Formation of sulfur trioxide during the SCR of NO with NH₃ over a V₂O₅/TiO₂ catalyst

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The oxidation of sulfur dioxide (SO₂) to sulfur trioxide (SO₃) is an undesirable reaction that occurs during the selective catalytic reduction (SCR) of nitrogen oxides (NOₓ) with ammonia (NH₃), 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 SO₃ formation over a V₂O₅/TiO₂ catalyst and to illustrate the formation mechanism of SO₃ in the presence of NOₓ, H₂O and NH₃. A fixed-bed reactor was combined with a Fourier transform infrared (FTIR) spectrometer and a Pentol SO₃ analyser to test the outlet concentrations of the multiple components. The results showed that the rate of SO₂ oxidation was zero-order in O₂, 0.77-order in SO₂ and -0.19-order in SO₃ and that the apparent activation energy for SO₃ oxidation was 74.3 kJ mol⁻¹ 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 SO₃ formation process is described here in detail. The adsorbed SO₂ was oxidized by V₂O₅ to produce adsorbed SO₃ in the form of bridge tridentate sulfate, and the adsorbed SO₃ was desorbed to the gas phase. NOₓ promoted the oxidation of the adsorbed SO₂ due to the promotion of the conversion of low-valent vanadium to high-valent vanadium. In addition, the desorption of the adsorbed SO₃ was inhibited by H₂O or NH₃ due to the conversion of tridentate sulfate to the more stable bidentate sulfate or ammonium bisulfate. Finally, the mechanism of the influence of NOₓ, H₂O and NH₃ on the formation of gaseous SO₃ was proposed.

1. Introduction

As the use of equipment for the selective catalytic reduction (SCR) of NOₓ has increased in recent years, the emission of SO₃ in coal-fired power plants has attracted more attention.¹⁻³ SO₃ 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.⁴⁻⁶ When the SO₃ concentration in flue gas is more than 5 ppm (18 mg m⁻³), an opaque plume is generated, and a “blue acid plume” appears in the downwind direction of the chimney.⁴⁻⁶ To solve the problem of SO₃ pollution, strict emission standards have been established.⁸ In the United States, 22 states have proposed SO₃ emission limits for coal-fired flue gas, of which 14 states have a limit of 6 mg m⁻³. The SO₃ emission limits in Singapore are 10 mg m⁻³ for flue gas from stationary sources. The daily SO₂ and SO₃ emission limits in Germany are 50 mg m⁻³. In China, regulations have been issued for “eliminating the white smoke” from industrial flue gas, aiming to expose the “blue” and “yellow” smoke from SO₂ and NOₓ, respectively, to achieve deep purification of the smoke.¹⁰⁻¹³ Therefore, research on the SO₃ formation process is very important and urgent.

There has been much discussion about the process of SO₂ oxidation to SO₃ on a V₂O₅/TiO₂ catalyst. Dunn J. P.¹²⁻¹³ studied the oxidation ability of several binary catalysts for SO₂ and found that the oxidation ability of V₂O₅ is greater than that of other transition metal oxides. In addition, the oxidation mechanism of SO₂ on a V₂O₅/TiO₂ catalyst has been proposed. SO₂ may adsorb and coordinate onto the vanadium–oxygen–support (V–O–M) bond, resulting in the (V⁵⁺–SO₃ ads) state. This process is followed by the cleavage of the V⁵⁺–O–SO₃ and formation of gaseous SO₃, which represents the rate determining step. The preferential adsorption of SO₃ results in stronger bonding of SO₃ to the surface vanadium species and competitive adsorption of SO₂ on the active sites. In contrast, Guo X. et al. studied the sulfate species on a V₂O₅/TiO₂ catalyst and concluded that sulfate species are formed on titanium instead of vanadium.¹⁶

H₂O and NH₃ in the atmosphere can inhibit the oxidation of SO₂ to SO₃, while NOₓ has a promotive influence.⁷⁻¹⁰⁻¹² 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...
and guiding appropriate process design. However, kinetic research on the oxidation process of SO\textsubscript{2} is limited. Therefore, it is necessary to simulate the process and influencing factors of SO\textsubscript{2} oxidation over the V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalyst. In this work, the effects of O\textsubscript{2} and SO\textsubscript{2} on SO\textsubscript{3} formation were studied, and the reaction order with respect to the reactants and the apparent activation energy during SO\textsubscript{2} oxidation were calculated to establish the basic kinetics of SO\textsubscript{2} oxidation on a V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalyst. Then, a proposed formation mechanism of SO\textsubscript{3} in a complex atmosphere was obtained by studying the effects of H\textsubscript{2}O, NO\textsubscript{x} and NH\textsubscript{3} on the SO\textsubscript{3} formation process.

2. Experimental

2.1. Catalyst preparation and characterization

The 5 wt% V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts were prepared by the wet impregnation method. Commercial P25 TiO\textsubscript{2} was calcined at 450 °C for 4 h. NH\textsubscript{4}VO\textsubscript{3}, the precursor for V\textsubscript{2}O\textsubscript{5}, was dissolved in distilled water at 80 °C; P25 TiO\textsubscript{2} was added into the NH\textsubscript{4}VO\textsubscript{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 μm.

The pore properties of the P25-TiO\textsubscript{2} and V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts were determined at 77 K through N\textsubscript{2} adsorption (NOVA3200e, Quantachrome, USA). The Brunauer–Emmett–Teller (BET) surface area (S\textsubscript{BET}) and the average pore diameter (\(d\)) were calculated by the BET method and Horvath–Kawazoe equation method, respectively. The total pore volume (V\textsubscript{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 Cu K\textsubscript{\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) TiO\textsubscript{2}. The diffraction peaks of V\textsubscript{2}O\textsubscript{5} (PDF #41-1426) at 15.4°, 20.4°, 21.7°, 26.2° and 31.0° were not observed, indicating that the V\textsubscript{2}O\textsubscript{5} was well distributed on the carrier, with no agglomerated microcrystals for the V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{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 V 2p\textsubscript{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\textsubscript{BET} (m\textsuperscript{2} g\textsuperscript{-1}) | V\textsubscript{t} (ml g\textsuperscript{-1}) | d (nm) |
|--------------|----------------------|---------------------|-------|
| P25-TiO\textsubscript{2} | 55                | 0.262             | 19.14 |
| V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} | 50                | 0.258             | 20.96 |

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

2.2. Activity measurement

The oxidation reactions of SO\textsubscript{2} to generate SO\textsubscript{3} were investigated in a quartz reactor with both an on-line FTIR spectrometer (Tensor 27, Bruker, Germany) capable of quantifying SO\textsubscript{2} with an error of 1% and an on-line SO\textsubscript{3} analyser (Pentol GmbH, Germany) capable of quantifying SO\textsubscript{3} with an error of 10%,\textsuperscript{23} as shown in Fig. 2. The gas flow rate for the standard state was 300 ml min\textsuperscript{-1} with an error of 1%. The gaseous hourly space velocity (GHSV) was approximately 19 000 h\textsuperscript{-1}.

The default reaction conditions for the SO\textsubscript{2} oxidation included 320 °C, 1000 ppm SO\textsubscript{2}, 6 vol% O\textsubscript{2}, and N\textsubscript{2} balance. When appropriate, 500 ppm NO\textsubscript{x} (NO accounted for approximately 90%, and the remainder was NO\textsubscript{2}), 500 ppm NH\textsubscript{3}, or 5 vol% H\textsubscript{2}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 SO\textsubscript{2} concentration varied between 500 and 1500 ppm, and the O\textsubscript{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 NH\textsubscript{3} had a significant impact on the measurement of SO\textsubscript{3}, so the NH\textsubscript{3} was turned off after a relatively short time, before it penetrated the catalyst, to reduce its influence on SO\textsubscript{3} detection. Assuming standard operating conditions, the SO\textsubscript{3} and O\textsubscript{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 μm, indicating that internal diffusion could be neglected. When the gas speed in a vacant tube is above 9.6 cm s\textsuperscript{-1}, the impact of external diffusion on the SO\textsubscript{3} conversion can be ignored. In this work, a catalyst particle size of 180–250 μm...
was selected, and the gas speed in the vacant tube was maintained at 10.6 cm s\(^{-1}\); thus, the effects of internal diffusion and external diffusion were eliminated.

For the temperature-programmed desorption (TPD) experiments, the V\(_2\)O\(_5\)/TiO\(_2\) catalyst was first processed in a 1000 ppm SO\(_2\) and 6 vol% O\(_2\) atmosphere at 320 °C for 180 min and then processed in a N\(_2\), 5 vol% H\(_2\)O or 500 ppm NH\(_3\) atmosphere, respectively, for 20 min. Finally, the TPD tests were carried out in N\(_2\) with a heating rate of 5 °C min\(^{-1}\) 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\(_2\) oxidation to SO\(_3\) at various temperatures, the effect of the O\(_2\) and SO\(_2\) concentrations on SO\(_3\) generation was evaluated, as shown in Fig. 3. In Fig. 3(a), even when the O\(_2\) concentration was zero, some SO\(_3\) was produced at various temperatures, indicating that the oxygen atom in V\(_2\)O\(_5\) participated in the oxidation of SO\(_2\). 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.\(^{24}\) With increasing O\(_2\) concentration,
the SO₃ concentration continued to increase, but the growth rate slowed until the O₂ concentration reached 1%. Thus, the reaction order was approximately zero when the O₂ concentration was more than 1%. Although the oxidation of SO₂ is an exothermic reaction, the increase in temperature was conducive to the formation of SO₃ because the reaction was far from the equilibrium. As shown in Fig. 3(b), as the SO₂ concentration increased from 500 ppm to 1500 ppm, the SO₃ 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 SO₂ conversion quantity increased linearly with the SO₂ concentration, and the higher the temperature was, the greater the slope of the curve was.

The chemical equation for SO₂ 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 reaction order of SO₂ was low in this experiment, so the following assumptions were made: (1) \( r_{SO_2} = [SO_3]/\tau \), and the residence time (\( \tau \)) is a constant; and (2) [SO₂] and [SO₃] are the averages of their import and export concentrations. The reaction order in O₂ was approximately zero. Thus, eqn (3) can be further simplified to eqn (4).

\[
2SO_2 + O_2 \rightarrow 2SO_3 \tag{1}
\]

\[
r_{SO_2} = k[SO_3][SO_3]/[O_2]^2 \tag{2}
\]

\[
\ln r_{SO_2} = \ln k + a \ln[SO_3] + b \ln[SO_3] + c \ln[O_2] \tag{3}
\]

\[
\ln[SO_3] = \frac{\ln k + a \ln[SO_3]}{1 - b} \tag{4}
\]

As shown in Fig. 4, the curves of ln[SO₃] versus ln[SO₂] 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 ± 0.05 and −0.19 ± 0.08, respectively. The reaction rate equation of SO₂ over the V₂O₅/TiO₂ catalyst is given by eqn (5).

\[
r_{SO_2} = k[SO_3]^{0.77}[SO_3]^{-0.19} \tag{5}
\]

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 kJ mol⁻¹ with an error of 2.4%. The reaction rate of SO₂ over the V₂O₅/TiO₂ catalyst is given by eqn (7).

\[
\ln k' = 0.19 \ln[SO_3] - 0.77 \ln[SO_3] \tag{6}
\]

\[
r_{SO_2} = A e^{-\frac{74.3}{RT}[SO_2]^{0.77}[SO_3]^{-0.19}} \tag{7}
\]

The apparent activation energy of SO₂ oxidation was approximately 84–209 kJ mol⁻¹, so the chemical reaction was a rate-limiting step, leading to both the shallow layer and deep layer of the catalyst being involved in the oxidation of SO₂. In contrast, the activation energy of the NO₃ reduction reaction was small at approximately 21 kJ mol⁻¹ and the chemical reaction rate was fast, resulting in only the shallow layer of the catalyst participating in the reduction of NO₃. According to the above differences, reducing the wall thickness of the catalyst was an effective method to reduce the oxidation rate of SO₂ while ensuring denitrification efficiency. In practice, the minimum thickness of the honeycomb walls is determined by their mechanical resistance.

### 3.2 Formation mechanism of SO₃

SO₃ formation was first characterized in a simple atmosphere of SO₂ and O₂, and then the effects of NO₃, H₂O and NH₃ on SO₃ formation were explored to further reveal the mechanism of SO₃ 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            |
O–H at 3550–3750 cm$^{-1}$ decreased. The high frequency peak at 3678 cm$^{-1}$ was attributed to an alkaline hydroxyl group, and the low frequency peak at 3627 cm$^{-1}$ was attributed to a neutral hydroxyl group. 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 cm$^{-1}$ belonged to the H–O–H bending motion of adsorbed H$_2$O, indicating that H$_2$O was formed during the adsorption of SO$_2$. The reduction of the surface hydroxyl group and the formation of adsorbed H$_2$O were a result of the SO$_2$ combining with the surface hydroxyl group on the TiO$_2$ and releasing sulfite species and H$_2$O. The half peaks at 1030–1150 cm$^{-1}$ indicated the existence of sulfite species on the catalyst surface.\textsuperscript{28–30}

The vibration peak at 1363–1385 cm$^{-1}$ belonged to the bridge tridentate sulfate species bound to the carrier.\textsuperscript{16,31–33} As the reaction proceeded, the peak intensity increased, indicating that the surface sulfate increased. As the peak gradually shifted from 1363 cm$^{-1}$ to 1385 cm$^{-1}$, the hydroxyl peak gradually shifted from 3678 cm$^{-1}$ to 3651 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 H$_2$O disappeared, but the wide peak at 1100–1300 cm$^{-1}$ increased significantly. These peaks belonged to the chelated bidentate sulfate, bridge bidentate sulfate and unidentate sulfate.\textsuperscript{34} This observation indicated that the bridge tridentate sulfate changed to bidentate sulfate or unidentate sulfate under the action of H$_2$O.

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

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

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

![Fig. 6](image6.png) **Fig. 6** *In situ* DRIFT spectra of the catalyst in the formation process of SO$_3$. (Conditions: 1000 ppm SO$_2$, 6 vol% O$_2$, and N$_2$).

![Fig. 7](image7.png) **Fig. 7** Transient effects of NO$_x$ on SO$_3$ formation (conditions: 1000 ppm SO$_2$, 500 ppm NO$_x$, 6 vol% O$_2$, and N$_2$).
approximately 60%. When the flow of NO\textsubscript{x} was stopped, the SO\textsubscript{3} concentration gradually decreased to the initial concentration. The enhancement may have been due to the oxidation of SO\textsubscript{2} by NO\textsubscript{x}, which was in the gas phase or adsorbed on the catalyst surface.

The effects of H\textsubscript{2}O on SO\textsubscript{3} formation are shown in Fig. 8. With the addition of H\textsubscript{2}O, the SO\textsubscript{3} concentration sharply increased from 11 ppm to 23 ppm and then gradually decreased to 8.5 ppm. Compared with the initial concentration, the SO\textsubscript{3} concentration first doubled and then decreased by 23%. It can be inferred that the SO\textsubscript{3} desorption from the active site into the gas phase was due to a competitive adsorption between H\textsubscript{2}O and SO\textsubscript{3}. When the flow of H\textsubscript{2}O was stopped, the SO\textsubscript{3} concentration sharply decreased to nearly zero and then returned to a constant of 12 ppm. The sharp decrease in the SO\textsubscript{3} concentration occurred because more active sites were released by the H\textsubscript{2}O desorption and more SO\textsubscript{3} was adsorbed.

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

In short, the process of gaseous SO\textsubscript{3} formation includes SO\textsubscript{2} adsorption, SO\textsubscript{2} oxidation and SO\textsubscript{3} desorption. To clarify in which step NO\textsubscript{x}, H\textsubscript{2}O and NH\textsubscript{3} affect SO\textsubscript{3} formation, the three steps were tested separately. The SO\textsubscript{2} oxidation was investigated first, followed by the SO\textsubscript{2} adsorption and SO\textsubscript{3} desorption.

### 3.4. Effects of NO\textsubscript{x}, H\textsubscript{2}O and NH\textsubscript{3} on SO\textsubscript{2} oxidation

To further investigate the effects of NO\textsubscript{x}, H\textsubscript{2}O and NH\textsubscript{3} on SO\textsubscript{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 NO\textsubscript{x}, the adsorption band of N\textsubscript{2}O at 1303 cm\textsuperscript{-1} appeared\textsuperscript{36,37}, the adsorption band of V\textsuperscript{3+} at 2041 cm\textsuperscript{-1} decreased, and the peak of tridentate sulfate at 1380–1386 cm\textsuperscript{-1} decreased. Thus, NO\textsubscript{x} was reduced to N\textsubscript{2}O while V\textsuperscript{3+} was oxidized to V\textsuperscript{5+}, and the increase in V\textsuperscript{5+} promoted...
the oxidation of the adsorbed SO₂. After the removal of the NOₓ, the adsorbed N₂O peak disappeared, and the tridentate sulfate peak returned to its initial state. Therefore, NOₓ promoted SO₂ oxidation by promoting the conversion of V³⁺ to V⁵⁺. No SO₃ formation was detected in the absence of the catalyst in the SO₂, O₂ and NOₓ atmospheres, indicating that the promotion effect of NOₓ on SO₂ oxidation acted on the catalyst surface instead of in the gas phase.

As shown in Fig. 11, after the addition of H₂O, the V=O peak at 2041 cm⁻¹ did not change significantly, the tridentate sulfate peak at 1379–1386 cm⁻¹ decreased slightly, and the bidentate sulfate peak at 1176–1240 cm⁻¹ increased. A bending vibration peak attributable to S–O–H was observed at 1295 cm⁻¹, indicating that H₂O promoted the transformation of tridentate sulfate to bidentate sulfate, which partly existed in the form of bisulfate. After the removal of the H₂O, the tridentate sulfate peak increased to its initial state, the bidentate sulfate peak increased further, and the bending vibration peak of S–O–H decreased, indicating that the proportion of hydrogen sulfate decreased.

As shown in Fig. 12, in the presence of NH₃, the peak position of tridentate sulfate shifted from 1387 cm⁻¹ to 1588 cm⁻¹, and the peak intensity decreased significantly. Further, new adsorption bands of NH₄⁺ at 1424 cm⁻¹ and S–O–H at 1301 cm⁻¹ appeared. NH₃ was partially oxidized on the catalyst surface to produce H₂O. In addition, there were hydroxyl groups on the catalyst surface. Thus, tridentate sulfate

**Fig. 11** In situ DRIFT spectra of the catalyst with H₂O flow (conditions: 1000 ppm SO₂, 5 vol% H₂O, 6 vol% O₂, and N₂).

**Fig. 12** In situ DRIFT spectra of the catalyst with NH₃ flow (conditions: 1000 ppm SO₂, 500 ppm NH₃, 6 vol% O₂, and N₂).

**Fig. 13** XPS characterization of the V₂O₅/TiO₂ catalysts after exposure to various gases (blank conditions: 1000 ppm SO₂ and N₂; other conditions: addition of 500 ppm NOₓ, 500 ppm NH₃ or 5% H₂O).
combined with NH₃ and hydroxyl or H₂O to produce ammonium bisulfate. The adsorption band of V⁵⁺ increased in the presence of NH₃, showing that V⁵⁺ was reduced to V³⁺ by NH₃. The decrease of V⁵⁺ inhibited the oxidation of the adsorbed SO₂.

To confirm the effects of NOₓ, H₂O and NH₃ on the valence state of vanadium, XPS characterization was performed on the V₂O₅/TiO₂ catalysts exposed to various atmospheres, and the spectra are shown in Fig. 13. The V 2p₃/₂ spectra were separated into two peaks by the Gaussian–Lorentzian deconvolution method, including the V³⁺ peak (515.0 eV) and V⁵⁺ peak (516.4 eV).⁴⁰,⁴¹ and the vanadium contents of various valences are shown in Table 4. Compared with the blank catalyst, the proportion of V⁵⁺ obviously increased from 46% to 72% in the presence of NOₓ, which may have been caused by the oxidation of V³⁺ by NOₓ. Similarly, the addition of H₂O led to a slight increase in the proportion of V⁵⁺. In contrast, the proportion of V⁵⁺ slightly decreased in the presence of NH₃ because of the reduction of V⁵⁺ by NH₃. The effect of NOₓ on the vanadium valence was generally more significant than that of H₂O and NH₃.

Based on the analysis of the results shown in Fig. 10–13, NOₓ promoted the conversion of V³⁺ to V⁵⁺, thereby accelerating the oxidation of the adsorbed SO₂. 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 SO₂ oxidation. It can be inferred that, in the presence of H₂O or NH₃, the tridentate sulfate transformed to the more stable bidentate sulfate and thereby inhibited the desorption of SO₃, which was verified by the TPD tests discussed below.

### 3.5. Effects of NOₓ, H₂O and NH₃ on SO₂ adsorption and SO₃ desorption

First, the effects of NOₓ, H₂O and NH₃ on SO₂ adsorption were investigated, and the breakthrough curves of SO₂ are shown in Fig. 14. For the blank, the SO₂ concentration increased rapidly, corresponding to the adsorption stage of SO₂, and tended to stabilize at 970 ppm, corresponding to the catalytic oxidation stage of SO₂, with a SO₂ conversion ratio of approximately 3%. After the addition of NOₓ, the SO₂ concentration decreased from 970 ppm to 960 ppm and tended to be stable, which was attributed to the promotion effect of NOₓ on the SO₂ oxidation instead of the SO₂ adsorption. After the addition of H₂O or NH₃, the SO₂ 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 H₂O or NH₃ promoted the SO₂ adsorption. Finally, the SO₂ concentration exceeded 970 ppm, which was due to the adsorption saturation of the alkaline sites from the adsorption of NH₃ and H₂O on the catalyst surface.

![Fig. 14](image1.png)

**Fig. 14** Effects of NOₓ, H₂O and NH₃ on SO₂ adsorption over the V₂O₅/TiO₂ catalyst (blank conditions: 1000 ppm SO₂ and N₂; other conditions: 500 ppm NOₓ, 500 ppm NH₃ or 5% H₂O).

![Fig. 15](image2.png)

**Fig. 15** Effects of NOₓ, H₂O and NH₃ on SO₃ desorption (blank conditions: 1000 ppm SO₂, 6 vol% O₂ and N₂; other conditions: 500 ppm NOₓ, 500 ppm NH₃ or 5% H₂O).

![Fig. 16](image3.png)

**Fig. 16** TPD curves of the catalysts adsorbed in various atmospheres (blank pretreatment conditions: N₂; other conditions: 500 ppm NH₃ or 5% H₂O).
The effects of NO\(_x\), H\(_2\)O and NH\(_3\) on SO\(_3\) desorption are shown in Fig. 15. For the blank, as the SO\(_2\) and O\(_2\) sources were removed, the SO\(_3\) concentration gradually decreased, showing that the adsorbed SO\(_2\) was desorbed in the flow of N\(_2\). After the addition of NO\(_x\), the desorption curves of SO\(_3\) coincided with that of the blank, indicating that NO\(_x\) did not influence the SO\(_3\) desorption. After the addition of H\(_2\)O, the SO\(_3\) concentration sharply doubled to a maximum and then gradually decreased. These results indicated that there was a strong competitive adsorption between H\(_2\)O and SO\(_3\). After the addition of NH\(_3\), the SO\(_3\) concentration gradually increased by approximately 2 ppm due to a mild competitive adsorption between NH\(_3\) and SO\(_3\). H\(_2\)O or NH\(_3\) and SO\(_3\) competitively adsorbed to promote SO\(_3\) desorption, but the promotion of SO\(_3\) desorption was not sustainable. Further, H\(_2\)O or NH\(_3\) combined with the adsorbed SO\(_3\) to form a more stable bidentate sulfate and ammonium bisulfate, which ultimately inhibited the SO\(_3\) desorption. This phenomenon was most obvious in the presence of NH\(_3\). Although the NH\(_3\) was removed, the SO\(_3\) concentration decreased to less than that of the blank.

The addition of NH\(_3\) and H\(_2\)O had an obvious inhibitory effect on the desorption of 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 SO\(_3\) desorption both increased by 60–70 °C in the presence of H\(_2\)O and increased significantly by 120–130 °C in the presence of NH\(_3\). These results showed that the presence of H\(_2\)O and NH\(_3\) made SO\(_3\) much more difficult to desorb and that NH\(_3\) inhibited SO\(_3\) desorption more effectively than did H\(_2\)O. The peak areas of 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 SO\(_3\) was approximately equal. Thus, H\(_2\)O and NH\(_3\) affected the adsorption state of SO\(_3\) but not the adsorption amount.

The formation of SO\(_3\) during the SCR of NO\(_x\) with NH\(_3\) in the presence of H\(_2\)O is summarized in Fig. 17. The formation of SO\(_3\) was obviously promoted by NO\(_x\), significantly inhibited by NH\(_3\), and slightly inhibited by H\(_2\)O. NO\(_x\) promoted the SO\(_2\) oxidation in that the NO\(_x\) promoted the transformation of low-valent vanadium to high-valent vanadium. H\(_2\)O and NH\(_3\) combined with the adsorbed SO\(_3\) to form bidentate sulfate and bisulfate, respectively, and the SO\(_3\) desorption was depressed. The inhibition of the SO\(_3\) desorption by NH\(_3\) was stronger than that by H\(_2\)O.

4. Conclusions

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

Conflicts of interest

There are no conflicts to declare.

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