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Effects of SO₂ and H₂O on low-temperature NO conversion over F-V₂O₅-WO₃/TiO₂ catalysts

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ABSTRACT

F-V₂O₅-WO₃/TiO₂ catalysts were prepared by the impregnation method. As the content of F ions increased from 0.00 to 0.35 wt.%, the NO conversion of F-V₂O₅-WO₃/TiO₂ catalysts initially increased and then decreased. The 0.2F-V₂O₅-WO₃/TiO₂ catalyst (0.2 wt.% F ion) exhibited the best denitration (De-NO_x) performance, with more than 95% NO conversion in the temperature range 160–360°C, and 99.0% N₂ selectivity between 110 and 280°C. The addition of an appropriate amount of F ions eroded the surface morphology of the catalyst and reduced its grain size, thus enhancing the NO conversion at low temperature as well as the sulfur and water resistance of the V₂O₅-WO₃/TiO₂ catalyst. After selective catalytic reduction (SCR) reaction in a gas flow containing SO₂ and H₂O, the number of NH₃ adsorption sites, active component content, specific surface area and pore volume decreased to different degrees. Ammonium sulfate species deposited on the catalyst surface, which blocked part of the active sites and reduced the NO conversion performance of the catalyst. On-line thermal regeneration could not completely recover the catalyst activity, although it prolonged the cumulative life of the catalyst. In addition, a mechanism for the effects of SO₂ and H₂O on catalyst NO conversion was proposed.

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Introduction

Nitrogen oxides (NO_x) are not only major atmospheric pollutants involved in environmental problems such as photochemical smog and urban haze pollution, but also important precursors and oxidants for the formation of nitrates and sulfates (Cheng et al., 2016). At present, the main control technology for stationary source NO_x emissions is selective catalytic reduction (SCR), which converts NO_x into N₂ and H₂O using NH₃ as a reducing agent (Bosch and Janssen, 1988; Busca et al., 1998; Lietti et al., 2000; Nova et al., 1998), and SCR

technology mainly uses V₂O₅-MoO₃/TiO₂ and V₂O₅-WO₃/TiO₂ catalysts. According to the flue gas temperature, the SCR catalysts are divided into medium-high temperature (>300°C) catalysts and low temperature (≤300°C) catalysts. Among these catalysts, the medium-high temperature SCR technology is mature, but the low-temperature SCR catalysts are easily affected in complex flue gas conditions: SO₂ is easily adsorbed onto the catalyst surface and part of the SO₂ is oxidized into SO₃ (Lietti et al., 2000). Then, SO₃ reacts with NH₃ to generate side reaction products, such as NH₄H₂SO₄, (NH₄)₂S₂O₇ and (NH₄)₂SO₄ in the presence of H₂O (Qi and Yang, 2003; Phil et al., 2008), which could plug the catalyst pore

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structure and prevent NO_x , NH_3 and O_2 from reaching the active surface of the catalyst, finally leading to a decrease in denitration (De-NO_x) activity (Liu and He, 2010; Song et al., 2016).

Furthermore, with the increasingly stringent NO_x emission limits and the enforcement of environmental regulations, the traditional medium-high temperature SCR technology can still meet the NO_x emission standards in the electric power industry. However, the exhaust temperature of non-electric industrial boilers is mostly lower than 300°C , and the gas composition varies greatly, so that medium-high temperature SCR technology cannot be successfully utilized in non-electric industries. Therefore, research on SCR catalysts that are high-activity and sulfur-resistant at low temperature has become a hotspot in the field of flue gas De-NO_x treatment.

In recent years, some scholars have tried to add F ions to improve the NO conversion performance of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts. For instance, F ions were incorporated into the TiO_2 lattice, replacing part of the lattice oxygen, which changed the surface morphology and formed V^{4+} , W^{5+} and Ti^{3+} ions by means of charge compensation and oxygen vacancies. Meanwhile, the added F ions increased the interaction between WO_3 and TiO_2 , promoted the dispersion of active components and the formation of superoxide groups, prevented grain growth, inhibited the phase transformation of TiO_2 from anatase to rutile, and produced more adsorbed active NH_3 species. At the same time, the NO adsorption capacity was increased, which was beneficial to the formation of the SCR intermediates NO_2 and NO_3 , and finally improved the NO conversion, sulfur and water resistance of the catalyst (Jin et al., 2017; Li and Zhong, 2009; Yang et al., 2016; Zhang and Zhong, 2012; Zhao et al., 2010, 2013; Zhang et al., 2012, 2014a, 2014b, 2015a, 2015b). Some scholars (Su et al., 2003; Wang et al., 2015) modified Al_2O_3 , TiO_2 and ZrO_2 with F ions, but this had no significant effect on the NO conversion of the catalysts, and even reduced the redox performance and chemically adsorbed oxygen concentration of Mn/TiO_2 catalysts, resulting in a decrease in catalyst activity.

Based on results in the literature, this study added F ions to improve the low-temperature NO conversion and the sulfur and water resistance of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts. Meanwhile, the effects of SO_2 and H_2O on the NO conversion of the catalysts were characterized by Brunauer-Emmett-Teller (BET), X-ray fluorescence (XRF), scanning electron microscope (SEM), X-ray diffraction (XRD), thermogravimetric (TG), Fourier transform infrared spectroscopy (FT-IR) and temperature programmed reduction with hydrogen (H_2 -TPR).

1. Materials and methods

1.1. Catalyst preparation

$\text{F-V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts were prepared by the impregnation method, and the precursor for F ions was NH_4F . The detailed preparation method was as follows: NH_4VO_3 , $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$, NH_4F and TiO_2 were mixed in dilute oxalic acid solution in the desired proportions and stirred for 2 hr at 50°C .

Subsequently, the formed viscous slurries were oven-dried at 105°C for 4 hr, then calcined at 490°C for 3 hr. Finally, the prepared $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts with F ion contents of 0.00, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35 wt.% were designated as 0F-3VWT, 0.05F-3VWT, 0.1F-3VWT, 0.15F-3VWT, 0.2F-3VWT, 0.25F-3VWT, 0.3F-3VWT and 0.35F-3VWT, respectively, and the samples after the SCR reaction containing SO_2 and H_2O were uniformly denoted as F-3VWTSH.

1.2. Catalyst activity test

Catalyst activity was tested in a fixed-bed flow reactor (inner diameter 20 mm) at $110\text{--}440^\circ\text{C}$. Reactant gases were controlled by mass flow meters and mixed before entering the reactor. The gas hourly space velocity (GHSV) was $30,000\text{ hr}^{-1}$ at a flow rate of 1500 mL/min. NO was detected online using a 42i-HL nitrogen oxides analyzer (42i-HL, Thermo Electron Co., USA) and SO_2 was determined by a Testo 350 flue gas analyzer (Testo 350, Testo Co., Germany). The selectivity of N_2 was analyzed by a Bruker Tensor 27 Fourier transform infrared spectrometer (Tensor 27, Bruker Co., Germany) and GC-2014C gas chromatograph (GC-2014C, Shimadzu, Japan). The NO conversion (C_{NO}), N_2 selectivity (S_{N_2}), and deactivation rate (DR) are calculated as follows:

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

$$S_{\text{N}_2} = [\text{N}_2]_{\text{out}} / ([\text{N}_2]_{\text{out}} + [\text{N}_2\text{O}]_{\text{out}} + 0.5[\text{NO}_2]_{\text{out}}) \times 100\% \quad (2)$$

$$\text{DR} = (C_{\text{NO-initial}} - C_{\text{NO-final}}) / t \quad (3)$$

where, $[\text{NO}]_{\text{in}}$, $[\text{NO}]_{\text{out}}$, $[\text{N}_2]_{\text{out}}$, $[\text{N}_2\text{O}]_{\text{out}}$, $[\text{NO}_2]_{\text{out}}$, $C_{\text{NO-initial}}$, $C_{\text{NO-final}}$ and t are inlet NO concentration, outlet NO concentration, outlet N_2 concentration, outlet N_2O concentration, outlet NO_2 concentration, initial NO conversion, final NO conversion and time, respectively.

1.3. Catalyst characterization

Specific surface areas and pore volumes of the catalysts were measured on an ASAP 2020 automatic physical adsorption instrument (ASAP 2020; Micromeritics Co., USA). Samples were vacuum pretreated at 250°C for 4 hr, and N_2 was statically adsorbed at -196°C . The BET (Brunauer-Emmett-Teller) method was used to calculate the specific surface area (S_{BET}). Catalyst components were analyzed using a Magix PW2403 X-ray fluorescence (XRF) spectrometer (Magix PW2403, PANalytical Co., Netherlands), and the concentration range analyzed was from 10^{-6} to 100%. Catalyst morphology was analyzed by a S-4300 (S-4300, Hitachi Science & Technology Corp., Japan) field emission scanning electron microscope (SEM). Samples were mounted face up and firmly adhered to the sample table with conductive adhesive. The samples were sputter-coated with gold to improve the conductivity and secondary electron production. Crystal structures of samples were obtained on a Bruker D8 Advance X-ray diffractometer (XRD, Bruker D8, Bruker Co., Germany) using $\text{Cu K}\alpha$ radiation (wavelength (λ) = 0.15406 nm) in the 2θ range from 10° to 80° . Fourier transform infrared spectroscopy (FT-IR) was performed using a Nicolet 6700 spectrometer (Nicolet 6700,

Thermo Co., USA) at wavenumbers ranging from 750 to 2250 cm^{-1} ; spectra were scanned 32 times with a resolution of 4 cm^{-1} . Thermogravimetric (TG) analysis was carried out on a TG/DTA6300 instrument (TG/DTA6300, NSK Ltd., Japan) from 25 to 600°C (heating rate was 10°C/min). Temperature programmed reduction with hydrogen (H_2 -TPR) was performed on an AutoChem II Model 2920 chemisorption instrument (2920, Micromeritics Co., USA) with 10 vol.% H_2/Ar at a constant flow rate of 50 mL/min (Chao et al., 2015; Liang et al., 2017; Song et al., 2014; Zhang et al., 2017).

2. Results and discussion

2.1. Effect of F ions on NO conversion over 3VWT catalysts

The results indicated that the NO conversion over the 3VWT catalysts at low temperature was improved by the addition of F ions as shown in Fig. 1. As the content of F ions increased, the NO conversion of the catalysts initially increased and then decreased. The 0.2F-3VWT catalyst exhibited the best De- NO_x performance, with more than 95% NO conversion in the temperature range 160–360°C and 99.0% N_2 selectivity between 110 and 280°C. However, the adsorption of NH_3 on the catalyst surface was slightly reduced by the presence of excess F ions, further leading to decline in the De- NO_x performance (Zhang et al., 2012, 2014a, 2014b, 2015a, 2015b; Zhang and Zhong, 2012; Zhao et al., 2010, 2013).

2.2. Effect of SO_2 on NO conversion over F-3VWT catalysts

NO conversion over the F-3VWT catalyst was evaluated in the presence of 0.03 vol.% SO_2 at 200°C, and the result is shown in Fig. 2. 99.9% NO conversion was achieved initially, which then decreased to 93.8% when the reaction time reached 928 hr.

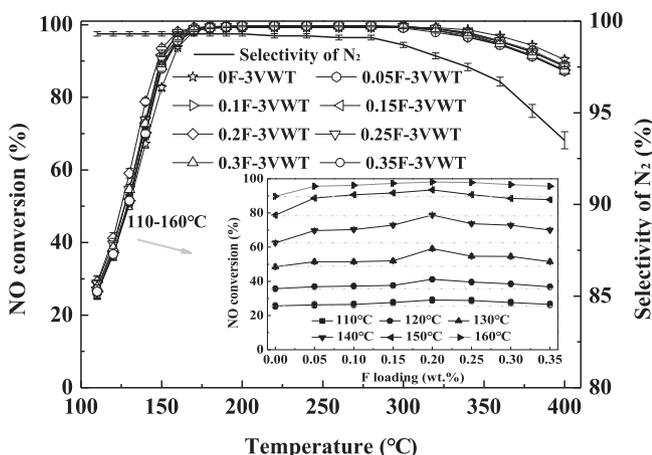


Fig. 1 – Effect of F ions on NO conversion over $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ (3VWT) catalysts. Reaction conditions: $[\text{NH}_3] = [\text{NO}] = 0.07$ vol.%, $[\text{O}_2] = 5$ vol.%, N_2 balance, gas hourly space velocity (GHSV) = 30,000 hr^{-1} . aF-3VWT refers to 3VWT catalysts with a wt.% F loading; [X] refers to the concentration of the X species.

The lowest NO conversion achieved during the overall experimental process was 92.4%. Under identical flue gas conditions, the sulfur resistance of the 0F-3VWT and 0.2F-3VWT catalysts was compared for the reaction time of 24 hr. In the absence of SO_2 , the NO conversion over the 0F-3VWT and 0.2F-3VWT catalysts was 99.3% and 99.9% respectively. After adding SO_2 to the fixed-bed system for 21 hr, the NO conversion of the 0F-3VWT catalyst dropped to 90.7%, while that of the 0.2F-3VWT catalyst remained steady at 99.9%. This indicated that the addition of an appropriate amount of F ions inhibited the adsorption of SO_2 and SO_3 on the catalyst surface and greatly promoted the sulfur resistance of 3VWT catalyst (Hou et al., 2014).

2.3. Effect of SO_2 and H_2O on NO conversion over F-3VWT catalysts

The catalyst was typically deactivated below 220°C (the dew point temperature of ammonium sulfate) in the presence of SO_2 and H_2O . Therefore, the sulfur resistance, water resistance and online thermal regeneration performance of the 0.2F-3VWT catalyst were investigated in the presence of 0.035 vol.% SO_2 and 15 vol.% H_2O at 240°C, as shown in Fig. 3a. The initial NO conversion of the catalyst was 99.9% without H_2O , and the activity decreased from 99.0% to 97.2% in the presence of 15 vol.% H_2O when the reaction time reached 100 hr. When 0.035 vol.% SO_2 and 15 vol.% H_2O were added to the fixed-bed system, the NO conversion decreased from 97.0% to 80.0% after 78 hr. However, the NO conversion rapidly recovered to 91.7% after stopping the addition of H_2O and SO_2 , which indicated that SO_2 and H_2O had a crucial influence on the activity of the catalyst.

The activities of the poisoned catalysts after regenerating at 350, 375, 400 and 425°C were compared in the presence of 0.035 vol.% SO_2 and 15 vol.% H_2O at 240°C. When the regeneration temperature was set at 350°C, the NO conversion returned to 94.2%, and the activity decreased to 80.0% after

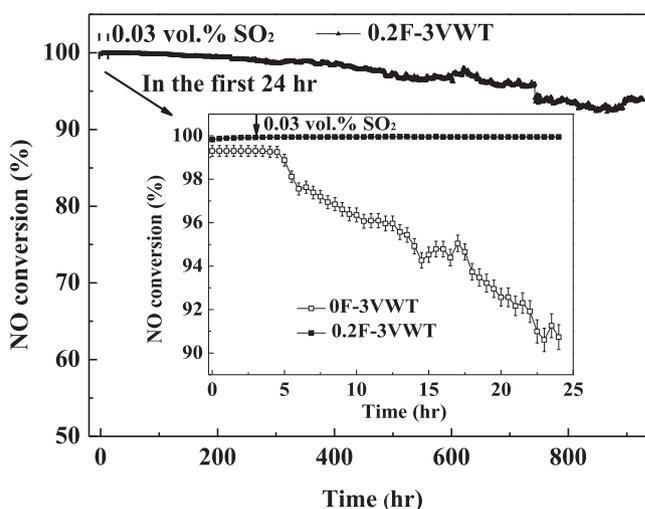


Fig. 2 – Effect of SO_2 on NO conversion over F-3VWT catalysts. Reaction conditions: $[\text{NH}_3] = [\text{NO}] = 0.07$ vol.%, $[\text{SO}_2] = 0.03$ vol.%, $[\text{O}_2] = 5$ vol.%, N_2 balance, GHSV = 30,000 hr^{-1} .

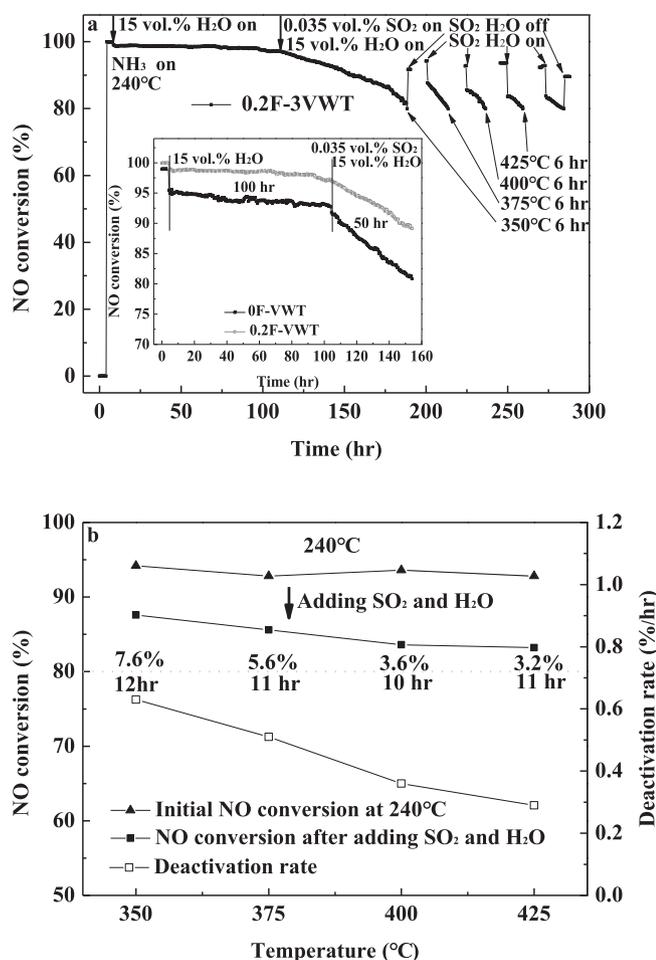


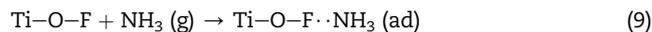
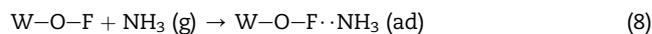
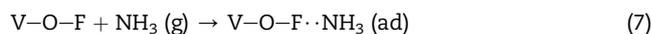
Fig. 3 – (a) Effect of SO₂ and H₂O on NO conversion over F-3VWT catalysts and (b) comparison of various parameters during the process of thermal regeneration at different temperatures. Reaction conditions: [NH₃] = [NO] = 0.07 vol.%, [O₂] = 5 vol.%, [SO₂] = 0.035 vol.%, [H₂O] = 15 vol.%, N₂ balance, GHSV = 30,000 hr⁻¹.

12 hr. When the regeneration temperature switched to 375°C, NO conversion returned to 92.8%, and the activity decreased to 80.0% after 11 hr. Subsequently, when the regeneration temperature was increased to 400°C, NO conversion returned to 93.6%, and the activity decreased to 80.0% after 10 hr. Finally, on further increase of the regeneration temperature to 425°C, NO conversion returned to 92.8%, and the activity decreased to 80.0% after 11 hr. It should be noted that the NO conversion recovered rapidly to 89.5% after stopping the introduction of H₂O and SO₂ after 288 hr.

The sulfur resistance and water resistance of 0F-3VWT and 0.2F-3VWT catalysts were also compared. When there was no H₂O or SO₂ in the reaction gas, the initial NO conversion over the 0F-3VWT and 0.2F-3VWT catalysts was 99.0% and 99.9% respectively. After adding 15 vol.% H₂O to the fixed-bed system for 100 hr, the NO conversion of the two catalysts first decreased to 95.5% and 99.0%, then dropped to 92.7% and 97.2%. This indicated that the 0.2F-3VWT catalyst effectively inhibited the sudden decrease of NO conversion and weakened the negative effect of H₂O on

NO conversion. Subsequently, when 0.035 vol.% SO₂ and 15 vol.% H₂O existed simultaneously in the reaction gas, the NO conversion decreased to 91.8% and 97.0%, respectively, and then dropped to 80.8% and 89.2% after 50 hr. The results showed that the sulfur resistance and water resistance of the catalysts were improved by adding an appropriate amount of F ions.

Based on the above experimental results, a mechanism for the effect of F ions on catalyst performance was proposed. The active F species could chemically adsorb onto V–O, W–O and Ti–O sites (Hou et al., 2014) over the surface of the V₂O₅-WO₃/TiO₂ catalysts, therefore, new V–O–F·NH₃, W–O–F·NH₃ and Ti–O–F·NH₃ intermediates were generated for NH₃ adsorption, changing the interaction laws between catalysts and NH₃, NO, SO₂, H₂O species. The specific reactions were as follows:



where (g) and (ad) refer to gas state and adsorption state, respectively.

A series of parameters were studied to understand the deactivation rates shown in Fig. 3b. The regeneration program was initiated when the NO conversion declined to 80.0%. With the increase of the regeneration temperature, the deactivation rate gradually decreased from 0.63%/hr for regeneration at 350°C to 0.29%/hr for regeneration at 425°C, but the initial NO conversion after adding SO₂ and H₂O also decreased gradually, which indicated that the catalyst was irreversibly poisoned to some extent under the experimental conditions.

2.4. Structural analysis

The specific surface areas of 0F-3VWT, 0.05F-3VWT, 0.1F-3VWT, 0.15F-3VWT, 0.2F-3VWT, 0.25F-3VWT, 0.3F-3VWT and 0.35F-3VWT are 82.1, 81.8, 82.3, 82.0, 81.7, 81.8, 81.8, and 82.1 m²/g, respectively. It was seen that the addition of trace amounts of F ions had almost no effect on the specific surface area of the catalyst, and the specific surface area basically remained steady at about 82.0 m²/g. From the upper part of Table 1, it can be seen that the specific surface area and pore volume of the catalyst after SCR reaction containing SO₂ and H₂O decreased significantly from 82.1 m²/g and 0.32 cm³/g to 52.6 m²/g and 0.21 cm³/g, respectively. The results showed that the side reaction products deposited on the catalyst surface and occupied the pore channels, reducing the contact frequency between the reaction gas and active sites, and resulted in a decrease in catalyst activity.

Table 1 – Comparison of physical properties of F-3VWT catalysts.

Characterization	List of content	0.2F-3VWT	0.2F-3VWTSH
Structure performance	BET (m ² /g)	82.1	52.6
	Pore volume (cm ³ /g)	0.32	0.21
	Average pore diameter (nm)	16.0	15.9
XRF	Component	Weight fraction (%)	
	TiO ₂	89.93	90.25
	V ₂ O ₅	2.99	2.20
	WO ₃	5.87	4.85
	P ₂ O ₅	0.93	0.87
	F	0.17	0.15
TG	SO ₃	0.1	1.67
	Temperature stages (°C)	Weight loss fraction (%)	
	25–600	4.26	8.84
	25–100	2.28	2.96
	220–440	0.73	4.28

BET: Brunauer-Emmett-Teller; XRF: X-ray fluorescence; TG: thermogravimetric.

2.5. Component analysis

A comparison of the components of 0.2F-3VWT catalysts before and after reaction in the presence of SO₂ and H₂O is shown in the middle part of Table 1. The contents of TiO₂, V₂O₅, WO₃, P₂O₅ and F in the fresh catalyst were almost the same as the theoretical contents, and trace S species were detected because the TiO₂ support itself contained some SO₄²⁻. After SCR reaction containing SO₂ and H₂O, the active component contents of the 0.2F-3VWT catalyst, including V₂O₅, WO₃ and P₂O₅, showed different degrees of loss, and the content of S species (SO₃) increased significantly, about 1.57% higher than that of the fresh catalyst, which indicated that the poisoned catalyst adsorbed a certain amount of S species and deposited sulfate.

2.6. SEM analysis

The SEM images of F-3VWT catalysts at magnifications of 10,000 and 5000 before and after reaction in the presence of SO₂ and H₂O are shown in Fig. 4. The fresh 0F-3VWT catalyst had a regular particle size, and the addition of F ions eroded the surface morphology of the VWT catalyst and reduced its grain size, which increased the contact frequency between the reaction gas and active sites. After SCR reaction containing SO₂ and H₂O, the surface of catalyst was filled and blocked by side products, and the pore volume was greatly reduced, finally resulting in a decrease in catalyst activity.

2.7. XRD analysis

Fig. 5 shows the XRD patterns of the five samples, showing that they mainly consisted of anatase TiO₂, with diffraction peaks appearing at 25.3°, 37.8°, 48.0°, 53.8°, 55.3°, 62.7°, 68.8°, 70.4° and 75.0°. Because of the homogeneous distribution of F ions, no diffraction peaks corresponding to fluoride phases

were detected. The diffraction peaks of sulfate and sulfite phases were weaker and almost did not appear in the pattern of the 0.2F-3VWTSH catalyst after reaction in the presence of SO₂ and H₂O, because sulfate or sulfite deposited uniformly on the catalyst surface or their diffraction peaks were overlapped by those of TiO₂.

2.8. FT-IR analysis

The FT-IR spectra of F-3VWT catalysts before and after reaction in the presence of SO₂ and H₂O are presented in Fig. 6. A strong band at 1630 cm⁻¹ due to the vibration of H₂O species appeared in the spectra of the two catalysts, which was due to water vapor adsorbed by the catalysts. Compared with the fresh catalysts with only one main peak, the poisoned catalysts showed a prominent NH₄⁺ absorption peak at 1394 cm⁻¹ and weak SO₄²⁻ absorption peaks at 958, 1038 and 1128 cm⁻¹. These results indicated that the poisoned catalysts adsorbed a certain amount of NH₃ and SO_x or had deposits of side reaction products containing NH₄⁺ and SO₄²⁻ (Liang et al., 2017).

2.9. TG analysis

The TG and weight loss curves of F-3VWT catalysts before and after reaction in the presence of SO₂ and H₂O at different stages are presented in Fig. 7 and the lower part of Table 1. The 0.2F-3VWTSH catalyst had greater weight loss than the 0.2F-3VWT catalyst, which was mainly distributed in two stages at 25–100 and 220–440°C. The first stage corresponded to the evaporation of water vapor, and the weight loss of the 0.2F-3VWTSH catalysts was 2.96% larger than the corresponding fresh catalyst, which was due to the 0.2F-3VWTSH catalyst adsorbing more water vapor during the SCR reaction. The second stage corresponded to the decomposition of side reaction products, which was in accordance with the decomposition temperature of NH₄HSO₄ and (NH₄)₂SO₄. The 0.2F-3VWT catalyst experienced almost no weight loss; however, the 0.2F-3VWTSH catalyst showed significant weight loss of about 4.28%, and the maximum weight loss rate was 0.048%/°C, which revealed that a certain amount of sulfate side products were deposited on the surface of the catalyst after SCR reaction containing SO₂ and H₂O, leading to a gradual decrease in the catalyst activity.

2.10. H₂-TPR analysis

H₂-TPR profiles of 0.2F-3VWT catalysts before and after reaction in the presence of SO₂ and H₂O are shown in Fig. 8. Addition of F ions caused the reduction peak of VO_x to be concentrated in the temperature range of 420–500°C. After SCR reaction containing SO₂ and H₂O, the VO_x reduction peak shifted to the lower temperature range of 370°C. At the same time, a reduction peak for ammonium sulfate or S species of the active component appeared at 550–650°C (Jin et al., 2017; Waqif et al., 1997; Wu et al., 2013; Yang et al., 2013; Zhang et al., 2015a, 2015b). The above two results indicated that the catalyst components may be sulfated, resulting in the irreversible poisoning of the catalyst.

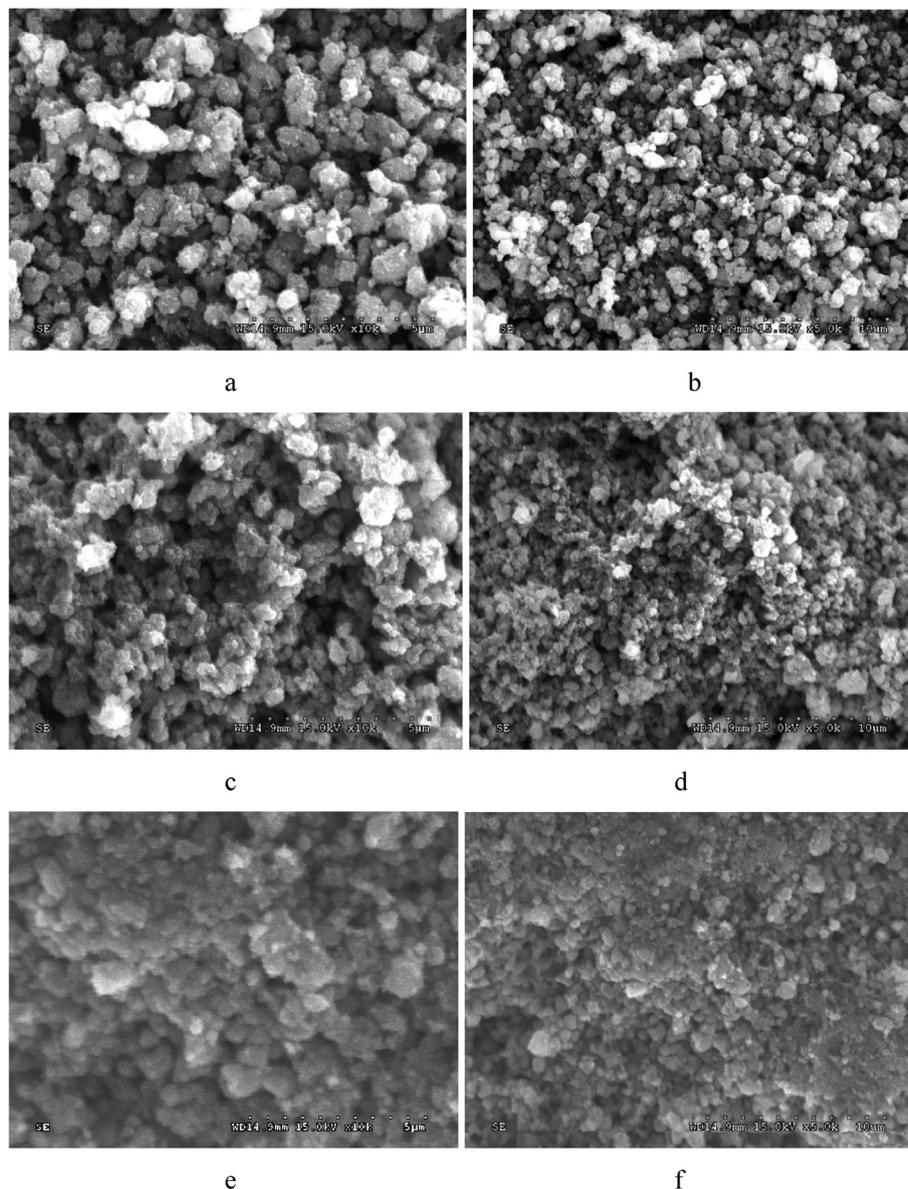


Fig. 4 – Scanning electron microscope (SEM) images of (a) 0F-3VWT \times 10,000, (b) 0F-3VWT \times 5000, (c) 0.2F-3VWT \times 10,000, (d) 0.2F-3VWT \times 5000, (e) 0.2F-3VWTSH \times 10,000, and (f) 0.2F-3VWTSH \times 5000. F-3VWTSH: the samples after the selective catalytic reduction (SCR) reaction containing SO_2 and H_2O .

2.11. Mechanism of the effects of SO_2 and H_2O on NO conversion over F-3VWT catalysts

Industrial boiler flue gas usually had a variety of gaseous species such as NO_x , NH_3 , O_2 , SO_2 , SO_3 , H_2O and other components. Chemical reactions usually occur between the catalyst and flue gas components or between flue gas components, consequently leading to a decline in the activity of the catalyst. In this part, the effect of SO_2 and H_2O on catalyst NO conversion will be discussed.

When H_2O was present in the reaction gas, the reasons for the decrease in VWT catalyst activity were as follows: (1) the H_2O generated during the SCR reaction (0.07 vol.% NO complete De- NO_x reaction generated 0.07–0.1 vol.% H_2O) was much lower than that of the H_2O concentration in the reaction gas, so the H_2O could not easily diffuse outward, shifting the

reaction balance to the left. (2) When the H_2O concentration in the reaction gas was high, NH_3 had difficulty being adsorbed onto the acid sites of the catalyst because H_2O competed with NH_3 for the same adsorption sites. Meanwhile, the adsorption of NH_3 onto H_2O sites affected the adsorption capacity of the catalyst, and finally hindered the De- NO_x reaction.

When SO_2 and H_2O existed simultaneously in the reaction gas, the reasons for catalyst deactivation included the following: (1) SO_2 and its oxidation product SO_3 competed with NO_x for adsorption sites on the catalyst surface, which reduced the adsorption performance of the catalyst for NO_x . (2) Side reactions occurred between SO_3 , H_2O and NH_3 to form NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$, which covered the active sites of the catalyst. (3) The active components were reacted in the presence of SO_2 and H_2O and formed sulfates with good thermal stability, such as $\text{V}_x(\text{SO}_4)_y\text{O}_z$, $\text{W}_x(\text{SO}_4)_y\text{O}_z$, $\text{Ti}_x(\text{SO}_4)_y\text{O}_z$, so that it

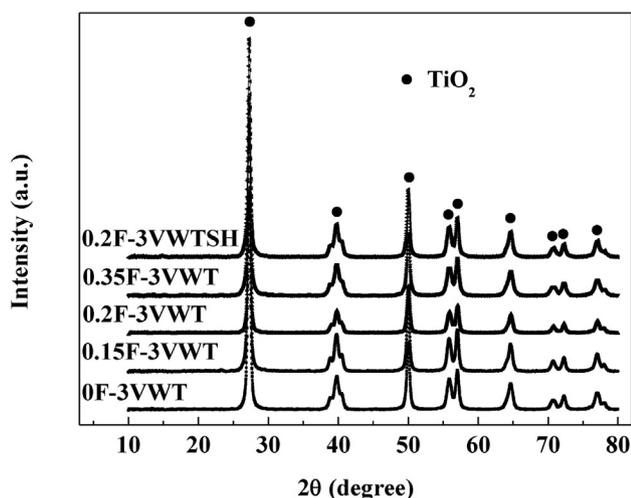


Fig. 5 – X-ray diffraction patterns of F-3VWT catalysts before and after reaction in the presence of SO₂ and H₂O.

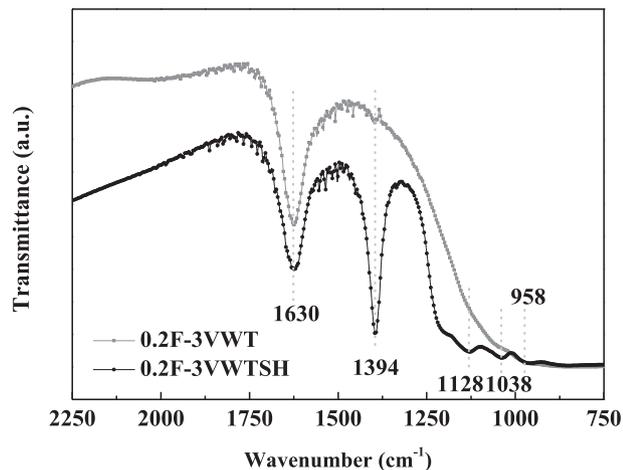


Fig. 6 – Fourier transform infrared spectroscopy (FT-IR) spectra of F-3VWT catalysts before and after reaction in the presence of SO₂ and H₂O.

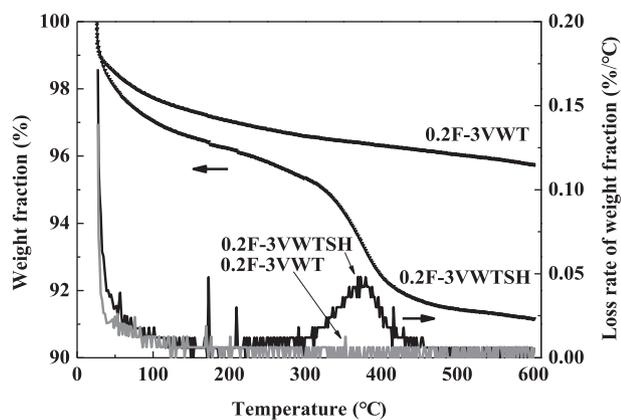


Fig. 7 – TG analysis of F-3VWT catalysts before and after reaction in the presence of SO₂ and H₂O.

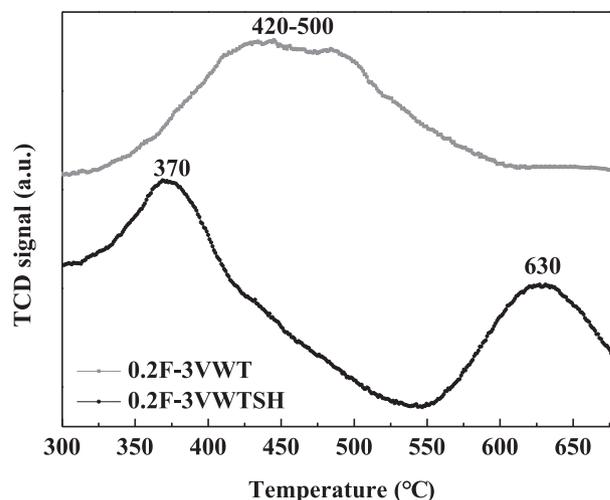


Fig. 8 – Temperature programmed reduction with hydrogen (H₂-TPR) profiles of 0.2F-3VWT catalysts before and after reaction in the presence of SO₂ and H₂O. TCD: thermal conductivity detector.

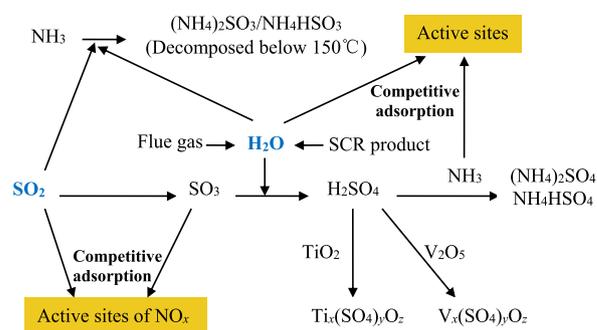
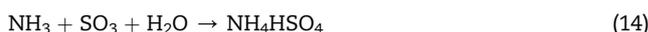
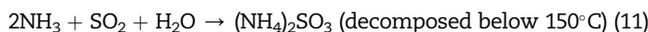
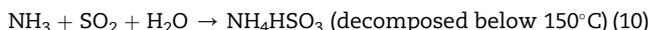
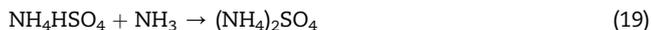


Fig. 9 – Mechanism of the effects of SO₂ and H₂O on NO conversion over the catalysts.

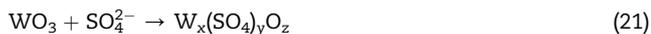
was difficult to recover catalyst activity by on-line thermal regeneration. In addition, the mechanism of the effects of SO₂ and H₂O on NO conversion over F-3VWT catalysts is shown in Fig. 9.

The main reversible side reactions were as follows:





The main irreversible side reactions were as follows:



3. Conclusions

As the content of F ions increased from 0.00 to 0.35 wt.%, the NO conversion of F-V₂O₅-WO₃/TiO₂ catalysts initially increased and then decreased. The 0.2F-3VWT catalyst exhibited the best De-NO_x performance, with more than 95% NO conversion in the temperature range of 160–360°C and 99.0% N₂ selectivity between 110 and 280°C. The addition of appropriate amounts of F ions eroded the surface morphology of the catalyst and reduced its grain size, thus enhancing the NO conversion at low temperature as well as the sulfur and water resistance of the V₂O₅-WO₃/TiO₂ catalyst under complex atmospheres. After SCR reaction in a gas flow containing SO₂ and H₂O, the number of NH₃ adsorption sites, the active component contents, specific surface area and pore volume decreased in different degrees. Ammonium sulfate species deposited on the catalyst surface, which blocked part of the active sites, and the catalyst was irreversibly poisoned to some extent under the experimental conditions. In addition, a mechanism for the effects of SO₂ and H₂O on catalyst NO conversion was proposed.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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