     | 304    | 429    | 476    | 542.35  |
| MnPrOₓ-S   | 402    | 569    | 630    | 625.65  |

References

- Guo et al. 2017
- Meng et al. 2015
- Shu et al. 2019
- Niu et al. 2021
- Liu et al. 2020a
- Sun et al. 2017
- Cheng et al. 2020
- Boningari et al. 2015
- Wu et al. 2020
- Tang et al. 2018
Fig. 5c showed the S 2p spectra of MnO$_x$-S and MnPrO$_x$-S catalysts. Each S 2p spectrum could be split into two peaks, which could be assigned to SO$_4^{2−}$ (168.8 eV) and HSO$_4^{−}$ (167.3 eV), respectively (Arfaoui et al. 2018; Sheng et al. 2018). The results indicated that sulfate species had been formed on the surface of MnO$_x$-S and MnPrO$_x$-S catalysts in SO$_2$ resistance tests, possibly as ammonium or Mn salts. As shown in Table S2, S atomic ratio of MnPrO$_x$-S catalyst was 3.48%, which was much higher than that of MnO$_x$-S catalyst (2.58%), indicating that more sulfate species had been formed or deposited on the surface of MnPrO$_x$-S catalyst compared with MnO$_x$-S catalyst. It implied that the enhancement effect of Pr modification on SCR performance might result from the sacrifice reaction between PrO$_x$ and SO$_2$, rather than inhibiting the formation or deposition of sulfate species on the catalyst surface.

**TG**

In order to further distinguish the sulfate species on the surface of SO$_2$-deactivated catalysts, thermogravimetric (TG) analysis of MnO$_x$-S and MnPrO$_x$-S catalysts was performed, and the TG-DTG curves were shown in Fig. S3. The weight loss in a temperature range of room temperature to 200 °C (step 1) could be attributed to the evaporation of physically absorbed water. The weight loss in a temperature range of 200–400 °C (step 2) could be ascribed to the decomposition of (NH$_4$)$_2$SO$_4$ or NH$_4$HSO$_4$. The weight loss in a temperature range of 400–700 °C (step 3) could be related to the phase transformation of metal oxides. The weight loss at >700 °C (step 4) could be assigned to the decomposition of metal sulfates (Sun et al. 2018; Tang et al. 2018).

It could be seen from Fig. S3(a) that, for MnO$_x$-S catalyst, there was no obvious weight loss in the temperature range of 200–400 °C (step 2), indicating that little (NH$_4$)$_2$SO$_4$ or NH$_4$HSO$_4$ could be found on the surface of MnO$_x$-S catalyst. The sharp declines in weight loss at 560 °C and 795 °C could be ascribed to the thermal transformation of MnO$_2$ to Mn$_2$O$_3$ and the decomposition of MnSO$_4$, respectively (Fan et al. 2018). In view of the above-mentioned XPS result, one could infer that the sulfate species on the surface of MnO$_x$-S catalyst might be metal sulfates. It indicated that the rapid deactivation of pristine MnO$_x$ catalyst was possibly due to the sulfation of Mn active sites.

As shown in Fig. S3(b), a weight loss of 0.916% in MnPrO$_x$-S catalyst could be observed in step 2, indicating that the introduction of Pr in MnO$_x$ catalyst would promote the formation of (NH$_4$)$_2$SO$_4$ or NH$_4$HSO$_4$ on the catalyst surface. The sharp declines in weight loss at 540 °C and 630 °C could be ascribed to the thermal transformation of MnO$_2$ to Mn$_2$O$_3$ and PrO$_2$ to Pr$_2$O$_3$, respectively (Fan et al. 2017). At high temperature above 700 °C, the weight loss owing to the
decomposition of manganese sulfates on MnPrOₓ-S catalyst surface was only 1.153%, which was much less than that for MnOₓ-S catalyst (3.394%). Namely, much less manganese sulfates had been formed on the MnPrOₓ-S catalyst surface compared with MnOₓ-S. Here, the sharp decline in weight loss at 910 °C could be ascribed to the decomposition of praseodymium sulfates (Yu et al. 2017). The above results suggested that, when SO₂ exists in feed gas, PrOₓ species in MnPrOₓ catalyst would preferentially react with SO₂, thus protecting Mn active sites. On the other hand, the introduction of Pr might promote the reaction between SO₂ and NH₃ rather than between SO₂ and Mn active sites, which was also conductive to protect Mn active sites to a great extent.

In situ DRIFTS

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

SO₂ + O₂ adsorption on the catalysts

Fig. 6 showed in situ DRIFT spectra of SO₂ + O₂ adsorption over MnOₓ and MnPrOₓ catalysts. For each test, the catalyst sample was pretreated by N₂ purging for 30 min, then 100 ppm SO₂ and 5 vol.% O₂ were introduced with a flow rate of 100 mL/min for 30 min, and IR spectra were recorded continuously.

As shown in Fig. 6a, with the introduction of SO₂ in feed gas, several bands at 1617, 1550, 1423, 1336, 1273, 1251, 1148 and 1052 cm⁻¹ appeared clearly in the IR spectrum of MnOₓ catalyst. The band at 1617 cm⁻¹ could be attributed to the adsorbed HSO₄⁻, while the band at 1423 cm⁻¹ could be assigned to the symmetrical stretching vibration of the adsorbed SO₂. The bands at 1336, 1273 and 1251 cm⁻¹ were assigned to the asymmetric stretching vibration of O=S=O (Tang et al. 2020). The band at 1148 cm⁻¹ was attributed 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). With the increase of SO₂ + O₂ exposure duration, most of the band intensities increased slightly. This result demonstrated that the presence of SO₂ had quickly led to the formation of sulfates on the MnOₓ catalyst surface, namely the sulfation of Mn active species, resulting in the instant deactivation of MnOₓ catalyst.

As shown in Fig. 6b, with the introduction of SO₂ in feed gas, several bands at 1641, 1535, 1146 and 1043 cm⁻¹ appeared obviously in the IR spectrum of MnPrOₓ catalyst. The band at 1636 cm⁻¹ could be assigned to the adsorbed H₂O (Wang et al. 2019a). The band at 1146 cm⁻¹ could be attributed to bulk metal sulfate, and the band at 1043 cm⁻¹ could be ascribed to the S–O stretching vibrations of bidentate sulfates located on the catalyst surface (Gao et al. 2019). Similarly, the band intensities increased obviously with the rising of SO₂ + O₂ exposure time. Since the band intensities corresponding to sulfates on the MnPrOₓ catalyst surface were much higher than those on the MnOₓ catalyst surface within the same SO₂ + O₂ exposure time, it indicated that much more metal sulfates had been formed on the MnPrOₓ catalyst surface. This result agreed well with the above-mentioned XPS and TG-DTG analysis results. It demonstrated that PrOₓ rather than MnOₓ was apt to react with SO₂ and PrOₓ acted as a sacrifice additive to protect Mn active species effectively. It was considered as the major cause for the enhancement effect of Pr modification on SO₂ resistance.

Effect of SO₂ on NH₃ adsorption on the catalysts

In situ DRIFTS experiments were conducted to investigate the effect of SO₂ on NH₃ adsorption on the surface of MnOₓ.
and MnPrO\textsubscript{x} catalysts. After pretreatment with N\textsubscript{2} purging for 30 min, each catalyst sample was exposed to 500 ppm NH\textsubscript{3} (100 mL/min) for 30 min, followed by introducing 100 ppm SO\textsubscript{2} in NH\textsubscript{3}/N\textsubscript{2} mixed gas for 30 min, and the IR spectrum was recorded with the increase of reaction time.

As shown in Fig. 7a, after NH\textsubscript{3} adsorption for 30 min, a saturated adsorption of NH\textsubscript{3} on MnO\textsubscript{x} catalyst surface would be reached, and several bands could be observed in the spectrum. The bands at 1192 and 1603 cm\textsuperscript{-1} could be assigned to coordinated NH\textsubscript{3} on Lewis acid sites. The band at 1427 cm\textsuperscript{-1} could be ascribed to NH\textsubscript{4}\textsuperscript{+} species on Brønsted acid sites (Fan et al. 2018). Note that, before the introduction of SO\textsubscript{2} in the feed gas, a new band (1678 cm\textsuperscript{-1}) assigned to coordinated NH\textsubscript{3} species on Lewis acid sites disappeared within 1 min. It suggested that NH\textsubscript{3} adsorbed on Lewis acid sites had been consumed completely due to the reactions between SO\textsubscript{2} and activated NH\textsubscript{3} species. Meanwhile, the bands (1268, 1144 and 1029 cm\textsuperscript{-1}) assigned to sulfate species appeared, and their intensities increased gradually with the rising of SO\textsubscript{2} injection duration. It implied that more and more SO\textsubscript{2} had been reacted with NH\textsubscript{3} and Mn active species to generate sulfates on the catalyst surface, thus resulting in the deactivation of MnO\textsubscript{x} catalyst.

Fig. 7b showed the change in absorbance bands of MnPrO\textsubscript{x} catalyst with SO\textsubscript{2} exposure duration. It could be seen that, after saturated adsorption of NH\textsubscript{3} for 30 min, several bands could also be observed in the spectrum of MnPrO\textsubscript{x} catalyst. The bands at 1181 and 1607 cm\textsuperscript{-1} might be assigned to coordinated NH\textsubscript{3} on Lewis acid sites. The bands at 1270 and 1421 cm\textsuperscript{-1} might be ascribed to NH\textsubscript{4}\textsuperscript{+} species on Brønsted acid sites. Similar to MnO\textsubscript{x} catalyst, NH\textsubscript{3} coordinated on Lewis acid sites and NH\textsubscript{4}\textsuperscript{+} species on Brønsted acid sites existed at a relatively low level on the MnPrO\textsubscript{x} catalyst surface before the introduction of SO\textsubscript{2} in NH\textsubscript{3}/N\textsubscript{2} mixed gas. With the increase of SO\textsubscript{2} exposure duration, the absorbance intensities of the bands (1181 and 1607 cm\textsuperscript{-1}) assigned to coordinated NH\textsubscript{3} species on Lewis acid sites increased gradually. Previous study reported that adsorbed NH\textsubscript{3} species on Lewis acid sites would play a key role in SCR reactions at low temperature (Zuo et al. 2014). The increase in band intensities of adsorbed NH\textsubscript{3} species on Lewis acid sites would impose a positive effect on SO\textsubscript{2} tolerance and SCR activity. Meanwhile, the new bands (1036 and 1122 cm\textsuperscript{-1}) assigned to metal sulfates had also appeared, and their intensities increased gradually with the rising of SO\textsubscript{2} injection duration. Obviously, the band intensities corresponding to sulfates on the MnPrO\textsubscript{x} catalyst surface were much higher than those on the MnO\textsubscript{x} catalyst surface; it implied that much more metal sulfates had been formed on the MnPrO\textsubscript{x} catalyst surface. It suggested that PrO\textsubscript{x} was apt to react with SO\textsubscript{2} in the presence of NH\textsubscript{3}, resulting in the formation of Pr sulfates rather than Mn sulfates. Thus, Pr worked well as a sacrificial additive to protect Mn active sites.
Effect of SO2 on NO + O2 adsorption on the catalysts

In situ DRIFTS experiments were performed to investigate the effect of SO2 on NO adsorption on the surface of MnOx and MnPrOx catalysts. Firstly, the catalyst was pretreated with 500 ppm NO and 5 vol.% O2 for 30 min, and then 100 ppm SO2 was introduced in the (NO + O2)/N2 mixed gas.

As shown in Fig. 8a, after the introduction of NO + O2 for 30 min, several bands (1627, 1545, 1345 and 1266 cm\(^{-1}\)) corresponding to the adsorbed NO species appeared in the spectrum of MnOx catalyst. These bands could be assigned to adsorbed NO2 species (1627 cm\(^{-1}\)), bidentate nitrate (1545 cm\(^{-1}\)), free NO3\(^-\) (1345 cm\(^{-1}\)), monodentate nitrate (1266 cm\(^{-1}\)), respectively (Fan et al. 2018; Gao et al. 2017a). It could be seen that, with the introduction of SO2, the absorbance intensities of these bands began to decrease quickly. Meanwhile, several new bands (1616, 1337, 1274, 1152 and 1057 cm\(^{-1}\)) assigned to sulfate species appeared after the injection of SO2 in feed gas, and their absorbance intensities increased gradually. It indicated that there was obvious competitive adsorption of SO2 and NO on the MnOx catalyst surface. In other words, SO2 would restrain NO adsorption on the catalyst surface, further inhibiting the SCR reactions occurred on MnOx catalyst via the L-H mechanism. Langmuir-Hinshelwood (L-H) mechanism: NO is adsorbed on the active site adjacent to the active site of the adsorbed NH3, and the transition intermediate state is generated through the reaction, and then decomposed into N2 and H2O. This might be the direct reason for the fast decline in NO conversion efficiency when MnOx catalyst was exposed to SO2 (Jin et al. 2014).

As shown in Fig. 8b, the inhibiting effect of SO2 on NO adsorption on the MnPrOx catalyst surface was similar to that for MnOx catalyst. But it was worth noting that the band (1545 cm\(^{-1}\)) attributed to bidentate nitrate on the MnOx catalyst surface disappeared just after exposing to SO2 for 5 min. By contrast, the corresponding band (1557 cm\(^{-1}\)) for MnPrOx catalyst could also be seen even after the injection of SO2 for 30 min. It suggested that the addition of Pr in MnOx catalyst could restrain the comparative adsorption of SO2 and NO on the catalyst surface, which was undoubtedly beneficial to maintain SCR reactions occurring through the L-H mechanism. This was a vital factor influencing the SCR activity and SO2 resistance performance of Pr-modified MnOx catalyst.

Discussion

The promoting effect of Pr modification on SO2 and H2O resistance

As shown in Table S2, S and N atomic ratios of MnPrOx-SH catalyst were 3.13% and 8.07%, respectively, which were a little lower than those of MnPrOx-S catalyst (3.48% and 8.35%). It implied that less sulfate species had been formed on the MnPrOx-SH catalyst surface compared with MnPrOx-S catalyst. As shown in Fig. S3, the weight loss in MnPrOx-SH catalyst in step 2 was 1.264%, which was obviously more than that for MnPrOx-S catalyst (0.916%). Here, it was considered that, in the presence of H2O and SO2 in feed gas, it might be comparatively easier for PrOx species in MnPrOx catalyst to promote the reaction between the adsorbed SO2/H2O and NH3 species. Thus, the introduction of Pr in MnOx catalyst could preferably protect Mn active species when H2O and SO2 coexisted in feed gas, resulting in an excellent resistance to H2O and SO2. At high temperature above 700 °C, the weight loss in MnPrOx-SH catalyst due to the decomposition of manganese sulfates was 1.045%, which was slightly less than that for MnPrOx-S catalyst (1.153%). It implied that, to some extent, the coexistence of H2O and SO2 in feed gas might be beneficial to decrease the consumption...
of PrO$_x$ species which acted as a sacrifice material to react with the adsorbed SO$_2$. In other words, PrO$_x$ in MnPrO$_x$ catalyst might suppress SO$_2$ adsorption on the catalyst surface in the presence of H$_2$O, resulting in forming less sulfate species and consuming less PrO$_x$, thus further enhancing the SCR performance of MnPrO$_x$ catalyst.

**The possible SCR reaction mechanism**

In this work, Pr-modified MnO$_x$ catalyst exhibited a superior SO$_2$ resistance over pristine MnO$_x$ catalyst. According to TG and in situ DRIFTS analysis results, it suggested that the presence of SO$_2$ would quickly lead to the sulfation of Mn active species, resulting in a fast deactivation of MnO$_x$ catalyst. However, Pr modification on MnO$_x$ catalyst would promote the reaction between SO$_2$ and NH$_3$ species rather than between SO$_2$ and Mn active sites. Besides, PrO$_x$ additive might preferentially react with SO$_2$ when SO$_2$ was injected in feed gas, thus protecting Mn active sites. For MnO$_x$ catalyst, there was strong competitive adsorption between SO$_2$ and NH$_3$/NO on the catalyst surface. Since the adsorption of NH$_3$ and NO on MnO$_x$ catalyst would be severely suppressed in the presence of SO$_2$, the relevant SCR reactions following either L-H or E-R mechanisms would be inhibited obviously. Eley-Rideal(E-R) mechanism: Gaseous NO reacts with adsorbed activated NH$_3$ to form a transitional intermediate state, which is further decomposed into N$_2$ and H$_2$O. But for Pr-modified MnO$_x$ catalyst, the presence of SO$_2$ in feed gas had little effect on NH$_3$ adsorption on the catalyst surface. In addition, the inhibiting effect of SO$_2$ on NO adsorption on MnPrO$_x$ catalyst was not so severe as the case for MnO$_x$ catalyst though competitive adsorption between SO$_2$ and NO could also be observed on the surface of Pr-modified MnO$_x$ catalyst. To the end, SCR reactions could still proceed in a near-normal way through the E-R mechanism on Pr-modified MnO$_x$ catalyst, while the SCR reactions through the L-H mechanism might be suppressed slightly. According to the above-mentioned discussion, the promoting effect of Pr modification on MnO$_x$ catalyst on SO$_2$ resistance and the possible reaction mechanism for NH$_3$-SCR of NO might be illustrated in Fig. 9.

**Conclusions**

In this work, the promoting effect and reaction mechanism of Pr modification on SO$_2$ resistance over MnO$_x$ catalyst had been investigated systematically. The results showed that MnPrO$_x$ catalyst exhibited much better SCR activity and resistance to H$_2$O and SO$_2$ than pristine MnO$_x$ catalyst. A nearly complete NO conversion efficiency of MnPrO$_x$ catalyst could be obtained in the temperature range of 120–220 °C. In the presence of H$_2$O, NO conversion efficiency of MnPrO$_x$ catalyst could maintain at ~100% at 200 °C. As to pristine MnO$_x$ catalyst, NO conversion efficiency decreased quickly down to ~20% after exposing to 100 ppm SO$_2$ for 1 h. But for Pr-modified MnO$_x$ catalyst, NO conversion efficiency just decreased down to 90.8% after exposing to SO$_2$ for 2.5 h. The characterization results showed that, compared with MnO$_x$ and MnO$_x$-S catalysts, MnPrO$_x$ catalyst exhibited much larger specific surface area, stronger reducibility, and more L acid sites, which was beneficial to improve the SCR performance. XPS analysis results showed that, compared with MnO$_x$ and MnO$_x$-S catalyst, MnPrO$_x$ catalyst also had higher Mn$_{4+}$/Mn$_{3+}$ ratio on the MnPrO$_x$-S catalyst surface, which could improve the SCR activity. XPS analysis results showed that the relative percentage of Mn$_{4+}$/Mn$_{3+}$ on the MnPrO$_x$-S catalyst surface was much higher than those of MnO$_x$ and MnO$_x$-S catalysts. It demonstrated that Pr modification was in favor of maintaining a high level of Mn$_{4+}$ proportion in Mn-based catalysts, thus improving the SCR performance and SO$_2$ resistance. TG analysis results showed that the rapid deactivation of pristine MnO$_x$ catalyst was possibly due to the sulfation of Mn active sites. But for
MnPrO\textsubscript{x} catalyst, Pr\textsubscript{y} species would preferentially react with SO\textsubscript{2} in the presence of SO\textsubscript{2} in feed gas, thus protecting the Mn active sites. In addition, the introduction of Pr might promote the reaction between SO\textsubscript{2} and NH\textsubscript{3} rather than between SO\textsubscript{2} and Mn active sites, which was also conducive to protect the Mn active sites to a great extent. In situ DRIFTS results confirmed that the presence of SO\textsubscript{2} had quickly led to the sulfation of Mn active species. As to MnPrO\textsubscript{x} catalyst, Pr\textsubscript{y} rather than Mn\textsubscript{x} was apt to react with SO\textsubscript{2}, thus acting as a sacrifice additive to protect Mn active species effectively. Since the adsorption of NH\textsubscript{3} and NO on MnO\textsubscript{x} catalyst would be severely suppressed in the presence of SO\textsubscript{2}, the relevant SCR reactions following either L-H or E-R mechanisms would be inhibited obviously. But for Pr-modified MnO\textsubscript{x} catalyst, the inhibiting effect of SO\textsubscript{2} on NO adsorption was not so severe as the case for MnO\textsubscript{x} catalyst. More importantly, the presence of NH\textsubscript{3} and NO on MnO\textsubscript{x} catalyst would be slightly. As to MnPrO\textsubscript{x} catalyst, the E-R mechanism on Pr-modified SCR reactions could still proceed in a near-normal way through Mn active sites to a great extent. In situ DRIFTS results confirmed Mn active species, which was also conductive to protect the Mn active species. Since the adsorption of NH\textsubscript{3} in the presence of SO\textsubscript{2}, the relevant SCR reactions following either L-H or E-R mechanisms would be inhibited obviously. But for Pr-modified MnO\textsubscript{x} catalyst, the inhibiting effect of SO\textsubscript{2} on NO adsorption was not so severe as the case for MnO\textsubscript{x} catalyst. More importantly, the presence of NH\textsubscript{3} and NO on MnO\textsubscript{x} catalyst, while SCR reactions through the L-H mechanism might be suppressed slightly.

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**Author contribution ZH:** Design experiments, revise manuscript. GZ: Conduct experiments, process data, write manuscript. HD: Analyze data. YG: Draw pictures. XP: Revise manuscript.

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