RESEARCH ARTICLE

Denitrification performance and sulfur resistance mechanism of Sm–Mn catalyst for low temperature NH₃-SCR

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Abstract MnO_r and Sm-Mn catalysts were prepared with the coprecipitation method, and they showed excellent activities and sulfur resistances for the selective catalytic reduction of NO_x by NH₃ between 50 and 300 °C in the presence of excess oxygen. 0.10Sm-Mn catalyst indicated better catalytic activity and sulfur resistance. Additionally, the Sm doping led to multi-aspect impacts on the phases, morphology structures, gas adsorption, reactions process, and specific surface areas. Therefore, it significantly enhances the NO conversion, N₂ selectivity, and sulfur resistance. Based on various experimental characterization results, the reaction mechanism of catalysts and the effect of SO2 on the reaction process about the catalysts were extensively explored. For 0.10Sm–Mn catalyst, manganese sulfate and sulfur ammonium cannot be generated broadly under the influence of SO₂ and the amount of surface adsorbed oxygen. The Bronsted acid sites strengthen significantly due to the addition of SO_2 , enhancing the sulfur resistance of the 0.10Sm–Mn catalyst.

Keywords MnO_x , Sm–Mn, catalyst, NH₃-SCR, sulfur resistance

1 Introduction

Nitrogen oxides (NO_x) can have a malign effect on human health and the ecological environment. The selective catalytic reduction with NH₃ (NH₃-SCR) has been considered the most appropriate method to

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mitigating and solving the pollution from NO_r, whereas the SCR catalyst is the key factor [1-4]. Many studies have demonstrated that MnO, has good low-temperature SCR catalytic activity. However, the physical and chemical properties of various manganese oxides differ. Therefore, the denitrification performances are also different [5–9]. It is worth emphasizing that Mn-based catalysts modified by element doping have excellent low temperature catalytic activity, and the NO conversion can even achieve 100% [10–12]. Despite the distinctive low temperature denitrification activity, Mn-based catalysts are vulnerable to SO₂ poisoning, and the substantial challenge is the main obstacle for industrial application [13]. There are two primary reasons for catalyst inactivation. On one hand, SO₂ can efficiently react with NH₃ to generate sulfur ammonium salts. These sulfur ammonium salts do not decompose under the active temperature window of MnO_x (below 200 °C) and deposit on the surface of the MnO_x catalyst, covering the active site of the catalyst and deactivating the catalyst. On the other hand, SO_2 will acidify the active component of the MnO_x catalyst and generate manganese sulfate, reducing the active component [13-15].

Recently, several researchers have concentrated on augmenting the sulfur resistance of manganese oxide catalysts. Additionally, there are four ways to enhance the sulfur resistance of Mn-based catalysts. Firstly, modify manganese oxide with other elements. The modifier protects the active component from sulfuration by preferentially adsorbing SO₂ [16,17]. Secondly, create multi-shell catalysts. The unique structure will improve the interaction between manganese oxide and auxiliaries, preventing sulfate formation [18]. Thirdly, alter the preparation method. By trying new methods, the structure and physical as well as chemical properties of the catalyst

are changed, improving the sulfur resistance [19]. Fourthly, modify the catalyst carrier to weaken the impact of SO_2 [20]. Although some accomplishments have been achieved in the sulfur resistance of Mn-based catalysts, the current research results still cannot meet the requirements of sulfur resistance at low temperatures. Among the above four ways to enhance sulfur resistance, elemental doping is currently the focus of research because of relatively simple, easy to operate, low cost, and high feasibility. As for various system catalysts of element doping, the Sm-Mn system catalyst indicates good low temperature denitrification performance with low activation temperature and a broad range of active temperatures. The introduction of Sm can obviously improve both water and SO₂ resistances over Sm-Mn catalyst [21-24]. However, in most research, only preparation factors (including Sm content, support, calcination temperature, and precipitant) and denitrification performances under the presence of SO₂ are explored for Sm-Mn catalyst, lacking a deep study of the SO₂ resistance mechanism. Therefore, several characterizations should be conducted to explain the SO₂ resistance mechanism of Sm-Mn catalyst in depth.

In this study, MnO_x and Sm-Mn catalysts were prepared with the coprecipitation method for the SCR of NO_x by NH_3 between 50 and 300 °C in the presence of excess oxygen. Meanwhile, using the pure MnO_x catalyst as the reference object, SCR activity, physicochemical properties of catalysts, and SCR reaction process in the sulfur-containing atmosphere were explored to further study the SO₂ resistance of MnO_x and Sm-Mn catalyst.

2 Experimental

2.1 Preparation of catalysts

Sm-Mn catalysts were prepared by the coprecipitation method. Sm(NO₃)₃·6H₂O and MnSO₄·H₂O mixed solutions were called A solution, and 0.2 mol·L⁻¹ Na₂CO₃ precipitant solution was called B solution. A and B solutions were added into an empty beaker with a separating funnel for mixing with pH = 9, and the mixture was stirred all the time when the B solution was dropped into the A solution. Following stirring for 24 h, the sample was filtrated and rinsed, and the obtained sample was dried at 110 °C for 12 h in an oven. Lastly, the sample was calcined at 450 °C for 4 h in a muffle furnace to obtain the Sm-Mn catalyst. During the precipitation process, Sm³⁺ and Mn²⁺ ions could be precipitated together by adding the precipitant (Na₂CO₃), forming the sediment mixture. During the calcining process, the sediment mixture could be thermally decomposed, and the interaction between Sm and Mn atoms might also occur, leading to forming an Sm-Mn catalyst. The

preparation of the MnO_x catalyst was like that of the Sm–Mn catalyst. $MnSO_4$ and 0.2 mol·L⁻¹ precipitant solutions were precipitated to obtain the MnO_x catalyst. The mol rates of Sm/Mn are 0, 0.05, 0.10, 0.15, and 0.20, and the catalysts are known as MnO_x , 0.05Sm–Mn, 0.10Sm–Mn, 0.15Sm–Mn, and 0.20Sm–Mn, respectively.

2.2 Experimental characterization

2.2.1 Denitrification performance of the catalyst

Denitrification performance tests of the catalysts were conducted in a fixed reaction bed designed by our research group. The denitrification activity experimental device mainly contains three parts: gas distribution system, reaction system, and gas analysis system. The simulated flue gas comprises 720 ppm NO, 800 ppm NH₃ and 3 vol % O_2 with N_2 balanced. The gas hourly space velocity was approximately 30000 h⁻¹. During the experiment, equilibrium gas N₂ was first introduced to exhaust the air in the reactor; subsequently, NO was introduced under the condition of N₂, and the maximum value of NO (named as [NO]_{in}) on the flue gas analyzer was recorded. Next, NH₃ and O₂ were introduced, and the catalytic reaction began. Following this, the reaction temperature is adjusted by the gradient. Furthermore, when the NO concentration indicator was stable at the corresponding temperature, the NO concentration value at the corresponding temperature (named as [NO]_{out}) was recorded. The conversion of NO was calculated as $([NO]_{in} - [NO_x]_{out})/[NO]_{in} \times 100\%$ and the N₂ selectivity was calculated as $\{1 - 2[N_2O]_{out}/([NO]_{in} - [NO_x]_{out})\} \times$ 100%, where $[NO_x] = [NO_2] + [NO]$. Our previous studies show the test details [25-28].

2.2.2 Sulfur resistance test

The sulfur resistance of the catalyst was still examined on the activity test equipment. Firstly, NO was added to the system when the material was steady and recorded. Secondly, the reaction bed temperature was increased to 160 °C, and the reaction conditions are the same as denitrification. Finally, after the NO indicator was stable for some time, 100 ppm SO₂ was injected into the system. Meanwhile, the change of catalyst denitration rate with time was obtained under the condition of SO₂.

2.2.3 Various characterizations

The phase composition of the catalyst was analyzed by Xray diffraction (XRD) with an X-ray diffractometer (Model Burker-D8 Advance). By comparing the changes in diffraction patterns of different catalysts, the influence of phase composition on the activity and sulfur resistance of catalysts were analyzed. The particular test conditions are as follows. The voltage is 40 kV, the target is Cu (K α ray), and the 2θ range is 5°–70°.

Morphologies of the catalysts were conducted by field emission scanning electron microscopy (FE-SEM). JEQL JSM-7100F FE-SEM was used to ascertain the micromorphology.

Specific surface area, pore volume, and pore size of the catalysts in this experiment were analyzed by Micromeritics ASAP 3020 specific surface area analyzer. Before the test, a 0.3–0.5 g catalyst sample was obtained and pretreated at 350 °C for 5 h in a vacuum to eliminate adsorbed impurities. Following the pretreatment, the adsorption and desorption of N₂ on the catalyst samples were estimated at –196 °C. The BET (Brunauer–Emmett–Teller) multimolecular adsorption model and Barrett–Joniner–Halenda model were used to calculate the specific surface area and pore size distribution.

Thermogravimetric (TG) analysis of the experiment was performed on a discovery thermogravimetric analyzer. Approximately 25 mg catalyst sample was placed in a clean crucible and tested in a platinum disk of the instrument. The temperature was increased from room temperature to 1000 °C at a rate of 10 °C·min⁻¹ in a nitrogen atmosphere to achieve the thermo-weight loss curve of the catalyst mass with the change of temperature.

The valence states and distribution of surface elements were estimated with X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, USA, Al K α radiation). According to the previous studies, results were corrected according to the C 1s peak (284.8 eV as the correction peak) [29,30].

Both temperature-programmed desorption (TPD) and temperature-programmed reduction (TPR) were conducted on the automated catalyst characterization apparatus (Chemisorb 2720, Micromeritics, USA) with a thermal conductivity detector. Before TPD experiments, the samples (0.03 g) were pretreated at 300 °C in a flow of pure He for 1 h, followed by NH₃/He adsorption at 110 °C for 1 h. Finally, the temperature was increased to 500 °C in flowing He at a rate of 10 °C ·min⁻¹. For hydrogen TPR (H₂-TPR), the samples were reduced by increasing the temperature from 50 to 800 °C at 10 °C ·min⁻¹.

In situ diffuse reflectance infrared transform spectroscopy analysis (DRIFTS) could trace and analyze the adsorption state of gas on catalyst surface, which could be used to explore the mechanism of gas-solid catalytic reaction. The Nicolet 6700 INFRARED spectrometer (Thermo Fisher) was used in this experiment. During the test, the wave number and scanning frequency were set as 4 cm⁻¹, and 64, respectively. Firstly, the high-purity N₂ was pumped into the sample tank to purge the sample surface until the scanning pattern no longer changed. The impurities adsorbed on the sample surface were basically cleared. The scanning pattern at this time was used as the back and bottom. Secondly, following the reaction sequence, other gases were introduced into the sample pool. The infrared spectra of the sample surface were continuously scanned to record the changes in the adsorption states of the gas on the catalyst surfaces. By exploring the changes of adsorbed species, the reaction mechanism of the catalyst on the surface was investigated.

3 Results and discussion

3.1 Performances of catalysts with different Sm content

The impacts of various Sm contents on NO conversion, N₂ selectivity, and sulfur resistance are presented in Fig. 1. SCR performances are conducted between 50 and 300 °C in excess oxygen. NO conversion promptly increased with the temperature and reached over 93% at 160 °C for 0.10Sm-Mn catalyst. The activity of Sm-Mn decreased obviously when the introduced amount of Sm exceeded 0.15. It could be described by the fact that the redox activity at low temperature was inhabited by more Sm addition. Figure 1(a) also presents the catalytic activation declined in the following sequence: 0.10Sm–Mn > 0.15Sm-Mn > 0.05Sm-Mn > MnO_x > 0.20Sm-Mn. The presence of SO₂ has a substantial toxic effect on MnO_{r} , where the NO conversion decreases from 78% to 38% within 8 h, decreasing by 40%. MnO_x catalyst shows the properties of particularly poor N2 selectivity and sulfur resistance. The doping of Sm can augment the significant improvement of the NO conversion, N₂ selectivity, and sulfur resistance, and the peculiar discovery is in agreement with the previous study [31,32].

3.2 XRD of catalysts before and after SO₂ poisoning

Catalysts are investigated by XRD to study the change of phase composition of MnO_x and 0.10Sm-Mn catalysts after being poisoned by SO₂ in Fig. 2. The fragile intensity of peaks suggests that most of the active ingredients are amorphous, which is quite beneficial for the catalyst to acquire the excellent SCR activities [33]. Before and after SO₂ poisoning, only the crystal diffraction peaks of MnO₂ (PDF#72-1982), Mn₂O₃ (PDF#41-1442), and Mn_3O_4 (PDF#16-0350) are detected in the MnO_x catalyst. While only SmO (PDF#33-1146) crystal diffraction peak is detected in the 0.10Sm-Mn catalyst. Before and after poisoning, XRD patterns of MnO_r and 0.10Sm–Mn catalysts do not change significantly, and no ammonium salts, sulfates, and sulfites are generated, demonstrating that the sulfate and ammonium salt are less or in an amorphous form.

3.3 Thermal stability of catalysts before and after SO_2 poisoning

Sulfur ammonium salts and manganese sulfate



Fig. 1 Performances of catalysts with different Sm content: (a) SCR activity; (b) N₂ selectivity; (c) sulfur resistance at 160 °C.



Fig. 2 XRD patterns of catalysts: (a) MnO_x before poisoning; (b) MnO_x after poisoning; (c) 0.10Sm–Mn before poisoning; (d) 0.10Sm–Mn after poisoning.

decompose at specific temperatures. Therefore, thermal analysis of MnO_x and 0.10Sm-Mn catalysts before and after poisoning is conducted to further determine whether the catalyst surface would generate sulfur ammonium salts and manganese sulfate after being poisoned by SO₂. According to the TG-DTG (derivative thermogravimetry) curves in Fig. 3, the weight loss of MnO_x sample before poisoning is primarily categorized into the following four stages: sample removal of adsorbed water and bound water (< 200 °C), decomposition of residual carbonate (approximately 541 °C), conversion of MnO_2 and Mn_2O_3

(approximately 585 °C), and conversion of Mn_2O_3 and Mn_3O_4 (approximately 730 °C). For the MnO_x after poisoning, new weight loss peaks appear at approximately 420, 646, and 800 °C. Among them, the peaks at approximately 420 and 800 °C are assigned to the decomposition of ammonium bisulfate and manganese sulfate, respectively [5,34]. According to Fig. 3, there is only 0.66 wt % weight loss of ammonium bisulfate and 2.64 wt % weight loss of manganese sulfate. As for the new peak near 646 °C, Sun et al. [31] discovered the same phenomenon in the SO₂ poisoning inactivation

study of MnO₂/TiO₂, which the phase transition of manganese oxide may cause. The TG of 0.10Sm-Mn samples before poisoning can be divided into the following three stages: the weight loss process of water (< 300 °C), decomposition of residual carbonate as well as the transformation of $MnO_2 \rightarrow Mn_2O_3$ (440–680 °C), and $Mn_2O_3 \rightarrow Mn_3O_4$ (700-800 °C) [6]. After poisoning, new weight loss peaks appear at 195 and 385 °C, which are the decomposition of ammonium sulfate and ammonium bisulfate, respectively, and the weight loss of ammonium sulfate is 2.5 wt %. The weight loss of ammonium sulfate is 1.06 wt %. Notably, the weight loss of MnO_x increased significantly from 700 to 840 °C after poisoning (approximately 2.64 wt %), whereas the weight loss of 0.10Sm–Mn changes little after 700 °C. Therefore, the content of manganese sulfate of 0.10Sm-Mn is higher than MnO_x catalyst after poisoning. Although the 0.10Sm-Mn catalyst will create more ammonium sulfate, this compound is rapidly broken down, does not deplete the manganese's active sites, and does not significantly reduce the catalyst's activity.

3.4 XPS analysis of catalysts before and after SO_2 poisoning

XPS tests are conducted on the samples to further analyze the changes of surface elements on MnO_y and 0.10Sm–Mn catalysts before and after poisoning [17,35], as depicted in Fig. 4. Oxygen atoms are found in two forms: lattice oxygen (O_a , peak at 529.7–530.0 eV) and surface adsorbed oxygen (O_{β}, peak at 531.5–531.8 eV) [3]. The surface atomic concentration and relative concentration ratios results are also presented in Table 1. After the poisoning, the adsorbed oxygen content on the surface increased for both catalysts. The proportion of adsorbed oxygen for the MnO_x catalyst increased from 16.77% to 31.65%, whereas that of the 0.10Sm-Mn catalyst increased from 51.12% to 64.66%. According to the standard binding energy spectrum, the oxygen binding energy in sulfate radical is approximately 531.5 eV, indicating that the oxygen may increase adsorbed oxygen on the surface in SO_4^{2-} . After poisoning, the S element was detected in the following two forms: SO_3^{2-} (peak at 168.5 eV) and SO_4^{2-} (peak at 169.6 eV) [17], demons-



Fig. 3 TG-DTG diagrams of MnO_x and 0.10Sm–Mn catalysts: (a) MnO_x before poisoning; (b) MnO_x after poisoning; (c) 0.10Sm–Mn before poisoning; (d) 0.10Sm–Mn after poisoning.



Fig. 4 O1s spectra of catalysts: (a) 0.10Sm–Mn after poisoning, (b) 0.10Sm–Mn before poisoning, (c) MnO_x after poisoning, (d) MnO_x before poisoning; S2p spectra of catalysts: (e) 0.10Sm–Mn after poisoning, (f) MnO_x after poisoning.

trating that the formation of materials that contain S on the catalyst surface due to the addition of SO₂. Based on the MnO_x and 0.10Sm–Mn catalysts before the poisoning, it can be inferred that there is more surface adsorbed oxygen on the surfaces of the 0.10Sm–Mn catalyst before poisoning than that of the MnO_x before the poisoning. In contrast, the higher proportion of surface adsorbed oxygen in catalysts can lead to better oxidation of NO to NO₂ in SCR reactions and enhance the catalytic activity [3].

3.5 SEM analysis of catalysts before and after SO_2 poisoning

 MnO_x and 0.10Sm–Mn catalysts generate sulfur ammonium salt (ammonium sulfate and ammonium bisulfate) after poisoning based on the thermal analysis. These sulfur ammonium salts deposited on the surface changed the microstructure. Therefore, SEM tests are conducted, as depicted in Fig. 5. Both MnO_x and 0.10Sm–Mn catalysts generate a lot of white precipitated particles

 Table 1
 Surface atomic concentration and relative concentration ratios by XPS

Sample	Surface atomic concentration/%			Relative concentration ratios/%
	Mn	Sm	S	$O_{\beta}/O_{a+\beta}$
MnO _x	18.24	-	-	16.77
MnO_x -S	27.59	_	2.45	31.65
$Sm-MnO_x$	18.13	6.49	-	51.12
Sm–MnO _x -S	14.87	5.68	4.68	64.66

after SO₂ poisoning. According to the TG-DTG and XPS results, these white particles should be sulfur ammonium salts. Additionally, more white particles were discovered in the MnO_x catalyst after poisoning, showing that MnO_x generated more sulfur ammonium salts. While the white particles of the 0.10Sm–Mn catalyst after poisoning are less, implying that 0.10Sm–Mn can hinder the formation of sulfur ammonium salt to a certain extent.

3.6 BET analysis of catalysts before and after SO_2 poisoning

Changes in particular surface area and pore structure of MnO_x and 0.10Sm–Mn catalysts before and after poisoning are presented in Table 2. The specific surface area of the 0.10Sm-Mn catalyst is significantly higher than that of the MnO_x catalyst. Specific surface area is a vital parameter in defining catalyst performance. The larger the surface area of the catalyst, the more contact sites between the reactants and the catalyst, and the smoother the mass transfer [14,22]. Therefore, the activity will be higher. As presented in Table 2, after adding Sm, the specific surface area of the catalyst was significantly enhanced, and the activity and sulfur resistance performance of Sm-Mn were also improved. In contrast, the specific surface areas of both catalysts decrease slightly after poisoning, and the difference is insignificant. Combined with the analysis of TG and SEM test results, the pore structure of the catalyst is blocked due to the deposition of sulfur ammonium salt; therefore, the pore volume and pore size of the catalyst decreased after poisoning.



Fig. 5 SEM images of MnO_x and 0.10Sm-Mn catalysts: (a) MnO_x before poisoning; (b) MnO_x after poisoning; (c) 0.10Sm-Mn before poisoning; (d) 0.10Sm-Mn after poisoning.

3.7 TPD of ammonia (NH₃-TPD) analysis of catalysts before and after SO₂ poisoning

NH₃-TPD experiments were conducted to explore the quantity and strength of the surface acids, and the results are shown in Fig. 6. All the samples have a pronounced desorption peak of approximately 113 °C, and their positions are not obviously different. Nevertheless, the peak area of 0.10Sm-Mn is more significant than that of MnO_x, implying that the 0.10Sm–Mn catalyst has more acidic sites. After introducing SO2, the number of acid sites of both MnO_x and 0.10Sm-Mn decreased. Meanwhile, it is interesting that the MnO_x catalyst after poisoning showed a new desorption peak at 264 °C, suggesting the formation of sulfates that afford new acid sites for the MnO_x catalyst after poisoning [22]. However, there is no new peak in the 0.10Sm-Mn-SO₂ sample, indicating SO₂ is difficute to form sulfate on the 0.10Sm-Mn catalyst. Therefore, Sm can effectively hinder the production of sulfate species, which is consistent with the results of TG-DTG.

3.8 H_2 -TPR analysis of catalysts before and after SO₂ poisoning

The redox performance of the catalysts was assessed by H_2 -TPR, and the results are shown in Fig. 7. For the MnO_x catalyst, two peaks were observed in the H_2 -TPR profile at 332 and 459 °C, which correspond to

Table 2 Surface area and pore structure of MnO_x and 0.10Sm–Mncatalysts before and after poisoning

Sample	Surface area/ $(m^2 \cdot g^{-1})$	Pore volume/($cm^3 \cdot g^{-1}$)	Pore size/nm
(a)	48.9	0.010	2.189
(b)	35.0	0.001	2.176
(c)	145.2	0.089	2.224
(d)	120.6	0.079	2.188

(a) MnO_x before poisoning; (b) MnO_x after poisoning; (c) 0.10Sm–Mn before poisoning; (d) 0.10Sm–Mn after poisoning.



Fig. 6 NH_3 -TPD profiles of MnO_x and 0.10Sm-Mn catalysts before and after poisoning.

 $Mn_2O_3 \rightarrow Mn_3O_4$ and $Mn_2O_3 \rightarrow Mn_3O_4$ respectively [14]. The reduction peaks shifted to lower temperatures of 307 and 437 °C in the H₂-TPR profile of the 0.10Sm–Mn catalyst. This indicated that the introduction of Sm improved the redox properties of the catalyst. Simultaneously, it can be discovered that after SO₂ poisoning, the peak shape of MnO_x at 329 °C has changed, which may be due to the effect of sulfate on the species of manganese in the sample. However, the position and intensity of the reduction peaks of 0.10Sm–Mn did not significantly change after SO₂ poisoning, implying that the influence of SO₂ on 0.10Sm–Mn was small. Therefore, it can be concluded that Sm could play a significant role in resisting SO₂ poisoning.

3.9 Reaction mechanism of catalysts before and after SO_2 poisoning

To further study the anti-SO₂ poisoning mechanism of Sm–Mn catalyst, it is quite necessary to explore the effect of SO₂ on the catalyst SCR reaction process. In this regard, the SCR reaction process of catalyst needs to be studied first. Previous studies indicated that the SCR reaction process varied depending on the catalyst [36]. This section selected MnO_x and 0.10Sm–Mn catalysts (with the best denitration and sulfur resistance performance) as samples. At 160 °C (0.10Sm–Mn catalyst has the highest NO conversion rate at 160 °C), *in situ* infrared reaction tracking research is carried out. This way, the SCR reaction mechanism of catalysts was explored to better discuss better the effect of SO₂ on their SCR reaction process.

3.9.1 SCR reaction mechanism of MnO_x

3.9.1.1 Adsorption and reaction of NH_3 on the surface of MnO_x catalyst

The adsorption of NH_3 on the catalyst surface has a vital influence on the SCR reaction [28]. Thus, this section will



Fig. 7 H₂-TPR profiles of MnO_x and 0.10Sm–Mn catalysts before and after poisoning.

first explore the adsorption and reaction of NH₃ on the surface of the MnO_x catalyst, and the resultes are shown in Fig. 8. Firstly, high-purity N₂ purged the MnO_x catalyst sample in the *in situ* reaction tank. Secondly, NH₃ was passed in after the scanning pattern no longer changed. Subsequently, the infrared pattern was scanned at different periods to record the adsorption state change of NH₃ on the catalyst surface. The results are shown in Fig. 8(a). After NH₃ was introduced for 5 min, firm absorption peaks started to appear at 1552 and 1425 cm⁻¹, which were the symmetric vibration peak of NH_4^+ formed at the Bronsted acid site $(\delta_{s}(NH_{4}^{+}))$ and the asymmetric vibration peak of coordination state NH₃ formed at the Lewis acid site ($\delta_{as}(NH_3)$), respectively [37,38]. Subsequently, weak absorption peaks appeared at 1238 and 1101 cm⁻¹, which were symmetric vibration peaks $(\delta_{s}(NH_{3}))$ and asymmetric vibration peaks $(\delta_{as}(NH_{3}))$ of coordination state NH₃ formed at Lewis acid sites, respectively [39]. Following 20 min, the adsorption reaction of NH₃ tended to saturation. It showed that there were Bronsted acid sites and Lewis acid sites on the surface of the MnO_x catalyst, and NH₃ was adsorbed at both acid sites to generate NH_4^+ and coordination NH_3 .

After NH₃ adsorption reached saturation, O₂ was

introduced into the reaction tank to detect the changes in the infrared spectrum. Subsequently, the effect of O₂ on NH₃ adsorption on the surface of the catalyst can be explored in Fig. 8(b). The symmetric vibration peak of NH₄⁺ ($\delta_s(NH_4^+)$) formed at the Bronsted acid site at 1552 cm⁻¹ strengthened with the addition of O₂. Additionally, new absorption peaks at 1745 and 1340 cm⁻¹ were generated, which were NH₄⁺ symmetric vibration peaks ($\delta_s(NH_4^+)$) formed at the Bronsted acid site. The above results indicate that the presence of O₂ can enhance the adsorption of NH₃ at the Bronsted acid site on the surface of the MnO_x catalyst.

With the introduction of N_2 , NH_3 and O_2 , NO was added into the reaction tank to observe the changes in the infrared spectrum and record the adsorption of a gas on the catalyst surface in different periods, as shown in Fig. 8(c). The absorption peak was enhanced at 1238 cm⁻¹, and a new absorption peak was generated at 1630 cm⁻¹. According to the literature [40], bridge nitrate was produced when NO was added, as evidenced by the two sites' absorption peaks matching those of the bridge nitrate. However, other absorption peaks were basically the same, suggesting that the derivatives formed after NH_3 adsorption would not react with NO.



Fig. 8 Adsorption of reaction gases on MnO_x catalyst surface: (a) NH_3 ; (b) NH_3 and O_2 ; (c) NH_3 , O_2 and NO.

3.9.1.2 Adsorption and the reaction of NO on the surface of MnO_x catalyst

NO will adsorb on the catalyst's surface and generate various nitrate and nitrite types (bridge nitrate, monotone nitrate, bicotone nitrate, bridge nitrite, monotone nitrite, bicotone nitrite, linear nitrite, nitryl compound) [41,42]. Therefore, the adsorption of NO on the catalyst surface is also crucial to the whole SCR reaction process. This experiment would study the adsorption and reaction of NO on the surface of the MnO_r catalyst, and the results are shown in Fig. 9. At first, high purity N2 was introduced into the in situ reaction tank, and NO was introduced after the infrared spectrum did not change. The infrared spectrum was scanned at different periods to record the change of the adsorption state of NO on the catalyst surface, as shown in Fig. 9(a). Following the introduction of NO, absorption peaks appeared at 1736, 1637, 1561, 1427, 1237 and 1066 cm⁻¹. Among them, the absorption peak at 1736 cm⁻¹ was from the nitryl compound [43]. The absorption peaks at 1637, 1561, 1237, and 1066 cm^{-1} were the absorption peaks of bridging nitrate [43], and the absorption peaks at 1427 cm^{-1} were the nitrite compounds on the surface of the catalyst. The absorption peaks at 1637, 1561, 1427, and 1237 cm^{-1}

were strong, and the absorption peaks at other locations were weak, demonstrating that NO was adsorbed on the surface of MnO_x catalyst and generated bridge nitrate and nitrite primarily, while generated nitrite compounds less.

After the NO absorption of NO on the surface of MnO_x catalyst reached saturation, O_2 was introduced to observe the changes in the infrared spectrum, as shown in Fig. 9(b). With the introduction of O_2 , the absorption peaks of bridge nitrate and nitrite at 1561, 1237, 1066 and 1427 cm⁻¹ gradually disappeared, whereas new absorption peaks appeared at 1502, 1292, and 1032 cm⁻¹. According to previous literature, the absorption peaks at 1502, 1292 and 1032 cm⁻¹ were from the bicotone nitrate [44], showing that bridge nitrate and nitrite on the surface of MnO_x catalyst were converted to bicotone nitrates in the presence of O_2 . Additionally, with the addition of O_2 , NO adsorption capacity also increases, indicating that O_2 could promote NO adsorption.

On the above basis, NH_3 was introduced into the reaction tank to observe the alterations in the infrared spectrum, as depicted in Fig. 9(c). The absorption peaks of bridge nitrate and bicotone nitrate at 1637 and 1502 cm⁻¹ significantly weakened, and the absorption peaks at 1292 cm⁻¹ shifted to 1314 cm⁻¹. This significant phenomenon might be due to the absorption peak of the



Fig. 9 Adsorption of reaction gases on MnO_x catalyst surface: (a) NO; (b) NO and O_2 ; (c) NO, O_2 and NH_3 .

NH₃ adsorption state overlapping with that of NO at this position. After NH₃ was introduced, NH₃ and NO coadsorbed at this position. However, the absorption peak strength of 1292–1314 cm⁻¹ also decreased with NH₃ entering. The absorption peaks at other locations did not significantly change. The results revealed that bridge nitrate and bicotone nitrate generated following NO adsorption on the surface of the MnO_x catalyst reacted with NH₃, while other adsorption states of NO did not.

3.9.1.3 Discussion on SCR reaction mechanism of MnO_x catalyst

The results of NO adsorption and reaction on the surface of MnO_x catalyst showed that NO adsorption primarily generates bridge nitrate, nitrite, and a small number of nitrite compounds. However, in the presence of O_2 , bridge nitrate and nitrite would be converted to bicotone nitrates. Through NH₃, bridge nitrate and bicotone nitrate reacted with gaseous NH₃. Firstly, NO was adsorbed on the catalyst surface to generate bridge nitrate and bicotone nitrate under O_2 conditions. Secondly, the bridge nitrate and bicotone nitrate reacted with NH₃ in the gaseous phase. 3.9.2 Study on SCR reaction mechanism of 0.10Sm–Mn catalyst

3.9.2.1 Adsorption and the reaction of NH_3 on 0.10Sm–Mn catalyst surface

The results of the adsorption and the rection of NH₃ on 0.10Sm-Mn catalyst are shown in Fig. 10. Among results, Fig. 10(a) shows the adsorption results of NH_2 on the surface of the Sm-Mn catalyst. With the introduction of NH₃, pronounced infrared absorption peaks at 1669, 1584, 1414 and 1084 cm⁻¹ could be observed. With the constant introduction of NH₃, the intensity of each absorption peak increased, and the adsorption reaction tended to saturation after 15 min. The absorption peaks at 1414 and 1084 cm⁻¹ were asymmetric vibration peaks $(\delta_{c}(NH_{3}))$ of coordination state NH₃ formed at Lewis acid sites [39]. The absorption peaks at 1669 and 1584 cm^{-1} were symmetric vibration peaks of NH_4^+ ($\delta_s(NH_4^+)$) generated at the Bronsted acid site [38]. The findings revealed that there were Bronsted and Lewis acid sites on the surface of the 0.10Sm-Mn catalyst, and NH₃ was adsorbed at both Bronsted and Lewis acid sites to generate NH_4^+ and coordination NH_3 .

After NH₃ was adsorbed on the surface of the



Fig. 10 Adsorption of reaction gases on 0.10Sm–Mn catalyst surface: (a) NH₃; (b) NH₃ and O₂; (c) NH₃, O₂ and NO.

0.10Sm–Mn catalyst to saturation, O_2 was introduced into the reaction tank, as depicted in Fig. 10(b). Compared with the adsorption of NH₃ alone, the peak strength at the 1414 cm⁻¹ peak increased after O_2 was introduced, whereas the absorption peaks at other locations did not change significantly. The peak at 1414 cm⁻¹ was the asymmetric vibration peak (δ_s (NH₃)) of the coordination state NH₃ formed with the Lewis acid site, demonstrating that O_2 improved the adsorption of NH₃ at the Lewis acid site.

After the infrared spectrum obtained by scanning the sample did not change, NO was injected into the reaction tank and the infrared spectrum was observed in Fig. 10(c). With the introduction of NO, the peak intensity at 1584 cm⁻¹ peak weakened, while the infrared absorption peaks at other locations did not change significantly, indicating that the reaction gradually consumed the corresponding amino groups at 1584 cm⁻¹. However, the peak at 1584 cm⁻¹ corresponded to the symmetric vibration peak of NH₄⁺ ($\delta_s(NH_4^+)$) formed by combining with Bronsted acid site, so NO mainly reacted with NH₄⁺ formed at Bronsted acid site, whereas NH₃ in coordination state formed at Lewis acid site did not participate in the reaction.

3.9.2.2 Adsorption and the reaction of NO on the 0.10Sm–Mn catalyst surface

The adsorption and the reaction of NO on the surface of 0.10Sm-Mn catalyst are depicted in Fig. 11. With the introduction of NO, obvious infrared absorption peaks appeared at 1734, 1664, 1633, 1429, 1310 and 1248 cm⁻¹, as is shown in Fig. 11(a). With time extension, the intensity of each absorption peak increased, and the adsorption response tended to saturation after 20 min. Among them, the absorption peak at 1734 cm⁻¹ corresponded to nitryl compound, and the absorption peaks at 1664. 1633, and 1248 cm⁻¹ were the absorption peaks of bridge nitrate [45], the absorption peak at 1310 cm^{-1} corresponded to bicotone nitrate [46], and the absorption peak at 1429 cm⁻¹ equivalent to the nitrite compound on the catalyst surface. Furthermore, the absorption peak at 1429 cm⁻¹ appeared first, which appeared 3 min after the introduction of NO, demonstrating that the nitrite compounds were generated rapidly after the adsorption of NO on the surface of the catalyst. In addition, the absorption peaks at 1664, 1633, 1429 and 1248 cm^{-1} were strong. In contrast, the absorption peaks at 1734 and 1310 cm⁻¹ were weak, indicating that bridge nitrate and nitrite compounds were mainly generated after NO



Fig. 11 Adsorption of reaction gases on 0.10Sm–Mn catalyst surface: (a) NO; (b) NO and O₂; (c) NO, O₂ and NH₃.

adsorption, while the nitryl compounds and nitrates were less.

After NO was introduced for 35 min, the infrared spectrum basically did not change. Next, O_2 was introduced into the reaction tank, and the infrared spectrum was observed to explore the change of NO adsorption state on the catalyst surface in the presence of O_2 in Fig. 11(b). NO adsorption did not significantly change with the extension of penetration time for O_2 , implying that O_2 did not have an obvious impact on the adsorption of NO.

Changes in the infrared spectrum were found in Fig. 11(c), when NH_3 was introduced into the reaction tank. With the extension of NH_3 adsorption time, the absorption peaks of bridging nitrate and bicotone nitrate at 1633 and 1310 cm⁻¹ significantly weakened. In contrast, the absorption peaks at other locations did not considerably change, implying that bridging nitrate and bicotone nitrate could react with NH_3 while other adsorptive species did not.

3.9.2.3 SCR reaction mechanism of 0.10Sm-Mn catalyst

For the Sm–Mn catalyst, NH_4^+ generated at the Bronsted acid site on the catalyst surface could react with NO, whereas NH₃ generated at the Lewis acid site did not. After NO was adsorbed on the surface of 0.10Sm-Mn catalyst, bridge nitrate, and nitrite compounds were primarily formed, with a small amount of bicotone nitrate and nitrite compounds. Among them, bridge nitrate and bicotone nitrate could react with NH₃; however, other adsorbing species did not participate in the reaction. Furthermore, O₂ enhanced the adsorption of NH₃ on the Lewis acid site but did not affect NO adsorption on the catalyst surface. There were three reaction pathways. Firstly, NH₃ and NO were adsorbed on the surface of catalyst, and their intermediate substances reacted to form N_2 and H_2O through the active center of the catalyst surface. Secondly, NH3 was adsorbed at the Bronsted acid site to generate NH_4^+ and reacted with gaseous NH_3 . Thirdly, NO was adsorbed on the surface of the catalyst to generate bridge nitrate and bicotone nitrate and subsequently reacted with gaseous NH₃.

According to the research results of the SCR reaction mechanism of the MnO_x catalyst, the incorporation of Sm changed the SCR mechanism of the Mn-based catalyst. There was only one SCR reaction pathway for pure MnO_x , whereas there were three reaction pathways for 0.10Sm–Mn catalyst. The increase of reaction pathways after incorporating Sm enhanced the reaction capacity of catalyst SCR and its resistance to SO₂ poisoning. The SCR reaction pathway of MnO_x was that NO was adsorbed on the surface of the catalyst to generate bridge nitrate and bicotone nitrate and subsequently reacted with NH₃ in the gaseous state. If SO₂ blocked NO adsorption, the SCR reaction would be blocked, and the catalyst

would be rapidly deactivated. However, the 0.10 Sm–Mn catalyst had many SCR reaction pathways. Even if SO₂ blocked one of the SCR reaction pathways, there were other reaction pathways as supplements, so it could still maintain a specific SCR reaction capacity. Thus, the impact of SO₂ on the SCR reaction process of MnO_x and 0.10 Sm–Mn catalysts will be explored in the follow-up study to explain the mechanism of 0.10 Sm–Mn catalyst against SO₂ poisoning.

3.9.3 Effect of SO_2 on SCR reaction of MnO_x and 0.10Sm–Mn catalysts

3.9.3.1 Effect of SO_2 on NH_3 adsorption for MnO_x and 0.10Sm–Mn catalysts

NH₃ adsorption is an essential step in the SCR reaction process. Therefore, this section will discuss the impact of SO₂ on NH₃ adsorption on the catalyst surface. Subsequently, an in-depth analysis of the mechanism of SO₂ poisoning on the catalyst can be conducted. Fresh MnO_x and 0.10Sm–Mn catalysts, as well as and MnO_x and 0.10Sm–Mn catalysts after 100 ppm SO₂ poisoning for 8 h were selected for the *in situ* infrared experiment. Firstly, the sample was purified using high-purity N₂ until the infrared spectrum no longer changed; at this time, the infrared spectrum was used as the background spectrum. Subsequently, NH₃ was introduced to record the changes in the infrared spectrum and observe its adsorption on the catalyst surface. The results are shown in Fig. 12.

For the fresh MnO_r catalyst (Fig. 8(a)), after NH₃ was introduced, infrared absorption peaks appeared at 1552, 1425, 1238 and 1101 cm⁻¹ were coordination states NH₃ and NH_4^+ formed at Lewis and Bronsted acid sites on the surface of MnO_x catalysts, respectively. As for the MnO_x catalyst poisoned by SO₂ Fig. 12(a), compared with the fresh MnO_x catalyst, the peaks at 1552 cm⁻¹ (the absorption peak of NH_4^+ formed at the Bronsted acid site) and 1425 cm⁻¹ (the asymmetric vibration peak ($\delta_{as}(NH_3)$)) of the coordination state NH₃ formed at the Lewis acid site) was obviously weakened. Meanwhile, the peak at 1101 cm⁻¹ (the symmetric vibration peak ($\delta_s(NH_3)$) of the coordination state NH₃ formed at the Lewis acid site) disappeared completely. The results revealed that the MnO_x catalyst would lose more Lewis and Bronsted acid sites under the action of SO₂; therefore, weakening the adsorption of NH₃.

As for the fresh 0.10Sm–Mn catalyst Fig. 9(a), pronounced infrared absorption peaks appeared at 1669, 1584, 1414 and 1084 cm⁻¹ after NH₃ was introduced. Among them, the peaks at 1414 and 1084 cm⁻¹ were the absorption peaks of NH₃ in the coordination state formed at the Lewis acid site of the catalyst [45]. The peaks at 1669 and 1584 cm⁻¹ were the absorption peaks of NH₄⁺ formed by NH₃ at the Bronsted acid site of the catalyst [47]. Additionally, for the Sm–Mn catalyst poisoned by



Fig. 12 (a) DRIFT results of NH₃ absorption for poisoned MnO_x poisoned by SO₂; (b) DRIFT results of NH₃ absorption for poisoned 0.10Sm–Mn poisoned by SO₂; (c) infrared spectra of NH₃ absorption for 30 min of fresh (1) and SO₂ poisoned (2) 0.10Sm–Mn catalysts.

 SO_2 (Fig. 12(b)), the absorption peak of NH_3 at 1414 and 1084 cm⁻¹ corresponding to the Lewis acid site weakened strongly. Moreover, a negative peak appeared at 1226 cm⁻¹, possibly because SO_4^{2-} was generated after SO_2 poisoned the catalyst. After NH_3 was adsorbed at SO_4^{2-} , SO_4^{2-} was shielded, and a negative peak was generated at 1226 cm⁻¹ [48]. Infrared spectra of NH₃ adsorbed on the fresh 0.10Sm-Mn catalyst and SO₂ poisoned 0.10Sm-Mn catalyst for 30 min were compared, as shown in Fig. 12(c). After SO₂ poisoned the catalyst, the absorption peaks of NH_4^+ at 1669 and 1584 cm⁻¹ corresponding to Bronsted acid sites were significantly improved. The findings revealed that under the action of SO2, 0.10Sm-Mn catalyst would lose Lewis acid site but improve Bronsted acid site significantly. Compared with the MnO_x catalyst, 0.10Sm-Mn catalyst could inhibit the loss of the Bronsted acid site under the action of SO_2 .

3.9.3.2 Effect of SO_2 on NO adsorption for MnO_x and 0.10Sm–Mn catalysts

This section investigated the effect of SO_2 on the adsorption of NO on MnO_x and 0.10Sm–Mn catalysts.

Fresh MnO_x and 0.10Sm–Mn catalysts and MnO_x and 0.10Sm–Mn catalysts that were poisoned for 8 h after 100 ppm SO₂ were selected for the *in situ* infrared experiment. High-purity N₂ was first injected into the *in situ* reaction tank to purge the sample surface, and NO was introduced after the infrared spectrum remained unchanged. The infrared spectrum was obtained by scanning at different periods to observe the change in the adsorption state of NO on the catalyst surface, and the results are shown in Fig. 13.

For fresh MnO_x catalyst, bridge nitrates (1637, 1561, 1237, 1066 cm⁻¹) [49], nitrite (1427 cm⁻¹) and nitryl compounds (1736 cm⁻¹) [43] were formed in Fig. 10(a), after NO was introduced. Nevertheless, for the MnO_x catalyst poisoned by SO₂ from Fig. 13(a), the strength of each absorption peak is greatly weakened, and NO adsorption is much decreased. The results showed that there was competitive adsorption between SO₂ and NO, and SO₂ inhibited the adsorption of NO on the surface of MnO_x catalyst.

As can be observed from Fig. 11(a), for the fresh 0.10Sm–Mn catalyst, various nitrate and nitrite compounds were generated after NO was introduced, primarily

Fig. 13 (a) DRIFT results of NO absorption for poisoned MnO_x poisoned by SO₂; (b) DRIFT results of NO absorption for poisoned 0.10Sm–Mn poisoned by SO₂; (c) infrared spectra of NO absorption for 30 min of fresh (1) and SO₂ poisoned (2) 0.10Sm–Mn catalysts.

including nitryl compounds (1734 cm^{-1}) [43], bridge nitrate (1664, 1633, 1248 cm⁻¹) [49], bicotone nitrate (1310 cm⁻¹) and nitrite (1429 cm⁻¹) [47]. For 0.10Sm-Mn catalyst poisoned by SO_2 from Figs. 13(b) and 13(c), compared with the fresh Sm-Mn catalyst, the absorption peaks of NO at 1734, 1633, and 1310 cm⁻¹ corresponding to nitrite compound, bridge nitrate, and bicotone nitrate disappeared respectively. At 1429 cm⁻¹, the absorption peak of nitrite compounds weakened strongly. However, new strong absorption peaks appeared at 1332 and 1558 cm⁻¹, which were linked to the absorption peak of bicotone nitrate [44], which may be a new adsorption site for NO by 0.10Sm-Mn sulfate generated after the action of SO₂. Although SO₂ can poison the 0.10Sm-Mn catalyst and inhibit the adsorption of NO at some active sites, 0.10Sm-Mn catalyst sulfate generated a new adsorption site for NO after the action of SO₂, which generated binate nitrate at this site.

3.10 Mechanism of Sm–Mn catalyst against SO₂ poisoning

The main reason why SO₂ could cause the rapid inactivation of MnO_x was that SO₂ would react with ammonia to generate sulfur ammonium salt based. These sulfur ammonium salts would not decompose under the active temperature window of Mn-based catalyst (< 200 °C); therefore, the sulfur ammonium salt deposited on the surface of the catalyst blocked the pore structure, decreased the specific surface area, and deactivated the catalyst. Additionally, the active component manganese oxide could be acidified by SO₂ to form the manganese sulfate, which reduced the active component and halted the catalyst. Compared with the MnO_x catalyst, the 0.10Sm-Mn catalyst also generated sulfur ammonium salts deposited on the surface after poisoning, but the content of sulfur ammonium salts was less. Moreover, the incorporation of Sm effectively inhibited the sulfuration of the active component manganese oxide. It protected the active component from being destroyed, so the 0.10Sm-Mn catalyst had a better ability to resist SO₂ poisoning.

By exploring the influence of SO_2 on the SCR reaction process, it was found that the presence of SO_2 would make the MnO_x catalyst lose part of the Lewis acid site and Bronsted acid site, thus affecting the adsorption and activation of NH₃ on the catalyst surface. Meanwhile, SO_2 would inhibit the adsorption of NO on the surface of the MnO_x catalyst due to the competitive adsorption between SO_2 and NO. Firstly, NO was adsorbed on the



catalyst surface to generate bridge nitrate and bicotone nitrate under O_2 conditions and subsequently reacted with gaseous or weakly adsorbed NH₃. After SO₂ hindered the adsorption of NO on the surface of MnO_x catalyst, the SCR reaction pathway would be seriously blocked to affect the progress of the SCR reaction and reduce the denitration activity. Therefore, inhibition of NO adsorption caused by SO₂ was one of the important reasons for the rapid deactivation of the MnO_x catalyst.

As for 0.10Sm–Mn catalyst, the Lewis acid site would lose by SO₂, but the Bronsted acid site was significantly strengthened. The previous research on the SCR reaction mechanism of 0.10Sm-Mn catalyst indicated various reaction pathways on the 0.10Sm-Mn catalyst. Firstly, NH₃ and NO were adsorbed on the surface of the catalyst, and their intermediate substances reacted to form N₂ and H₂O through the active center of the catalyst surface. Secondly, NH₃ was adsorbed at the Bronsted acid site to generate NH_4^+ and reacted with gaseous NH_3 . Thirdly, NO was adsorbed on the surface of the catalyst to develop bridge nitrate and bicotone nitrate and then reacted with gaseous NH₃. NH₄⁺ formed at the Bronsted acid site on the surface of Sm-Mn catalyst could react with NO. Although NO adsorption on the active site and NH₃ on the Lewis acid site were inhibited by SO_2 , NH_4^+ formed at the enhanced Bronsted acid site on the catalyst surface could still react with gaseous or weakly adsorbed NO by SCR, and 0.10Sm-Mn catalyst still maintained a particular catalytic activity. Specifically, compared with MnO_x catalysts, the sulfur resistance of 0.10Sm-Mn catalysts improved.

4 Conclusions

The denitrification activity and physicochemical properties of MnO_x and Sm–Mn catalysts in a sulfur-containing atmosphere are investigated, and the impact of SO₂ on the SCR reaction process of MnO_x and 0.10Sm–Mn catalysts are analyzed deeply by the DRIFTS study. The doping of Sm can enhance the significant advancement of the NO conversion, N₂ selectivity, and sulfur resistance. The active component manganese oxide could be acidified by SO₂, leading to the formation of manganese sulfate (sulfation) and inactivation of active ingredients (MnO_x). The slight sulfation took place on the 0.10Sm-Mn catalyst according to the TG, FE-SEM, NH₃-TPD, and H_2 -TPR, achieving a better ability to resist SO_2 poisoning. In situ infrared experimental results indicated that the presence of SO₂ would impact the adsorption and activation of NH₃ and NO on the MnO_r and 0.10Sm-Mn catalyst surfaces. For the 0.10Sm-Mn catalyst, the increase of Bronsted acid level led to the formation of more NH_4^+ , which could react with gaseous or weakly adsorbed NO. Therefore, the increased Bronsted acid

level benefited from decelerating resistance to SO_2 poisoning.

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