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## Formation of sulfur trioxide during the SCR of NO with NH<sub>3</sub> over a V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst

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The oxidation of sulfur dioxide (SO<sub>2</sub>) to sulfur trioxide (SO<sub>3</sub>) is an undesirable reaction that occurs during the selective catalytic reduction (SCR) of nitrogen oxides (NO<sub>x</sub>) with ammonia (NH<sub>3</sub>), which is a process applied to purify flue gas from coal-fired power plants. The objectives of this work were to establish the fundamental kinetics of SO<sub>3</sub> formation over a V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst and to illustrate the formation mechanism of SO<sub>3</sub> in the presence of NO<sub>x</sub>, H<sub>2</sub>O and NH<sub>3</sub>. A fixed-bed reactor was combined with a Fourier transform infrared (FTIR) spectrometer and a Pental SO<sub>3</sub> analyser to test the outlet concentrations of the multiple components. The results showed that the rate of SO<sub>2</sub> oxidation was zero-order in O<sub>2</sub>, 0.77-order in SO<sub>2</sub> and -0.19-order in SO<sub>3</sub> and that the apparent activation energy for SO<sub>2</sub> oxidation was 74.3 kJ mol<sup>-1</sup> over the range of studied conditions. Based on *in situ* diffuse reflectance infrared Fourier transform (*in situ* DRIFT) spectroscopy, X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) tests, the SO<sub>3</sub> formation process is described here in detail. The adsorbed SO<sub>2</sub> was oxidized by V<sub>2</sub>O<sub>5</sub> to produce adsorbed SO<sub>3</sub> in the form of bridge tridentate sulfate, and the adsorbed SO<sub>3</sub> was desorbed to the gas phase. NO<sub>x</sub> promoted the oxidation of the adsorbed SO<sub>2</sub> due to the promotion of the conversion of low-valent vanadium to high-valent vanadium. In addition, the desorption of the adsorbed SO<sub>3</sub> was inhibited by H<sub>2</sub>O or NH<sub>3</sub> due to the conversion of tridentate sulfate to the more stable bidentate sulfate or ammonium bisulfate. Finally, the mechanism of the influence of NO<sub>x</sub>, H<sub>2</sub>O and NH<sub>3</sub> on the formation of gaseous SO<sub>3</sub> was proposed.

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## 1. Introduction

As the use of equipment for the selective catalytic reduction (SCR) of NO<sub>x</sub> has increased in recent years, the emission of SO<sub>3</sub> in coal-fired power plants has attracted more attention.<sup>1–3</sup> SO<sub>3</sub> increases the acid dew point of flue gas, and sulfuric acid forms when the flue gas is cooled, which corrodes the downstream equipment and pipelines.<sup>4,5</sup> When the SO<sub>3</sub> concentration in flue gas is more than 5 ppm (18 mg m<sup>-3</sup>), an opaque plume is generated, and a “blue acid plume” appears in the downwind direction of the chimney.<sup>6–9</sup> To solve the problem of SO<sub>3</sub> pollution, strict emission standards have been established.<sup>6</sup> In the United States, 22 states have proposed SO<sub>3</sub> emission limits for coal-fired flue gas, of which 14 states have a limit of 6 mg m<sup>-3</sup>. The SO<sub>3</sub> emission limits in Singapore are 10 mg m<sup>-3</sup> for flue gas from stationary sources. The daily SO<sub>2</sub> and SO<sub>3</sub> emission limits in Germany are 50 mg m<sup>-3</sup>. In China, regulations have been issued for “eliminating the white smoke” from

industrial flue gas, aiming to expose the “blue” and “yellow” smoke from SO<sub>3</sub> and NO<sub>2</sub>, respectively, to achieve deep purification of the smoke.<sup>10,11</sup> Therefore, research on the SO<sub>3</sub> formation process is very important and urgent.

There has been much discussion about the process of SO<sub>2</sub> oxidation to SO<sub>3</sub> on a V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst. Dunn J. P.<sup>12–15</sup> studied the oxidation ability of several binary catalysts for SO<sub>2</sub> and found that the oxidation ability of V<sub>2</sub>O<sub>5</sub> is greater than that of other transition metal oxides. In addition, the oxidation mechanism of SO<sub>2</sub> on a V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst has been proposed. SO<sub>2</sub> may adsorb and coordinate onto the vanadium-oxygen-support (V-O-M) bond, resulting in the (V<sup>5+</sup>)·SO<sub>2-ads</sub> state. This process is followed by the cleavage of the V<sup>5+</sup>-O-SO<sub>2</sub> and formation of gaseous SO<sub>3</sub>, which represents the rate determining step. The preferential adsorption of SO<sub>3</sub> results in stronger bonding of SO<sub>3</sub> to the surface vanadium species and competitive adsorption of SO<sub>2</sub> on the active sites. In contrast, Guo X. *et al.* studied the sulfate species on a V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst and concluded that sulfate species are formed on titanium instead of vanadium.<sup>16</sup>

H<sub>2</sub>O and NH<sub>3</sub> in the atmosphere can inhibit the oxidation of SO<sub>2</sub> to SO<sub>3</sub>, while NO<sub>x</sub> has a promotive influence.<sup>7,17–22</sup> However, the mechanisms of these effects have not been described in detail. Kinetics research is of great significance for revealing the reaction mechanism, evaluating the influence of various factors

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and guiding appropriate process design. However, kinetic research on the oxidation process of  $\text{SO}_2$  is limited. Therefore, it is necessary to simulate the process and influencing factors of  $\text{SO}_2$  oxidation over the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst. In this work, the effects of  $\text{O}_2$  and  $\text{SO}_2$  on  $\text{SO}_3$  formation were studied, and the reaction order with respect to the reactants and the apparent activation energy during  $\text{SO}_2$  oxidation were calculated to establish the basic kinetics of  $\text{SO}_2$  oxidation on a  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst. Then, a proposed formation mechanism of  $\text{SO}_3$  in a complex atmosphere was obtained by studying the effects of  $\text{H}_2\text{O}$ ,  $\text{NO}_x$  and  $\text{NH}_3$  on the  $\text{SO}_3$  formation process.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

The 5 wt%  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts were prepared by the wet impregnation method. Commercial P25  $\text{TiO}_2$  was calcined at 450 °C for 4 h.  $\text{NH}_4\text{VO}_3$ , the precursor for  $\text{V}_2\text{O}_5$ , was dissolved in distilled water at 80 °C; P25  $\text{TiO}_2$  was added into the  $\text{NH}_4\text{VO}_3$  solution, and then the solution was stirred for 1 h and subsequently dried by a rotary evaporator. The obtained powder was calcined in air at 450 °C for 4 h and pulverized to a size of 180–250  $\mu\text{m}$ .

The pore properties of the P25- $\text{TiO}_2$  and  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts were determined at 77 K through  $\text{N}_2$  adsorption (NOVA3200e, Quantachrome, USA). The Brunauer–Emmett–Teller (BET) surface area ( $S_{\text{BET}}$ ) and the average pore diameter ( $d$ ) were calculated by the BET method and Horvath–Kawazoe equation method, respectively. The total pore volume ( $V_t$ ) was calculated directly. The results are shown in Table 1. The carrier and catalyst both displayed a mesoporous structure.

Powder X-ray diffraction (XRD, Empyrean, PANalytical B.V., Netherlands) patterns were recorded on a diffractometer (Rigaku D/Max-RA) at 40 kV and 150 mA employing  $\text{Cu K}\alpha$  radiation, and the results are shown in Fig. 1. The XRD patterns of the catalyst exhibited a mixed phase of anatase (PDF #21-1272) and rutile (PDF #21-1276)  $\text{TiO}_2$ . The diffraction peaks of  $\text{V}_2\text{O}_5$  (PDF #41-1426) at 15.4°, 20.4°, 21.7°, 26.2° and 31.0° were not observed, indicating that the  $\text{V}_2\text{O}_5$  was well distributed on the carrier, with no agglomerated microcrystals for the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst.

X-ray photoelectron spectroscopy (XPS) was used to characterize the vanadium on the catalyst surface using a hemispherical energy analyser (ESCALAB 250Xi, Thermo Fisher, USA). The main C 1s peak at 284.6 eV was used as an internal standard to calibrate the binding energies. The areas of the main peaks for  $\text{V} 2\text{p}_{3/2}$  were detected, and the Gaussian–Lorentzian deconvolution method was utilized to calculate the vanadium contents of the various valences.

Table 1 Pore properties of the carrier and catalyst

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$V_t$ ( $\text{ml g}^{-1}$ )	$d$ (nm)
P25- $\text{TiO}_2$	55	0.262	19.14
$\text{V}_2\text{O}_5/\text{TiO}_2$	50	0.258	20.96

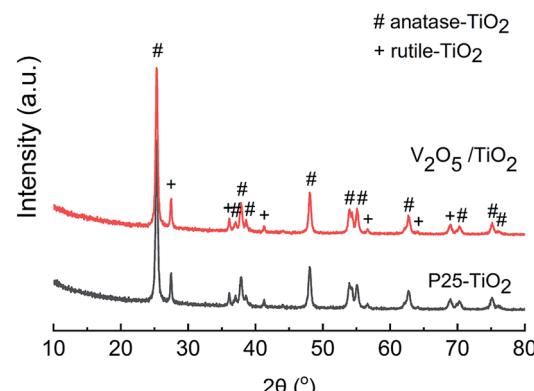


Fig. 1 XRD patterns of the carrier and catalyst.

*In situ* diffuse reflectance infrared Fourier transform (*in situ* DRIFT) spectra were collected on a Fourier transform infrared (FTIR) spectrometer (Tensor 27, Bruker, Germany) to investigate the oxidation of  $\text{SO}_2$ . The spectra were obtained by averaging 16 scans with a resolution of  $2 \text{ cm}^{-1}$ .

### 2.2. Activity measurement

The oxidation reactions of  $\text{SO}_2$  to generate  $\text{SO}_3$  were investigated in a quartz reactor with both an on-line FTIR spectrometer (Tensor 27, Bruker, Germany) capable of quantifying  $\text{SO}_2$  with an error of 1% and an on-line  $\text{SO}_3$  analyser (Pentol GmbH, Germany) capable of quantifying  $\text{SO}_3$  with an error of 10%,<sup>23</sup> as shown in Fig. 2. The gas flow rate for the standard state was 300  $\text{ml min}^{-1}$  with an error of 1%. The gaseous hourly space velocity (GHSV) was approximately 19 000  $\text{h}^{-1}$ .

The default reaction conditions for the  $\text{SO}_2$  oxidation included 320 °C, 1000 ppm  $\text{SO}_2$ , 6 vol%  $\text{O}_2$ , and  $\text{N}_2$  balance. When appropriate, 500 ppm  $\text{NO}_x$  (NO accounted for approximately 90%, and the remainder was  $\text{NO}_2$ ), 500 ppm  $\text{NH}_3$ , or 5 vol%  $\text{H}_2\text{O}$  was introduced to the mixture gas. The reaction temperature ranged from 180 °C to 400 °C with an error of 0.1 °C. The  $\text{SO}_2$  concentration varied between 500 and 1500 ppm, and the  $\text{O}_2$  concentration ranged from 0.1 vol% to 10 vol%. In various sections of this work, the different components of the mixture gas were evaluated and are shown in Table 2.

Water vapor was prepared according to the saturation method (ISO 6145-9: 2009, IDT). As shown in orange in Fig. 2, the pipelines through which the water vapor flowed were insulated and maintained at 80–90 °C. Note that the  $\text{NH}_3$  had a significant impact on the measurement of  $\text{SO}_3$ , so the  $\text{NH}_3$  was turned off after a relatively short time, before it penetrated the catalyst, to reduce its influence on  $\text{SO}_3$  detection. Assuming standard operating conditions, the  $\text{SO}_2$  and  $\text{O}_2$  gas diffusivities were calculated, and then the effectiveness factors were calculated to be 0.99–1.00 for the catalyst particle sizes tested from 150 to 550  $\mu\text{m}$ , indicating that internal diffusion could be neglected. When the gas speed in a vacant tube is above 9.6  $\text{cm s}^{-1}$ , the impact of external diffusion on the  $\text{SO}_2$  conversion can be ignored. In this work, a catalyst particle size of 180–250  $\mu\text{m}$



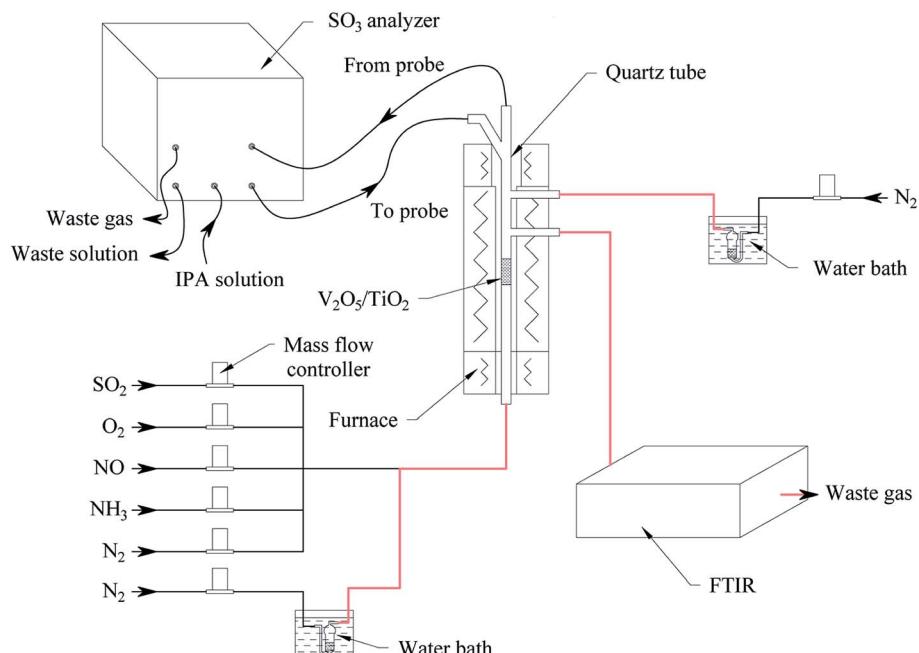


Fig. 2 The schematic diagram of the activity measurement.

Table 2 Components of the mixture gas for various testing purposes

Section	Components of the mixture gas
3.1, 3.2	SO <sub>2</sub> , O <sub>2</sub> and N <sub>2</sub>
3.3, 3.4	SO <sub>2</sub> , O <sub>2</sub> and N <sub>2</sub> ; NO <sub>x</sub> , NH <sub>3</sub> or H <sub>2</sub> O (if used)
3.5	SO <sub>2</sub> and N <sub>2</sub> ; O <sub>2</sub> , NO <sub>x</sub> , NH <sub>3</sub> or H <sub>2</sub> O (if used)

was selected, and the gas speed in the vacant tube was maintained at  $10.6 \text{ cm s}^{-1}$ ; thus, the effects of internal diffusion and external diffusion were eliminated.

For the temperature-programmed desorption (TPD) experiments, the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was first processed in a 1000 ppm SO<sub>2</sub> and 6 vol% O<sub>2</sub> atmosphere at 320 °C for 180 min and then processed in a N<sub>2</sub>, 5 vol% H<sub>2</sub>O or 500 ppm NH<sub>3</sub> atmosphere, respectively, for 20 min. Finally, the TPD tests were carried out

in N<sub>2</sub> with a heating rate of 5 °C min<sup>-1</sup> until the temperature reached 800 °C.

### 3. Results and discussion

#### 3.1. Reaction order and apparent activation energy

To determine the reaction order of SO<sub>2</sub> oxidation to SO<sub>3</sub> at various temperatures, the effect of the O<sub>2</sub> and SO<sub>2</sub> concentrations on SO<sub>3</sub> generation was evaluated, as shown in Fig. 3. In Fig. 3(a), even when the O<sub>2</sub> concentration was zero, some SO<sub>3</sub> was produced at various temperatures, indicating that the oxygen atom in V<sub>2</sub>O<sub>5</sub> participated in the oxidation of SO<sub>2</sub>. This result was consistent with the Mars-van-Krevelen (M-K) mechanism, in which the first step involves reduction of the oxygen vacancy produced by the reactants and catalysts and the second step involves replacement of the oxygen vacancies with oxygen adsorbed by dissociation.<sup>24</sup> With increasing O<sub>2</sub> concentration,

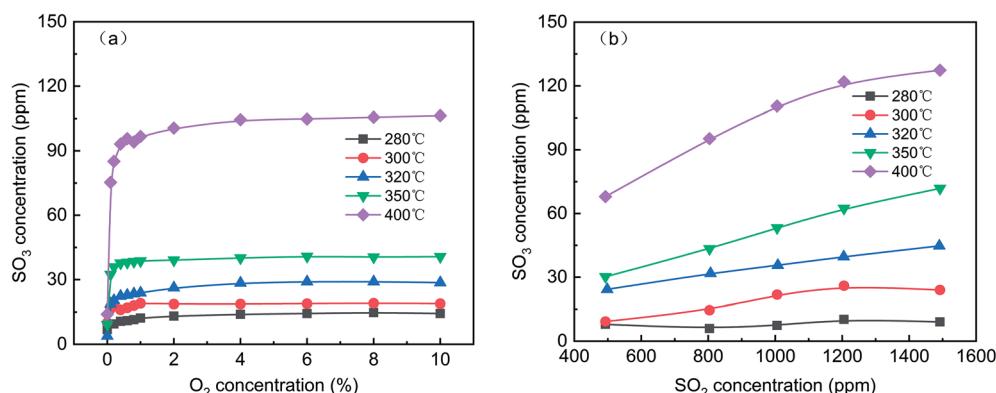
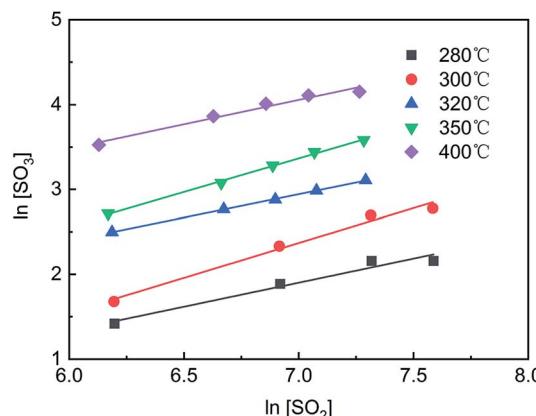


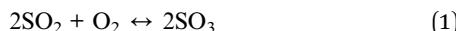
Fig. 3 Effect of the O<sub>2</sub> (a) and SO<sub>2</sub> (b) concentrations on SO<sub>3</sub> generation (default conditions: 1000 ppm SO<sub>2</sub>, 6 vol% O<sub>2</sub>, and N<sub>2</sub>).



Fig. 4  $\ln[\text{SO}_3]$ – $\ln[\text{SO}_2]$  at various temperatures.

the  $\text{SO}_3$  concentration continued to increase, but the growth rate slowed until the  $\text{O}_2$  concentration reached 1%. Thus, the reaction order was approximately zero when the  $\text{O}_2$  concentration was more than 1%. Although the oxidation of  $\text{SO}_2$  is an exothermic reaction, the increase in temperature was conducive to the formation of  $\text{SO}_3$  because the reaction was far from the equilibrium. As shown in Fig. 3(b), as the  $\text{SO}_2$  concentration increased from 500 ppm to 1500 ppm, the  $\text{SO}_3$  concentration increased from 7.9 ppm to 9.0 ppm at 280 °C and from 68.0 ppm to 127.4 ppm at 400 °C. The  $\text{SO}_2$  conversion quantity increased linearly with the  $\text{SO}_2$  concentration, and the higher the temperature was, the greater the slope of the curve was.

The chemical equation for  $\text{SO}_2$  oxidation is shown in eqn (1). The generalized reaction rate equation is shown in eqn (2), and the linearized form is shown in eqn (3). The oxidation rate of  $\text{SO}_2$  was low in this experiment, so the following assumptions were made: (1)  $r_{\text{SO}_2} = [\text{SO}_3]/\tau$ , and the residence time ( $\tau$ ) is a constant; and (2)  $[\text{SO}_2]$  and  $[\text{SO}_3]$  are the averages of their import and export concentrations. The reaction order in  $\text{O}_2$  was approximately zero. Thus, eqn (3) can be further simplified to eqn (4).

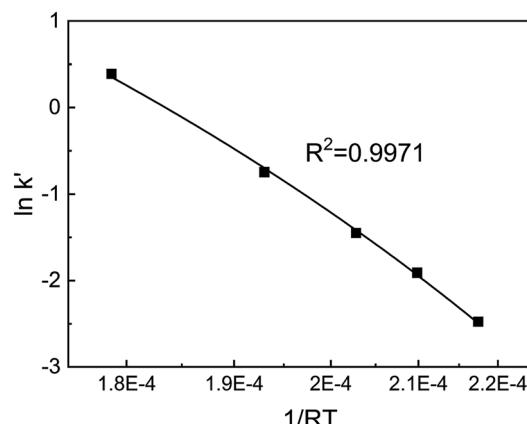


$$r_{\text{SO}_2} = k[\text{SO}_2]^a[\text{SO}_3]^b[\text{O}_2]^0 \quad (2)$$

$$\ln r_{\text{SO}_2} = \ln k + a \ln[\text{SO}_2] + b \ln[\text{SO}_3] + c \ln[\text{O}_2] \quad (3)$$

$$\ln[\text{SO}_3] = \frac{\ln k' + a \ln[\text{SO}_2]}{1 - b} \quad (4)$$

As shown in Fig. 4, the curves of  $\ln[\text{SO}_2]$  versus  $\ln[\text{SO}_3]$  were fitted using eqn (4), and a series of  $a$  and  $b$  values were obtained at various temperatures and are listed in Table 3. The average values of  $a$  and  $b$  were  $0.77 \pm 0.05$  and  $-0.19 \pm 0.08$ ,

Fig. 5 Curve of  $1/RT$ – $\ln k'$  for  $\text{SO}_2$  oxidation.

respectively. The reaction rate equation of  $\text{SO}_2$  over the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst is given by eqn (5).

$$r_{\text{SO}_2} = k'[\text{SO}_2]^{0.77}[\text{SO}_3]^{-0.19} \quad (5)$$

Substituting the values of  $a$  and  $b$  into eqn (4) yields eqn (6). After a series of  $\ln k'$  values at various temperatures was calculated by eqn (6), the resulting curve of  $1/RT$  versus  $\ln k'$  was obtained, as shown in Fig. 5. The slope of the curve was equal to the apparent activation energy, approximately 74.3  $\text{kJ mol}^{-1}$  with an error of 2.4%. The reaction rate of  $\text{SO}_2$  over the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst is given by eqn (7).

$$\ln k' = 0.19 \ln[\text{SO}_3] - 0.77 \ln[\text{SO}_2] \quad (6)$$

$$r_{\text{SO}_2} = A e^{-\frac{74.3}{RT}} [\text{SO}_2]^{0.77} [\text{SO}_3]^{-0.19} \quad (7)$$

The apparent activation energy of  $\text{SO}_2$  oxidation was approximately 84–209  $\text{kJ mol}^{-1}$ , so the chemical reaction was a rate-limiting step,<sup>25</sup> leading to both the shallow layer and deep layer of the catalyst being involved in the oxidation of  $\text{SO}_2$ . In contrast, the activation energy of the  $\text{NO}_x$  reduction reaction was small at approximately 21  $\text{kJ mol}^{-1}$ ,<sup>26</sup> and the chemical reaction rate was fast, resulting in only the shallow layer of the catalyst participating in the reduction of  $\text{NO}_x$ . According to the above differences, reducing the wall thickness of the catalyst was an effective method to reduce the oxidation rate of  $\text{SO}_2$  while ensuring denitrification efficiency. In practice, the minimum thickness of the honeycomb walls is determined by their mechanical resistance.

### 3.2. Formation mechanism of $\text{SO}_3$

$\text{SO}_3$  formation was first characterized in a simple atmosphere of  $\text{SO}_2$  and  $\text{O}_2$ , and then the effects of  $\text{NO}_x$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  on  $\text{SO}_3$  formation were explored to further reveal the mechanism of  $\text{SO}_3$  formation in complex atmospheres. *In situ* DRIFT spectra for the reaction in a simple atmosphere at various times are shown in Fig. 6. As the reaction proceeded, the stretching vibration of

Table 3 Reaction orders ( $a, b$ ) at various temperatures

$T$ (°C)	280	300	320	350	400
$a$	0.71	0.86	0.71	0.86	0.73
$b$	-0.25	-0.05	-0.29	-0.08	-0.26
$R^2$	0.8895	0.9522	0.9993	0.9955	0.949



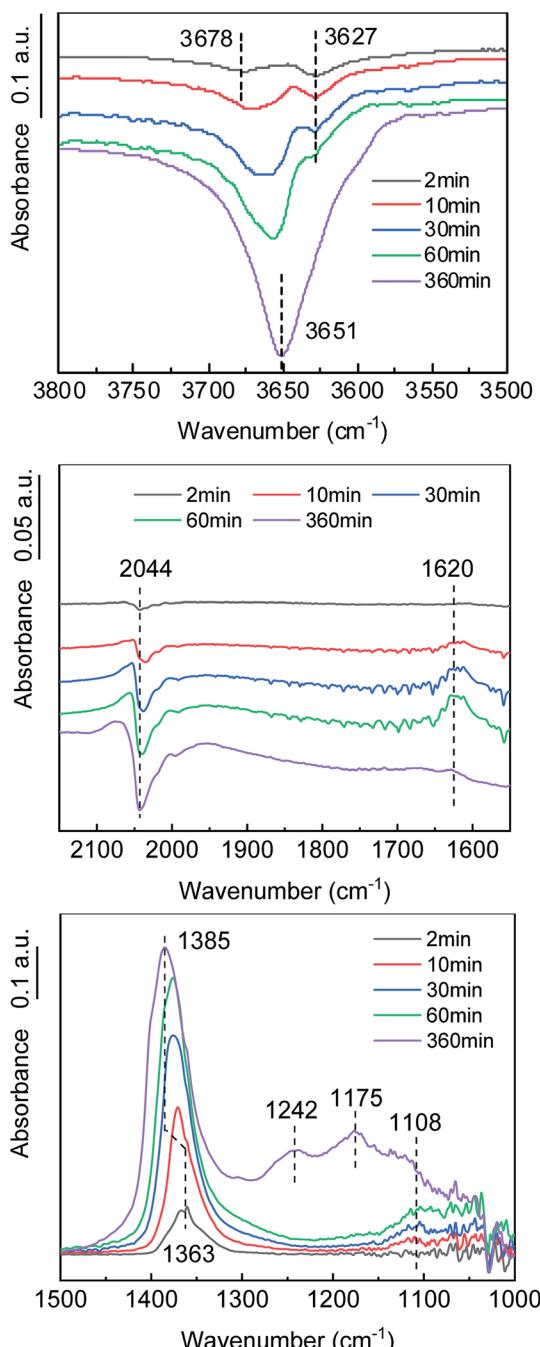


Fig. 6 *In situ* DRIFT spectra of the catalyst in the formation process of  $\text{SO}_3$ . (Conditions: 1000 ppm  $\text{SO}_2$ , 6 vol%  $\text{O}_2$ , and  $\text{N}_2$ ).

$\text{O-H}$  at 3550–3750  $\text{cm}^{-1}$  decreased. The high frequency peak at 3678  $\text{cm}^{-1}$  was attributed to an alkaline hydroxyl group, and the low frequency peak at 3627  $\text{cm}^{-1}$  was attributed to a neutral hydroxyl group.<sup>27</sup> Based on the variation of the peak strength with reaction time, it was inferred that the alkaline hydroxyl groups were preferentially consumed. The peak at 1620  $\text{cm}^{-1}$  belonged to the  $\text{H-O-H}$  bending motion of adsorbed  $\text{H}_2\text{O}$ ,<sup>28</sup> indicating that  $\text{H}_2\text{O}$  was formed during the adsorption of  $\text{SO}_2$ . The reduction of the surface hydroxyl group and the formation of adsorbed  $\text{H}_2\text{O}$  were a result of the  $\text{SO}_2$  combining with the

surface hydroxyl group on the  $\text{TiO}_2$  and releasing sulfite species and  $\text{H}_2\text{O}$ . The half peaks at 1030–1150  $\text{cm}^{-1}$  indicated the existence of sulfite species on the catalyst surface.<sup>28–30</sup>

The vibration peak at 1363–1385  $\text{cm}^{-1}$  belonged to the bridge tridentate sulfate species bound to the carrier.<sup>16,31–33</sup> As the reaction proceeded, the peak intensity increased, indicating that the surface sulfate increased. As the peak gradually shifted from 1363  $\text{cm}^{-1}$  to 1385  $\text{cm}^{-1}$ , the hydroxyl peak gradually shifted from 3678  $\text{cm}^{-1}$  to 3651  $\text{cm}^{-1}$ , which indicated that the bridge tridentate sulfate species was preferentially bound first to the basic hydroxyl group and then to the neutral hydroxyl group on the carrier. A comparison of the spectra at 60 min and 360 min revealed that the bending motion peak of  $\text{H}_2\text{O}$  disappeared, but the wide peak at 1100–1300  $\text{cm}^{-1}$  increased significantly. These peaks belonged to the chelated bidentate sulfate, bridge bidentate sulfate and unidentate sulfate.<sup>34</sup> This observation indicated that the bridge tridentate sulfate changed to bidentate sulfate or unidentate sulfate under the action of  $\text{H}_2\text{O}$ .

The negative peak at 2044  $\text{cm}^{-1}$  belonged to the overtones of  $\text{V=O}$ .<sup>35</sup> The gradual deepening of the negative peak indicated that the ratio of the high-valent vanadium ( $\text{V}^{5+}$ ) was decreasing, which was consistent with the mechanism of the K-M reaction. As an active component, the  $\text{V}_2\text{O}_5$  was reduced to low-valent vanadium ( $\text{V}^{3+}$ ) when the  $\text{SO}_2$  was oxidized, and then the  $\text{V}^{3+}$  was oxidized to  $\text{V}^{5+}$  by  $\text{O}_2$ , thus completing a catalytic cycle. The formation process of gaseous  $\text{SO}_3$ , accompanied by the transformation between high-valent vanadium and low-valent vanadium, can be roughly divided into three steps. (1) Gaseous  $\text{SO}_2$  is chemically adsorbed on the surface of the carrier through hydroxyl groups. (2) The chemically adsorbed  $\text{SO}_2$  is oxidized by high-valent vanadium to form adsorbed  $\text{SO}_3$ . (3) The adsorbed  $\text{SO}_3$  is desorbed to generate gaseous  $\text{SO}_3$ .

### 3.3. Effects of $\text{NO}_x$ , $\text{H}_2\text{O}$ and $\text{NH}_3$ on gaseous $\text{SO}_3$ formation

The effects of  $\text{NO}_x$  on  $\text{SO}_3$  formation are shown in Fig. 7. With the addition of  $\text{NO}_x$ , the  $\text{SO}_3$  concentration gradually increased from 11 ppm to 17.5 ppm and then remained constant, showing that  $\text{NO}_x$  promoted the generation of gaseous  $\text{SO}_3$  by

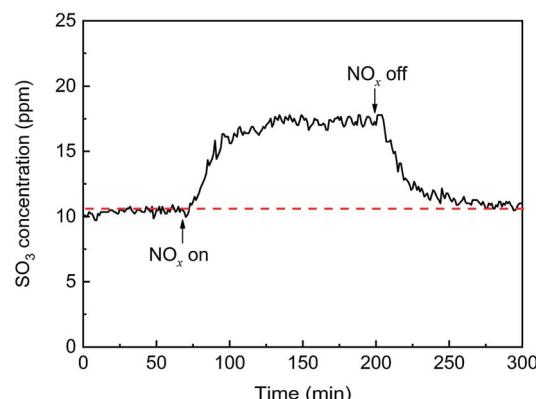


Fig. 7 Transient effects of  $\text{NO}_x$  on  $\text{SO}_3$  formation (conditions: 1000 ppm  $\text{SO}_2$ , 500 ppm  $\text{NO}_x$ , 6 vol%  $\text{O}_2$ , and  $\text{N}_2$ ).

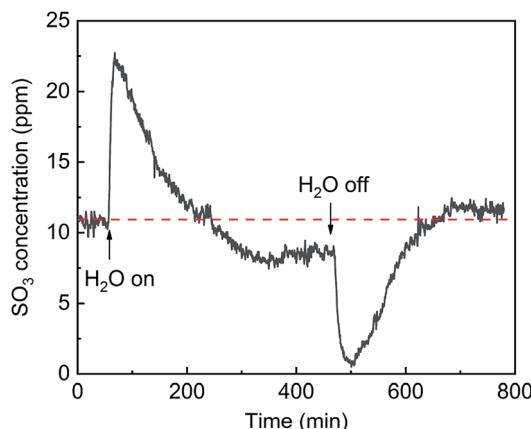


Fig. 8 Transient effects of  $\text{H}_2\text{O}$  on  $\text{SO}_3$  formation (conditions: 1000 ppm  $\text{SO}_2$ , 5 vol%  $\text{H}_2\text{O}$ , 6 vol%  $\text{O}_2$ , and  $\text{N}_2$ ).

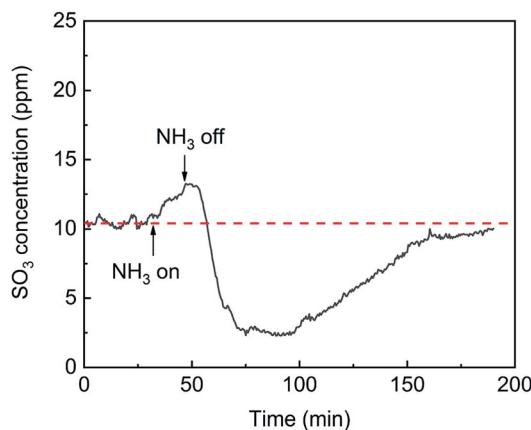


Fig. 9 Transient effects of  $\text{NH}_3$  on  $\text{SO}_3$  formation (conditions: 1000 ppm  $\text{SO}_2$ , 500 ppm  $\text{NH}_3$ , 6 vol%  $\text{O}_2$ , and  $\text{N}_2$ ).

approximately 60%. When the flow of  $\text{NO}_x$  was stopped, the  $\text{SO}_3$  concentration gradually decreased to the initial concentration. The enhancement may have been due to the oxidation of  $\text{SO}_2$  by  $\text{NO}_x$ , which was in the gas phase or adsorbed on the catalyst surface.

The effects of  $\text{H}_2\text{O}$  on  $\text{SO}_3$  formation are shown in Fig. 8. With the addition of  $\text{H}_2\text{O}$ , the  $\text{SO}_3$  concentration sharply increased from 11 ppm to 23 ppm and then gradually decreased to 8.5 ppm. Compared with the initial concentration, the  $\text{SO}_3$  concentration first doubled and then decreased by 23%. It can be inferred that the  $\text{SO}_3$  desorption from the active site into the gas phase was due to a competitive adsorption between  $\text{H}_2\text{O}$  and  $\text{SO}_3$ . When the flow of  $\text{H}_2\text{O}$  was stopped, the  $\text{SO}_3$  concentration sharply decreased to nearly zero and then returned to a constant of 12 ppm. The sharp decrease in the  $\text{SO}_3$  concentration occurred because more active sites were released by the  $\text{H}_2\text{O}$  desorption and more  $\text{SO}_3$  was adsorbed.

The effects of  $\text{NH}_3$  on  $\text{SO}_3$  formation are shown in Fig. 9. With the addition of  $\text{NH}_3$ , the  $\text{SO}_3$  concentration slightly increased from 11 ppm to 13 ppm. When the flow of  $\text{NH}_3$  was stopped, the  $\text{SO}_3$  concentration sharply decreased to 3 ppm and then recovered and remained constant. The desorption of  $\text{SO}_3$  was promoted by the competitive adsorption between  $\text{NH}_3$  and  $\text{SO}_3$  and was inhibited by the combination of  $\text{SO}_3$  and adsorbed  $\text{NH}_3$ . When  $\text{NH}_3$  was initially introduced, competitive adsorption dominated the process, and the release of  $\text{SO}_3$  increased slightly. When the  $\text{NH}_3$  was withdrawn, the competitive adsorption basically stopped, but the combination of  $\text{SO}_3$  and adsorbed  $\text{NH}_3$  remained, which greatly inhibited the desorption of  $\text{SO}_3$  and led to a sharp drop in the  $\text{SO}_3$  concentration.

In short, the process of gaseous  $\text{SO}_3$  formation includes  $\text{SO}_2$  adsorption,  $\text{SO}_2$  oxidation and  $\text{SO}_3$  desorption. To clarify in which step  $\text{NO}_x$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  affect  $\text{SO}_3$  formation, the three steps were tested separately. The  $\text{SO}_2$  oxidation was investigated first, followed by the  $\text{SO}_2$  adsorption and  $\text{SO}_3$  desorption.

### 3.4. Effects of $\text{NO}_x$ , $\text{H}_2\text{O}$ and $\text{NH}_3$ on $\text{SO}_2$ oxidation

To further investigate the effects of  $\text{NO}_x$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  on  $\text{SO}_2$  oxidation, *in situ* DRIFT spectroscopy was used to determine the intermediate products, and the results are shown in Fig. 10–12. As shown in Fig. 10, in the presence of  $\text{NO}_x$ , the adsorption band of  $\text{N}_2\text{O}$  at  $1303\text{ cm}^{-1}$  appeared,<sup>36,37</sup> the adsorption band of  $\text{V}=\text{O}$  at  $2041\text{ cm}^{-1}$  decreased, and the peak of tridentate sulfate at  $1386\text{--}1380\text{ cm}^{-1}$  decreased. Thus,  $\text{NO}_x$  was reduced to  $\text{N}_2\text{O}$  while  $\text{V}^{3+}$  was oxidized to  $\text{V}^{5+}$ , and the increase in  $\text{V}^{5+}$  promoted

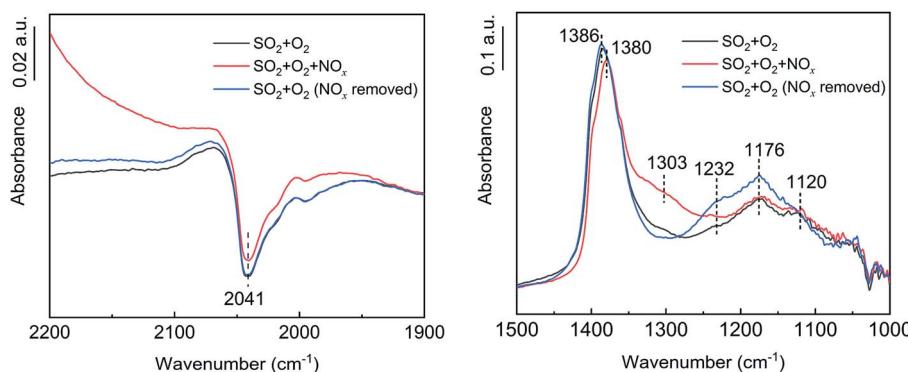


Fig. 10 *In situ* DRIFT spectra of the catalyst with  $\text{NO}_x$  flow (conditions: 1000 ppm  $\text{SO}_2$ , 500 ppm  $\text{NO}_x$ , 6 vol%  $\text{O}_2$ , and  $\text{N}_2$ ).

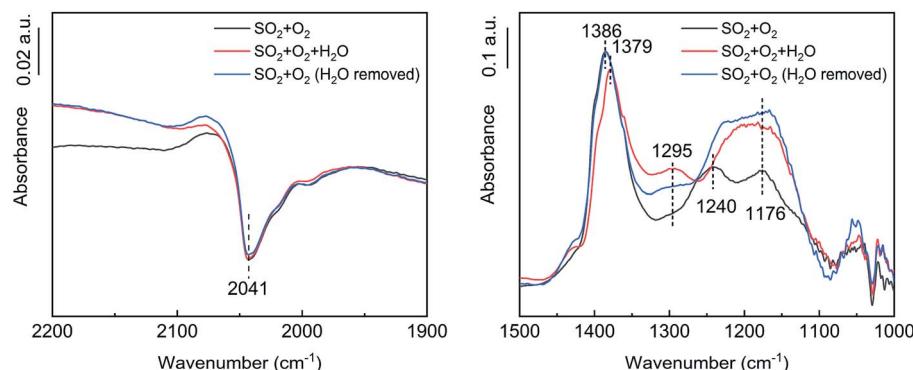


Fig. 11 *In situ* DRIFT spectra of the catalyst with  $\text{H}_2\text{O}$  flow (conditions: 1000 ppm  $\text{SO}_2$ , 5 vol%  $\text{H}_2\text{O}$ , 6 vol%  $\text{O}_2$ , and  $\text{N}_2$ ).

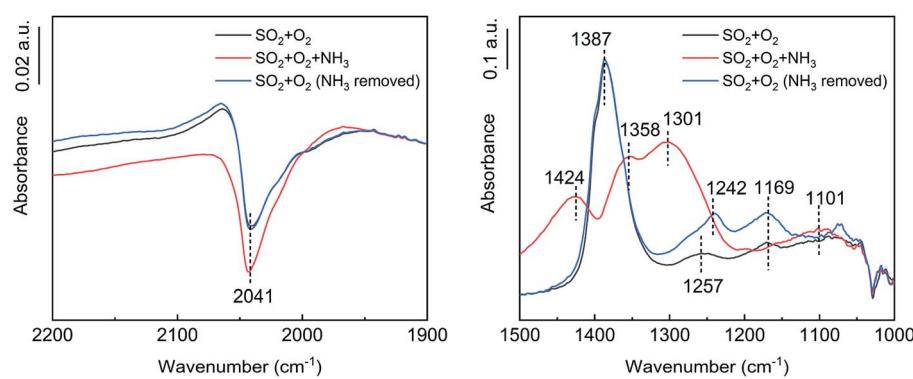


Fig. 12 *In situ* DRIFT spectra of the catalyst with  $\text{NH}_3$  flow (conditions: 1000 ppm  $\text{SO}_2$ , 500 ppm  $\text{NH}_3$ , 6 vol%  $\text{O}_2$ , and  $\text{N}_2$ ).

the oxidation of the adsorbed  $\text{SO}_2$ . After the removal of the  $\text{NO}_x$ , the adsorbed  $\text{N}_2\text{O}$  peak disappeared, and the tridentate sulfate peak returned to its initial state. Therefore,  $\text{NO}_x$  promoted  $\text{SO}_2$  oxidation by promoting the conversion of  $\text{V}^{3+}$  to  $\text{V}^{5+}$ . No  $\text{SO}_3$  formation was detected in the absence of the catalyst in the  $\text{SO}_2$ ,  $\text{O}_2$  and  $\text{NO}_x$  atmospheres, indicating that the promotion effect of  $\text{NO}_x$  on  $\text{SO}_2$  oxidation acted on the catalyst surface instead of in the gas phase.

As shown in Fig. 11, after the addition of  $\text{H}_2\text{O}$ , the  $\text{V}=\text{O}$  peak at  $2041\text{ cm}^{-1}$  did not change significantly, the tridentate sulfate peak at  $1379\text{--}1386\text{ cm}^{-1}$  decreased slightly, and the bidentate sulfate peak at  $1176\text{--}1240\text{ cm}^{-1}$  increased. A bending vibration peak attributable to  $\text{S}-\text{O}-\text{H}$  was observed at  $1295\text{ cm}^{-1}$ ,<sup>38</sup> indicating that  $\text{H}_2\text{O}$  promoted the transformation of tridentate sulfate to bidentate sulfate, which partly existed in the form of bisulfate. After the removal of the  $\text{H}_2\text{O}$ , the tridentate sulfate peak increased to its initial state, the bidentate sulfate peak increased further, and the bending vibration peak of  $\text{S}-\text{O}-\text{H}$  decreased, indicating that the proportion of hydrogen sulfate decreased.

As shown in Fig. 12, in the presence of  $\text{NH}_3$ , the peak position of tridentate sulfate shifted from  $1387\text{ cm}^{-1}$  to  $1358\text{ cm}^{-1}$ , and the peak intensity decreased significantly. Further, new adsorption bands of  $\text{NH}_4^+$  at  $1424\text{ cm}^{-1}$  and  $\text{S}-\text{O}-\text{H}$  at  $1301\text{ cm}^{-1}$  appeared.<sup>39</sup>  $\text{NH}_3$  was partially oxidized on the catalyst surface to produce  $\text{H}_2\text{O}$ . In addition, there were hydroxyl groups on the catalyst surface. Thus, tridentate sulfate

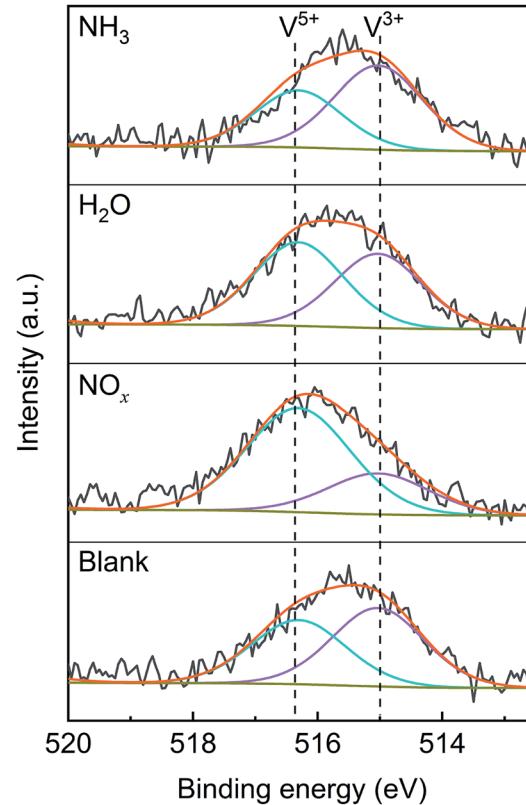
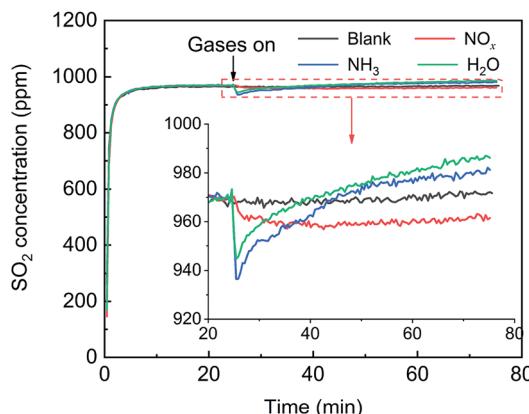


Fig. 13 XPS characterization of the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts after exposure to various gases (blank conditions: 1000 ppm  $\text{SO}_2$  and  $\text{N}_2$ ; other conditions: addition of 500 ppm  $\text{NO}_x$ , 500 ppm  $\text{NH}_3$  or 5%  $\text{H}_2\text{O}$ ).



**Table 4** XPS analysis for the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts after exposure to various gases

Sample	Blank	$\text{NO}_x$	$\text{H}_2\text{O}$	$\text{NH}_3$
$\text{V}^{5+}/(\text{V}^{5+} + \text{V}^{3+})$	46%	72%	53%	40%

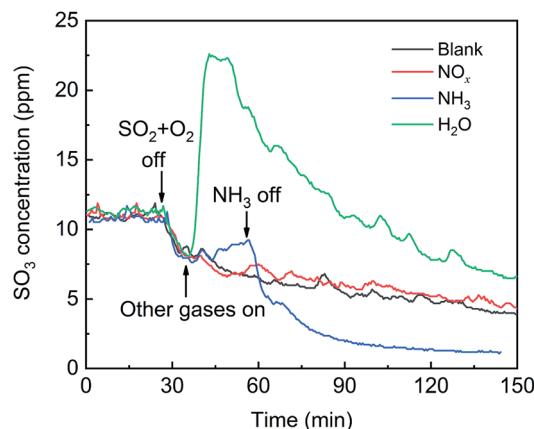


**Fig. 14** Effects of  $\text{NO}_x$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  on  $\text{SO}_2$  adsorption over the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst (blank conditions: 1000 ppm  $\text{SO}_2$  and  $\text{N}_2$ ; other conditions: 500 ppm  $\text{NO}_x$ , 500 ppm  $\text{NH}_3$  or 5%  $\text{H}_2\text{O}$ ).

combined with  $\text{NH}_3$  and hydroxyl or  $\text{H}_2\text{O}$  to produce ammonium bisulfate. The adsorption band of  $\text{V}=\text{O}$  increased in the presence of  $\text{NH}_3$ , showing that  $\text{V}^{5+}$  was reduced to  $\text{V}^{3+}$  by  $\text{NH}_3$ . The decrease of  $\text{V}^{5+}$  inhibited the oxidation of the adsorbed  $\text{SO}_2$ .

To confirm the effects of  $\text{NO}_x$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  on the valence state of vanadium, XPS characterization was performed on the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts exposed to various atmospheres, and the spectra are shown in Fig. 13. The  $\text{V} 2\text{p}_{3/2}$  spectra were separated into two peaks by the Gaussian–Lorentzian deconvolution method, including the  $\text{V}^{3+}$  peak (515.0 eV) and  $\text{V}^{5+}$  peak (516.4 eV),<sup>40,41</sup> and the vanadium contents of various valences are shown in Table 4. Compared with the blank catalyst, the proportion of  $\text{V}^{5+}$  obviously increased from 46% to 72% in the presence of  $\text{NO}_x$ , which may have been caused by the oxidation of  $\text{V}^{3+}$  by  $\text{NO}_x$ . Similarly, the addition of  $\text{H}_2\text{O}$  led to a slight increase in the proportion of  $\text{V}^{5+}$ . In contrast, the proportion of  $\text{V}^{5+}$  slightly decreased in the presence of  $\text{NH}_3$  because of the reduction of  $\text{V}^{5+}$  by  $\text{NH}_3$ . The effect of  $\text{NO}_x$  on the vanadium valence was generally more significant than that of  $\text{H}_2\text{O}$  and  $\text{NH}_3$ .

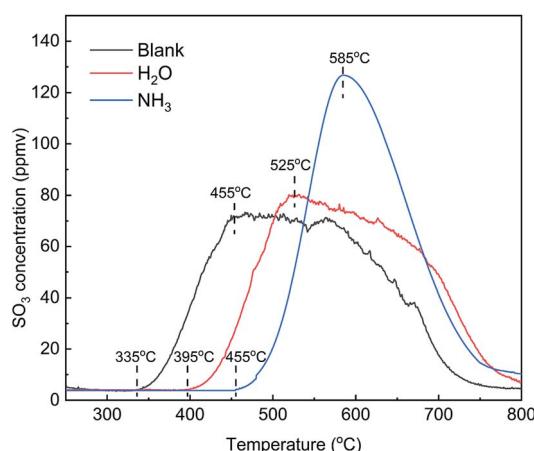
Based on the analysis of the results shown in Fig. 10–13,  $\text{NO}_x$  promoted the conversion of  $\text{V}^{3+}$  to  $\text{V}^{5+}$ , thereby accelerating the oxidation of the adsorbed  $\text{SO}_2$ . The tridentate sulfate peak changed with the atmosphere, while the bidentate sulfate peak always increased, indicating that the bidentate sulfate was more stable than the tridentate sulfate, and the tridentate sulfate may have been the key intermediate product of the  $\text{SO}_2$  oxidation. It can be inferred that, in the presence of  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , the tridentate sulfate transformed to the more stable bidentate sulfate and thereby inhibited the desorption of  $\text{SO}_3$ , which was verified by the TPD tests discussed below.



**Fig. 15** Effects of  $\text{NO}$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  on  $\text{SO}_3$  desorption (blank conditions: 1000 ppm  $\text{SO}_2$ , 6 vol%  $\text{O}_2$  and  $\text{N}_2$ ; other conditions: 500 ppm  $\text{NO}$ , 500 ppm  $\text{NH}_3$  or 5%  $\text{H}_2\text{O}$ ).

### 3.5. Effects of $\text{NO}_x$ , $\text{H}_2\text{O}$ and $\text{NH}_3$ on $\text{SO}_2$ adsorption and $\text{SO}_3$ desorption

First, the effects of  $\text{NO}_x$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  on  $\text{SO}_2$  adsorption were investigated, and the breakthrough curves of  $\text{SO}_2$  are shown in Fig. 14. For the blank, the  $\text{SO}_2$  concentration increased rapidly, corresponding to the adsorption stage of  $\text{SO}_2$ , and tended to stabilize at 970 ppm, corresponding to the catalytic oxidation stage of  $\text{SO}_2$ , with a  $\text{SO}_2$  conversion ratio of approximately 3%. After the addition of  $\text{NO}_x$ , the  $\text{SO}_2$  concentration decreased from 970 ppm to 960 ppm and tended to be stable, which was attributed to the promotion effect of  $\text{NO}_x$  on the  $\text{SO}_2$  oxidation instead of the  $\text{SO}_2$  adsorption. After the addition  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , the  $\text{SO}_2$  concentration rapidly decreased and then gradually increased and finally stabilized at more than 970 ppm. These characteristics are typical of adsorption breakthrough curves, indicating that the presence of  $\text{H}_2\text{O}$  or  $\text{NH}_3$  promoted the  $\text{SO}_2$  adsorption. Finally, the  $\text{SO}_2$  concentration exceeded 970 ppm, which was due to the adsorption saturation of the alkaline sites from the adsorption of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  on the catalyst surface.



**Fig. 16** TPD curves of the catalysts adsorbed in various atmospheres (blank pretreatment conditions:  $\text{N}_2$ ; other conditions: 500 ppm  $\text{NH}_3$  or 5%  $\text{H}_2\text{O}$ ).



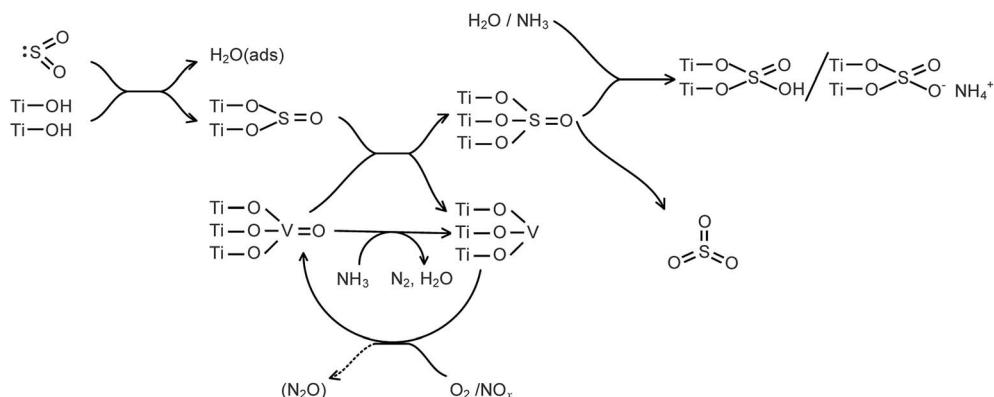


Fig. 17 Formation of  $\text{SO}_3$  during the SCR of  $\text{NO}_x$  with  $\text{NH}_3$  in the presence of  $\text{H}_2\text{O}$ .

The effects of  $\text{NO}_x$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  on  $\text{SO}_3$  desorption are shown in Fig. 15. For the blank, as the  $\text{SO}_2$  and  $\text{O}_2$  sources were removed, the  $\text{SO}_3$  concentration gradually decreased, showing that the adsorbed  $\text{SO}_3$  was desorbed in the flow of  $\text{N}_2$ . After the addition of  $\text{NO}_x$ , the desorption curves of  $\text{SO}_3$  coincided with that of the blank, indicating that  $\text{NO}_x$  did not influence the  $\text{SO}_3$  desorption. After the addition of  $\text{H}_2\text{O}$ , the  $\text{SO}_3$  concentration sharply doubled to a maximum and then gradually decreased. These results indicated that there was a strong competitive adsorption between  $\text{H}_2\text{O}$  and  $\text{SO}_3$ . After the addition of  $\text{NH}_3$ , the  $\text{SO}_3$  concentration gradually increased by approximately 2 ppm due to a mild competitive adsorption between  $\text{NH}_3$  and  $\text{SO}_3$ .  $\text{H}_2\text{O}$  or  $\text{NH}_3$  and  $\text{SO}_3$  competitively adsorbed to promote  $\text{SO}_3$  desorption, but the promotion of  $\text{SO}_3$  desorption was not sustainable. Further,  $\text{H}_2\text{O}$  or  $\text{NH}_3$  combined with the adsorbed  $\text{SO}_3$  to form a more stable bidentate sulfate or ammonium bisulfate, which ultimately inhibited the  $\text{SO}_3$  desorption. This phenomenon was most obvious in the presence of  $\text{NH}_3$ . Although the  $\text{NH}_3$  was removed, the  $\text{SO}_3$  concentration decreased to less than that of the blank.

The addition of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  had an obvious inhibitory effect on the desorption of  $\text{SO}_3$ . To compare the effects of the two gases, TPD tests were carried out on the catalysts pretreated in various atmospheres, and the results are shown in Fig. 16. Compared with the blank, the initial temperature and peak temperature of  $\text{SO}_3$  desorption both increased by 60–70  $^\circ\text{C}$  in the presence of  $\text{H}_2\text{O}$  and increased significantly by 120–130  $^\circ\text{C}$  in the presence of  $\text{NH}_3$ . These results showed that the presence of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  made  $\text{SO}_3$  much more difficult to desorb and that  $\text{NH}_3$  inhibited  $\text{SO}_3$  desorption more effectively than did  $\text{H}_2\text{O}$ . The peak areas of  $\text{SO}_3$  desorption were 19 615, 20 185 and 21 011 ppm min in three kinds of atmospheres. In view of the measurement error of approximately 10%, the desorption amount of  $\text{SO}_3$  was approximately equal. Thus,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  affected the adsorption state of  $\text{SO}_3$  but not the adsorption amount.

The formation of  $\text{SO}_3$  during the SCR of  $\text{NO}_x$  with  $\text{NH}_3$  in the presence of  $\text{H}_2\text{O}$  is summarized in Fig. 17. The formation of  $\text{SO}_3$  was obviously promoted by  $\text{NO}_x$ , significantly inhibited by  $\text{NH}_3$ , and slightly inhibited by  $\text{H}_2\text{O}$ .  $\text{NO}_x$  promoted the  $\text{SO}_2$  oxidation

in that the  $\text{NO}_x$  promoted the transformation of low-valent vanadium to high-valent vanadium.  $\text{H}_2\text{O}$  and  $\text{NH}_3$  combined with the adsorbed  $\text{SO}_3$  to form bidentate sulfate and bisulfate, respectively, and the  $\text{SO}_3$  desorption was depressed. The inhibition of the  $\text{SO}_3$  desorption by  $\text{NH}_3$  was stronger than that by  $\text{H}_2\text{O}$ .

## 4. Conclusions

Over the range of conditions studied, the rate of  $\text{SO}_2$  oxidation was zero-order in  $\text{O}_2$ , 0.77-order in  $\text{SO}_2$  and -0.19-order in  $\text{SO}_3$ , and the apparent activation energy for  $\text{SO}_2$  oxidation was 74.3  $\text{kJ mol}^{-1}$ . The chemical reaction process can be roughly divided into three steps, including (1)  $\text{SO}_2$  adsorption on the active site to generate adsorbed  $\text{SO}_2$ , (2) the oxidation of adsorbed  $\text{SO}_2$  to produce adsorbed  $\text{SO}_3$  in the form of tridentate sulfate and (3) the desorption of  $\text{SO}_3$  from the catalyst surface to the gas phase.  $\text{NO}_x$  promoted the transformation of low-valent vanadium to high-valent vanadium, which promoted  $\text{SO}_2$  oxidation and resulted in a significant increase in  $\text{SO}_3$ . However, the presence of  $\text{NO}_x$  had no obvious effect on the  $\text{SO}_2$  adsorption and  $\text{SO}_3$  desorption. The presence of  $\text{H}_2\text{O}$  or  $\text{NH}_3$  promoted  $\text{SO}_2$  adsorption and had no significant effect on  $\text{SO}_2$  oxidation. However,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  combined with tridentate sulfate to form a more stable bidentate sulfate and ammonium bisulfate, respectively, and  $\text{SO}_3$  desorption was depressed. The difference was that the inhibition of  $\text{SO}_3$  desorption by  $\text{NH}_3$  was more obvious than that by  $\text{H}_2\text{O}$ . Thus, the formation of gaseous  $\text{SO}_3$  was significantly inhibited by  $\text{NH}_3$  and slightly inhibited by  $\text{H}_2\text{O}$ .

## Conflicts of interest

There are no conflicts to declare.

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