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SO₂ promoted in situ recovery of thermally deactivated Fe₂(SO₄)₃/TiO₂ NH₃-SCR catalysts: From experimental work to theoretical study

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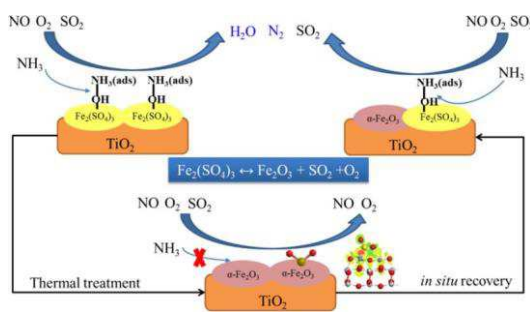
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HIGHLIGHTS

- Thermally deactivated Fe₂(SO₄)₃/TiO₂ (FeTi-T) was obtained by thermal treatment.
- Fe₂(SO₄)₃ decomposition causes Brønsted acid sites loss and catalyst deactivation.
- The in situ recovery of FeTi-T is achieved by SO₂ in the flue gas.
- Fe₂(SO₄)₃ is formed by SO₂/O₂ and Fe₂O₃ under NH₃-SCR reaction conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Due to high catalytic activity and excellent resistance to SO₂ and H₂O, sulfate materials are considered to be promising vanadium-free catalysts for selective catalytic reduction of NO_x with NH₃ (NH₃-SCR). Despite this, investigations about thermal stability of sulfate SCR catalysts are limited, which is surprising given that sulfates are typically susceptible to thermal decomposition. In this work, the thermal stability of Fe₂(SO₄)₃/TiO₂ catalysts was investigated. It was determined that the thermal decomposition of Fe₂(SO₄)₃ resulted in NO_x conversion decreased from 90% to 60% at 350 °C. Interestingly however, the introduction of SO₂ into the gas stream was found to reverse the effects of the thermal deactivation and the NO_x conversion of 90% (350 °C) was once again observed. Extensive characterization of each catalyst sample and density functional theory (DFT) calculations were subsequently conducted. The reduction in catalytic activity after the thermal treatment was attributed to the transformation of Fe₂(SO₄)₃ to α-Fe₂O₃, which reduced the quantity of Brønsted acid sites on the catalyst. The presence of SO₂ in the gas stream was found to reverse this phase transformation which ultimately led to the recovery of Brønsted acid sites. DFT calculations indicated that SO₂ adsorbed selectively on Fe atoms of the thermal deactivated catalysts and S-Fe bond should mainly be formed by electrons from p orbitals of S and Fe atoms. Then NH₃ could be adsorbed on the surface by N-S bond with SO₂. The recoverable property of this catalyst provides a promising outlook for the commercial application, especially given that industrial flue gas streams regularly contain SO₂.

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1. Introduction

The selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is an effective approach to controlling the emission of NO_x from the combustion of fossil fuels [1–4]. This approach has also been shown to be highly successful for NO_x abatement in the exhausts of diesel engines [5–7]. Current commercial SCR catalysts are typically vanadium-based materials which are due to their high efficiency for NO_x removal and excellent tolerance of SO₂. Nevertheless, it is vitally important that novel vanadium-free SCR catalysts are developed because of the bio-logical toxicity of vanadium-based catalysts and their undesirable activity for SO₂ oxidation [8–10]. There are numerous examples of transition metal (e.g., Mn, Ce, Fe, and Cu) oxide catalysts which are highly active for NH₃-SCR [11–14]. However, in many cases these catalysts are exceptionally susceptible to deactivation in the presence of SO₂ (a common component in flue gas), which has greatly limited the application of these vanadium-free catalysts [15–18]. The deactivation of these vanadium-free catalysts is believed to be a result of interactions between SO₂/O₂ and active sites, which leads to changes in the surface acidity and reducibility and ultimately results in the deactivation of these catalytic materials [15–18]. Various sulfate catalysts have also been investigated for their application in NH₃-SCR [19,20]. Interestingly, it was revealed that some of these sulfate catalysts possessed an abundance of acid sites and displayed reasonable SCR activity and SO₂ resistance. Fe₂(SO₄)₃/TiO₂ catalysts for instance were found to be highly active as NO_x conversion up to 90% were observed at reaction temperatures in excess of 350 °C [19]. Even higher NO_x conversions were observed over a CuSO₄/TiO₂ catalyst (> 90%) in temperatures ranging from 280 to 380 °C [20]. In addition, both of these sulfate catalysts displayed excellent resistances to SO₂, underlining their potential as catalysts for industrial NO_x reduction [19,20].

The thermal stability of catalysts is an important property to investigate when assessing the commercial viability of a catalyst for NH₃-SCR [21,22]. In commercial flue gas streams, large fluctuations in temperature are common and temperatures in excess of 600 °C can be observed under certain conditions [22]. At such elevated temperatures, the destruction of the framework/pore structure of oxide-based materials has been shown to occur which is considered to be another mechanism commonly associated with catalytic deactivation [23,24]. Typically, sulfates are prone to decomposition at high temperatures (e.g., the initial decomposition of Fe₂(SO₄)₃ and CuSO₄ in flowing air was 507 and 586 °C, respectively [25]), which may also lead to the thermal deactivation of sulfate catalysts. As such, the poor thermal stability of these sulfate catalysts may hinder their practical application in NH₃-SCR systems. However, few researchers have highlighted the issues associated with the thermal deactivation of these materials in NH₃-SCR.

The promotional effect of SO₂ on some vanadium-free oxide catalysts at given temperatures have been reported [26–29]. L. Ma et al. [28] studied the influence of SO₂ sulfation treatment on CeO₂ cubes and nanospheres and they found the treatment could significantly increase the SCR activity of the catalyst at temperatures higher than 200 °C due to the formation of surface Ce₂(SO₄)₃, which could supply abundant Brønsted acid sites. F. Liu et al. [29] found that SO₂ treatment could lead to the formation of the sulfate species with iron sites, resulting in the enhancement of acid strength on FeTiO_x catalysts, thus increased the SCR activity at temperatures higher than 325 °C. As such, it is rational to postulate that the presence of SO₂ in flue gas may assist in the regeneration of sulfate species on the surface of sulfate catalysts which have undergone thermal deactivation in NH₃-SCR. If this theory is correct, the in situ recovery may be achieved and thermally-deactivated sulfate catalysts may not have to be replaced. This would be highly advantageous both practically and economically from an industrial perspective and as such, would provide a novel approach for the future catalyst design of SCR catalysts.

Density functional theory (DFT) is thought to be an efficient method in the study of catalysts deactivation and regeneration [30,31]. In this

work, both experimental methods and DFT calculations were employed to investigate the thermal deactivation and regeneration of Fe₂(SO₄)₃/TiO₂ SCR catalysts. Fe₂(SO₄)₃ was selected preferentially over CuSO₄ due to its lower thermal stability [25]. In order to investigate the effect of thermal stability on the performance of this catalyst for NO_x conversion, the prepared catalyst was calcined under a flow of N₂ at 630 °C for 1 h. The recovery in the catalytic activity of the thermally-deactivated catalyst was assessed in the presence of SO₂ at 350 °C. N₂ adsorption-desorption, X-Ray diffraction (XRD), Thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Temperature-programmed desorption of NH₃ (NH₃-TPD), Temperature-programmed reduction of H₂ (H₂-TPR) and in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) were used to investigate the mechanism of thermal deactivation and recovery of catalytic activity. DFT calculations were performed to investigate the adsorption of SO₂ on the thermally deactivated catalysts and the influence of SO₂ on NH₃ adsorption.

2. Experimental section

2.1. Catalyst preparation

Fe₂(SO₄)₃/TiO₂ catalyst was synthesized by a solid-state impregnation method. Firstly, a sol-gel method was used to obtain anatase TiO₂ support material [20]. Subsequently, Fe₂(SO₄)₃ (0.6 g) was added to the synthesized TiO₂ (6.0 g) in an agate mortar and ground to uniformity. The powdered mixture was then calcined at 500 °C in air for 5 h to yield the fresh Fe₂(SO₄)₃/TiO₂ catalyst (FeTi). A thermal treatment of this material was subsequently performed in a tubular furnace. For this, the fresh Fe₂(SO₄)₃/TiO₂ catalyst was calcined under N₂ flow at 630 °C for 1 h to yield the thermally deactivated catalyst (FeTi-T).

2.2. NO_x conversion tests

The NO_x conversion of each catalyst material was tested using a fixed-bed quartz reactor (φ 10 mm × 600 mm). The gas mixture contained NO (600 ppm), NH₃ (600 ppm), H₂O (4.0%) and O₂ (4.0%) in N₂. The total gas flow rate was maintained at 1200 mL/min, which corresponded to a gas hourly space velocity (GHSV) of 60 000 h⁻¹. Concentrations of NO and NO₂ in the gas were detected using a T-340 flue gas analyzer (Testo Company, Germany). A SENMA IR Sensor (Madur Company, Austria) was used to analyze the concentration of N₂O in the outlet. NO_x conversion was calculated by Eq. (1):

$$x = \frac{\text{NO}_{x,\text{in}} - \text{NO}_{x,\text{out}}}{\text{NO}_{x,\text{in}}} \times 100\% \quad (1)$$

where NO_{x,in} and NO_{x,out} were concentrations of NO_x (NO + NO₂) in the inlet and outlet of the reactor, respectively.

N₂O is the main by-product of SCR reaction and the N₂ selectivity was calculated by Eq. (2):

$$S_{\text{N}_2} = 1 - \frac{2\text{N}_2\text{O}_{\text{out}}}{\text{NO}_{x,\text{in}} - \text{NO}_{x,\text{out}}} \times 100\% \quad (2)$$

where N₂O_{out} was the concentrations of N₂O in the outlet of the reactor.

2.3. Activity recovery of the thermally-deactivated catalyst

A similar experimental set up was also used to investigate the recovery of catalytic activity. The fixed-bed quartz reactor was filled with 1.2 mL of the thermally-deactivated material (FeTi-T). The gas mixture (1200 mL/min) containing NO (600 ppm), NH₃ (600 ppm), H₂O (4.0%), O₂ (4.0%) and SO₂ (1000 ppm) in N₂ was introduced into the reactor at 350 °C for approximately 30 h to yield the regenerated material (FeTi-S). Concentrations of NO and NO₂ in the outlet were

detected by a T-340 flue gas analyzer.

2.4. Catalyst characterizations

N₂ adsorption-desorption was conducted at -196 °C using a Quantachrome NOVA 2000e surface area and pore size analyzer. The sample was first degassed under vacuum at 300 °C for 3 h. The Brunauer-Emmett-Teller (BET) method was subsequently used to calculate the specific surface area of each material. Powder XRD of each material was conducted using a PANalytical B.V. X'Pert Pro XRD diffractometer with Cu K α radiation and the X-ray tube was operated at 40 kV and 40 mA. TGA was carried out on a HCT-1 thermoanalyzer (Beijing Hengjiu Company, China) in a flowing N₂. The heating rate was 10 °C/min. FTIR was conducted on a Bruker Vertex 70 infrared spectrometer with a resolution of 4 cm⁻¹ (64 scans). XPS was performed on

a Thermo Fisher Scientific ESCALAB 250 spectrometer, using Al K α radiation. The binding energy of each material was compensated with the adventitious C 1 s peak at 284.6 eV. H₂-TPR was performed on a Quantachrome ChemBET-3000 TPR-TPD chemisorption analyzer using a gas feed of 5% H₂/Ar. Before switching to the H₂/Ar feed, the sample (50 mg) was pretreated under a helium flow at 400 °C for 1 h. During the TPR experiment, the temperature was progressively increased from 50 to 900 °C at a rate of 10 °C/min. An online mass spectrometer (MS, DYCOR LC-D100, Ametek Company, USA) was used as the detector. NH₃-TPD was also performed on the ChemBET-3000 TPR-TPD chemisorption analyzer with an on-line MS as detector. For this, each sample (50 mg) was pretreated under flowing helium at 400 °C for 1 h and then cooled to 50 °C. After that, 5% NH₃/Ar was introduced for 30 min and then the carrier gas was switched to helium. To remove any weakly adsorbed NH₃ from the surface of the material, the material was purged with helium at 100 °C for 1 h. The temperature was then increased to 600 °C at a ramp rate of 10 °C/min. In situ DRIFTS was performed on a Bruker Vertex 70 infrared spectrometer with a MCT detector. A Harrick Scientific reaction cell with ZnSe windows was used. The powdered sample in the reaction cell was first treated under N₂ at 400 °C for 1 h and then cooled to 350 °C. Background spectra were re-recorded at 350 °C. Afterwards, the target mixture gas was introduced and the spectrum was recorded at a given time by 100 scans with a resolution of 4 cm⁻¹.

2.5. Calculation methods

The first-principle density functional theory calculations (including structural and electronic investigations) were conducted based on the Cambridge Sequential Total Energy Package (CASTEP) and used to investigate the adsorption of SO₂ and NH₃ on the catalyst model. The model of TiO₂ (0 0 1) surfaces was used because the stability of (0 0 1) surfaces of anatase TiO₂ was the lowest and should play an important role in catalytic reaction [30]. More details could be found in our previous work [32,33].

3. Results and discussion

3.1. NO_x conversion over catalysts

NO_x conversion observed over all prepared samples is displayed in Fig. 1a. The FeTi material exhibited an exceptionally high catalytic activity with over 90% of NO_x converted between 350 and 450 °C, in line with previous reports [19]. A significant decrease of catalytic activity was observed over FeTi-T material, suggesting that the thermal treatment had a negative effect on the activity of Fe₂(SO₄)₃/TiO₂ catalyst. For FeTi-T material, NO_x conversion was found to be lower than 70% at all the temperatures. The catalytic activity of FeTi-S material was subsequently investigated and a significant increase in the conversion of NO_x was observed. The catalytic activity was found to be comparable with that of FeTi material. N₂O is an important greenhouse

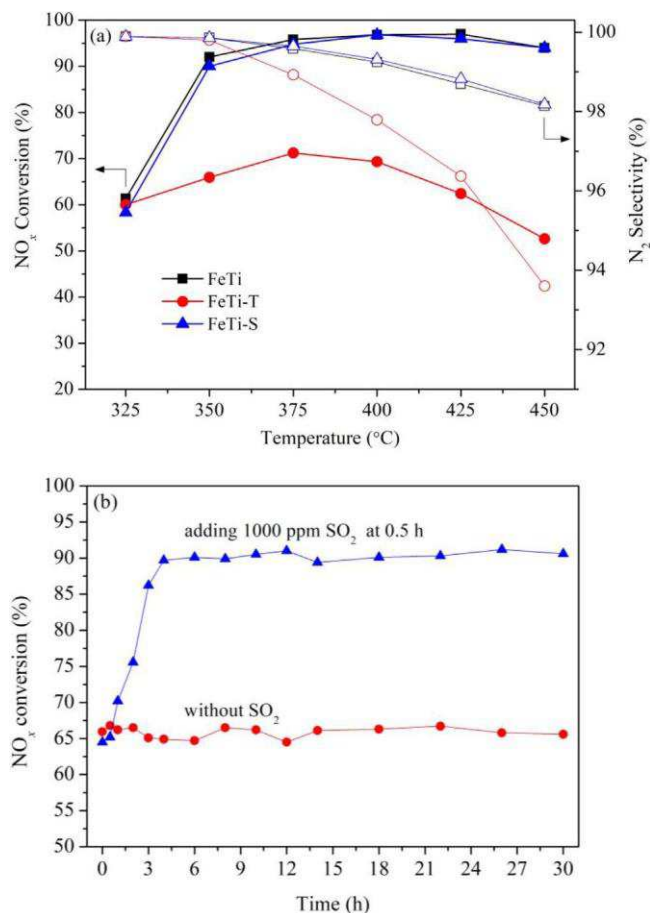


Fig. 1. (a) NO_x conversion and N₂ selectivity of the prepared catalysts. (b) Time-on-stream NO_x conversion of FeTi-T catalyst with and without SO₂ at 350 °C. (Reaction conditions: GHSV = 60 000 h⁻¹, [NO] = [NH₃] = 500 ppm, [H₂O] = 4.0%, [O₂] = 4.0%).

gas and it's the main by-product of NH₃-SCR reaction [34]. The N₂ selectivity of prepared materials is shown in Fig. 1a. The N₂ selectivity was higher than 98% within the test temperatures for FeTi material, in accordance with other researches [19]. After the thermal treatment, the N₂ selectivity showed a significant decrease. However, N₂ selectivity recovered after FeTi-T material was sulfated by SO₂.

The time-on-stream data for the activity recovery experiment is displayed in Fig. 1b. The addition of SO₂ into the gas mixture at 350 °C resulted in a noticeable increase of the NO_x conversion over FeTi-T material; NO_x increased rapidly from 65% to 90% after only 2.5 h and remained stable until the end of the experiment. By comparison, the NO_x conversion observed over FeTi-T material (in the absence of SO₂) only reached and maintained at 65% across the test period. It can therefore be concluded that the thermal pretreatment causes the de-activation of the Fe₂(SO₄)₃/TiO₂ catalyst. It was also clear that flowing SO₂ over this material leads to a recovery in its catalytic performance.

3.2. Characterization of synthesized catalysts

3.2.1. Structural and surface properties

Table 1 shows the specific surface area (SBET), total pore volume (V_p) and average pore diameter (D_p) of each material. The SBET and D_p of Fe₂(SO₄)₃/TiO₂ catalyst was 64.3 m²/g and 7.5 nm, respectively. After the thermal treatment under N₂, a significant structural change in the Fe₂(SO₄)₃/TiO₂ catalyst occurred; the SBET decreased from 64.3 to 54.1 m²/g with the D_p increased from 7.5 to 8.5 nm. The sintering of the carrier might occur under the thermal treatment and thus caused the

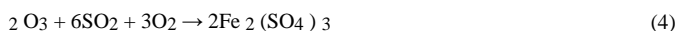


Table
Physico-chemical properties of each catalyst.

Sample	S_{BET} (m^2/g)	V_p^a (cm^3/g)	D_p (nm)	d_{cryst} (nm)	T_{acid}^c (mmol/g)
F	6				
FeTi	5				
FeT	5				

^a Obtained at P/P₀ = 0.99.

^b Calculated by the Scherrer formula based on the (1 0 1) plane of anatase TiO₂ in XRD patterns.

^c Calculated by the integral area of the desorption peak in NH₃-TPD.

reduction of specific surface area. After sulfation by SO₂, the S_{BET} of FeTi-T material did not appear to decrease significantly, indicating that the sulfation had little effect on the carrier. In general, the decrease of the specific surface area could cause the deactivation of catalysts. The S_{BET} of FeTi-S material was significantly lower than that of FeTi material; however, their catalytic activities were almost the same. Therefore, it could be concluded that the decrease of the specific surface area should not be the main reason for the deactivation of the catalyst after thermal treatment.

XRD patterns of all the materials are displayed in Fig. 2. The most intense diffraction peaks observed on FeTi material corresponded to anatase TiO₂ and diffraction peaks associated with Fe₂(SO₄)₃ phases were very weak, suggesting that the Fe₂(SO₄)₃ species were likely to be well dispersed on TiO₂ support. After the thermal treatment, however, the diffraction peaks associated with Fe₂(SO₄)₃ disappeared completely and diffraction peaks corresponded to α -Fe₂O₃ phase were observed, suggesting that significant quantities of the Fe₂(SO₄)₃ decomposed during the heat treatment according to Eq. (3). In addition, there were no obviously peaks assigned to rutile TiO₂, suggesting that the phase transitions from anatase to rutile might not occur. For FeTi-S material, new small diffraction peaks associated with Fe₂(SO₄)₃ were observed, implying that Fe₂(SO₄)₃ could be recovered according to Eq. (4). The average crystallite size of anatase TiO₂ (d_{cryst}) is often used to determine the degree of TiO₂ sintering at high temperatures [23,24]. The d_{cryst} of each material was calculated using the Scherrer equation based on full width at half maximum (FWHM) of the TiO₂ (1 0 1) plane, the results of which are also displayed in Table 1. The d_{cryst} associated with FeTi material was calculated to be 21.7 nm, which was similar to the results reported in the literature [23,24]. After the thermal treatment, the d_{cryst} of FeTi-T material increased to 24.3 nm, suggesting that the sintering of anatase TiO₂ occurred, which also aligned with the decrease observed in the S_{BET} .

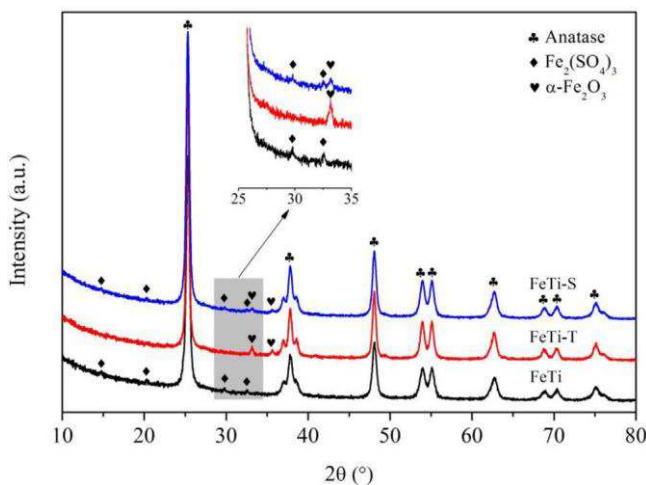
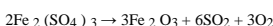


Fig. 2. XRD results of prepared catalysts.

TGA was subsequently used to assess the mass loss of all materials, as shown in Fig. S1. For FeTi material, the mass loss started from 400 °C and a mass loss of 5.5% was observed at approximately 850 °C, while a mass loss of only 0.5% was observed for FeTi-T material. This indicated that a significant proportion of the Fe₂(SO₄)₃ was likely to have de-composed during the thermal treatment, in accordance with the conclusions drawn from the XRD (Fig. 2). Interestingly, after FeTi-T material was subjected to the activity recovery step, an increase in the quantity of mass loss in the TGA was observed (4.0% for FeTi-S material). Most of Fe₂(SO₄)₃ should be recovered, according to Eq. (4).

The FTIR spectra of prepared materials are shown in Fig. S2. A board peak in the range from 900 to 400 cm⁻¹ and three peaks at 1221, 1136, 1045 cm⁻¹ could be found on Fe₂(SO₄)₃/TiO₂ catalysts. The board peak could be associated with anatase TiO₂ and those three peaks could be associated with the stretching motion of adsorbed HSO₄⁻ and SO₄²⁻ on the surface of the catalyst [35,36]. After the thermal treatment, the board peak split into two peaks centered at 702 and 521 cm⁻¹, respectively, indicating that the sintering of TiO₂ carrier occurred, in accordance with the results of XRD and other researches [36]. The three peaks assigned to adsorbed HSO₄⁻ and SO₄²⁻ almost disappeared, suggesting that most of the Fe₂(SO₄)₃ decomposed on FeTi-T material. However, the three peaks were largely recovered on FeTi-S material, suggesting that most of sulfate should recover after the sulfation, in accordance with the results of XRD and TGA.

XPS was subsequently used to determine the chemical states of Fe, Ti, O and S in prepared materials, as displayed in Fig. 3. An intense peak could be observed in all materials at a binding energy of around 711.4 eV, which suggested that iron predominantly existed in a Fe³⁺ state [37]. In the XPS spectrum of FeTi material, two peaks at 459.0 and 464.7 eV were also observed and could be attributed to the spin-split orbitals components of Ti 2p. From the XPS spectrum of this material after the thermal treatment, both of these peaks appeared to have shifted to 459.4 and 465.0 eV, which was further evidence to suggest that the thermal treatment facilitated the sintering of TiO₂. It is re-ported that the sintering could increase the size of TiO₂ nanoparticles and thus caused the peaks shift to higher binding energies to some extent [38]. For all synthesized materials, O 1s curves could be fitted into three peaks, which respectively assigned to the lattice oxygen (O_α), surface OH group (O_β) and weakly adsorbed oxygen (O_γ, Table 2) [39–41]. For FeTi material, O_β of the total oxygen was 43.4%. After the thermal treatment, the ratio of O_β decreased largely (12.4%) on FeTi-T material, suggesting that the thermal treatment would cause the disappearance of a large number of surface OH group. Most of surface OH

(3) group recovered after sulfation and the O_β increased to 39.4%. Surface OH group could supply Brønsted acid sites on the surface of catalysts and benefit the occurrence of NH₃-SCR reaction [20,42]. The recovery of surface OH group should be one of the main reasons for the activity recovery of the deactivated catalysts. In the S 2p region of the spectrum, a large peak at 168.4 eV (indicative of HSO₄⁻ species) and a shoulder peak at 169.8 eV (indicative of SO₄²⁻ species) was observed on FeTi material [43]. After the thermal treatment, the intensity of S 2p peaks decreased significantly and the peak assigned to HSO₄⁻ species almost disappeared. Only a small peak at 169.3 eV assigned to SO₄²⁻ could be found, suggesting that a large proportion of the sulfate especially hydro-sulfate species on the surface of the catalyst decomposed during the thermal treatment, which correlated well with the conclusions drawn from XRD, TGA and FTIR (Figs. 2, S1 and S2). Upon exposure to SO₂ however, the intensity of S 2p peaks increased once again, suggesting that the activity recovery step led to formation of sulfate and hydro-sulfate species on the surface of the material. As Fig. 3 showed, the shape of Fe 2p_{3/2} and S 2p for FeTi-S sample was similar to the shape of FeTi sample, thus we concluded that most of Fe₂(SO₄)₃ should be recovered after the sulfation, be in line with the results of XRD, TGA and FTIR.

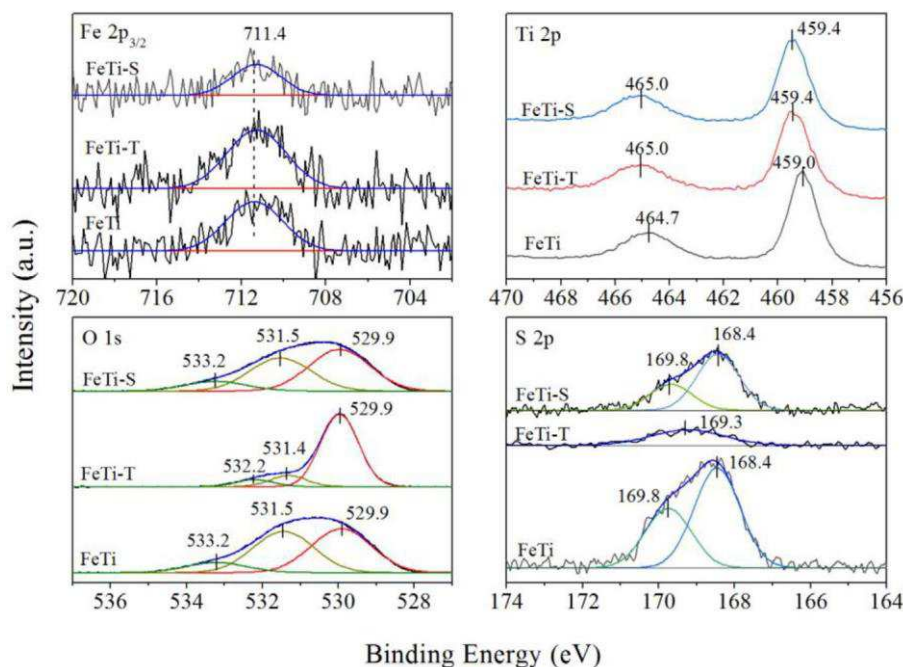


Fig. 3. XPS results of Fe 2p_{3/2}, Ti 2p, O 1s and S 2p for prepared materials.

Table 2
The content of O and S species in different catalysts.

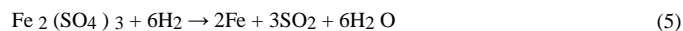
Sample	O 1s			S 2p	
	O _a (%)	O _β (%)	O _γ (%)	S _a (%)	S _β (%)
FeTi	46.0 (529.9)	43.4 (531.5)	10.6 (533.2)	37.8 (168.4)	62.2 (169.8)
FeTi-T	79.8 (529.9)	12.4 (531.4)	7.8 (532.2)	/	100 (169.3)
FeTi-S	49.1 (529.9)	39.4 (532.2)	11.5 (533.2)	35.7 (168.4)	64.3 (169.8)

^a O_a: lattice oxygen, O_β: surface OH group, O_γ: adsorbed oxygen; S_a: HSO₄⁻, S_β: SO₄²⁻ (Data in parentheses means the position of the peak (eV)).

3.2.2. Reducibility and surface acidity

Previous works have proved that the surface reducibility can affect the activity of SCR catalysts [44,45]. For this reason, H₂-TPR was used to determine the effect the thermal treatment on surface reducibility of the catalyst. The corresponding data for these experiments is displayed in Fig. 4. A broad H₂ (m/e = 2) consumption peak was observed in H₂-

TPR of FeTi material between the temperatures of 400 and 650 °C (centered at 565 °C). The release of H₂S, SO₂ and SO₃ during H₂-TPR process was also measured by MS and only the signal of SO₂ (m/e = 64) could be detected (Fig. 4). It was determined that the emission of SO₂ occurred almost in parallel with the H₂ consumption, suggesting that the H₂ consumption was likely indicative of Fe₂(SO₄)₃ reduction according to Eq. (5) and was in line with reports from previous publications [20]. The H₂ consumption peak of FeTi-T material shifted to 510 °C and the intensity decreased significantly, which was likely attributed to the presence of α-Fe₂O₃ (Eq. (6)) (confirmed by XRD). As Eqs. (5) and (6) showed, the H₂ consumption quantity over Fe₂O₃ was smaller than that of Fe₂(SO₄)₃. In addition, a much smaller quantity of SO₂ was emitted for FeTi-T material. After exposure to SO₂ (FeTi-S material), a broader H₂ consumption peak centered at 554 °C was presented and the release of SO₂ increased significantly, providing further evidence to suggest that the activity recovery procedure facilitated the production of new Fe₂(SO₄)₃.



Typically, in NH₃-SCR reactions, the absorption of NH₃ onto the surface acid sites is considered to be one of the key steps in the reaction [46–48]. In order to determine how the thermal treatment affected this, NH₃-TPD was conducted on all materials (Fig. 5). NH₃ desorption on FeTi material began at approximately 100 °C and ended at approximately 600 °C with the total amount of acid sites (T_{acid}) calculated to be approximately 0.352 mmol/g. After the thermal treatment, the T_{acid} decreased significantly and was calculated to be approximately 0.072 mmol/g (20% of that observed over FeTi material). After the subsequent exposure to SO₂, the T_{acid} increased to 0.274 mmol/g (78% of that observed over FeTi material). It can be therefore concluded that the thermal treatment caused a decrease in the amount of acid sites on the surface of the catalyst and that the sulfation step partly facilitated the recovery of some acid sites.

In situ DRIFTS was subsequently used to investigate the nature of the acid sites on each material. The DRIFTS spectra depicting the adsorption of NH₃ onto each material at 350 °C are displayed in Fig. 6. Several bands were observed in the spectrum of FeTi material after exposure to

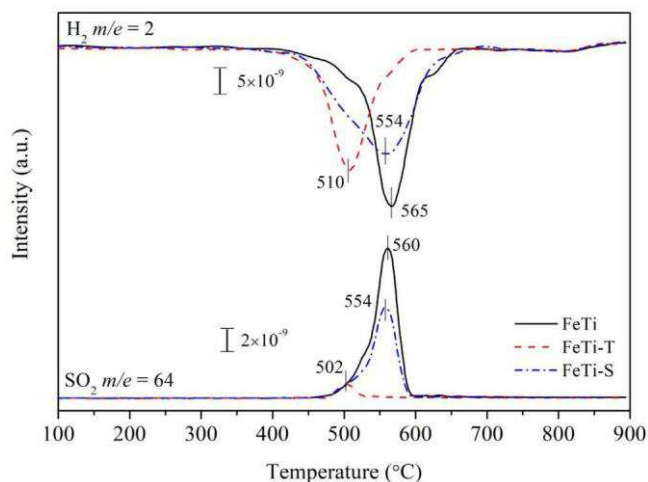


Fig. 4. H₂-TPR profiles and the release of SO₂ during H₂-TPR for synthesized materials.

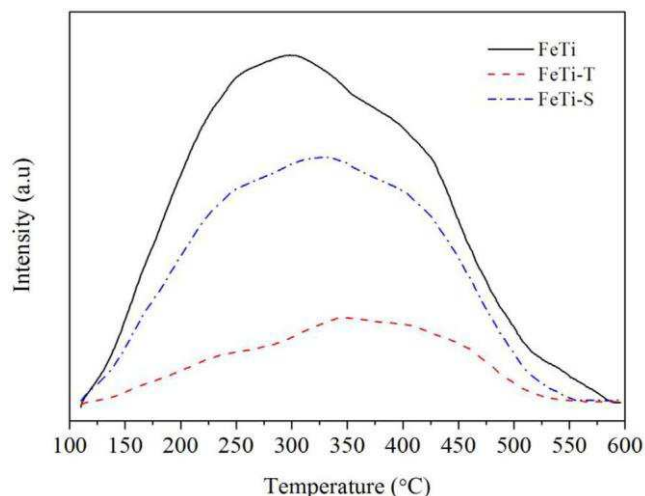


Fig. 5. NH_3 -TPD profiles of prepared materials.

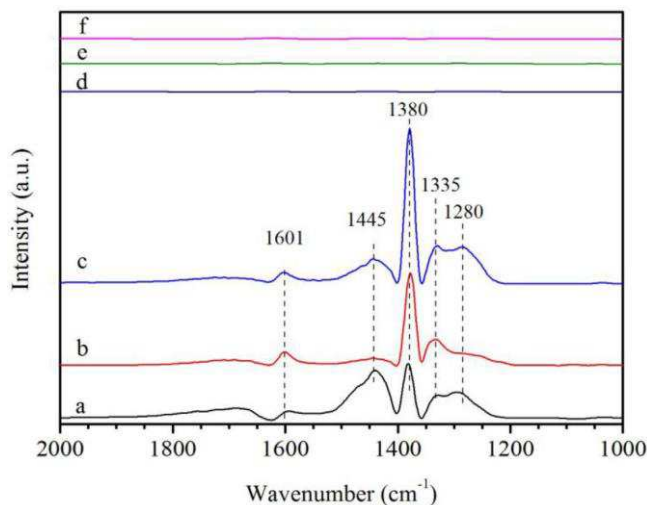


Fig. 6. DRIFTS spectra corresponding to the adsorption of NH_3 (a–c) and $\text{NO} + \text{O}_2$ (d–f) on various samples at $350\text{ }^\circ\text{C}$. (a, d: FeTi material; b, e: FeTi-T material; c, f: FeTi-S material).

NH_3 for 15 min and purged with N_2 for another 10 min. The band at 1445 cm^{-1} and the broad band from 1635 – 1850 cm^{-1} were assigned to NH_4^+ species chemisorbed onto Brønsted acid sites [49,50]. The band at 1601 cm^{-1} was indicative of NH_3 adsorbed onto Lewis acid sites [49,50]. The bands at 1380 , 1335 and 1280 cm^{-1} were attributed to NH_2 wagging [51,52]. The thermal treatment of FeTi material did not appear to have a significant effect on Lewis acid sites as no significant change was observed for the band at 1601 cm^{-1} . A significant reduction in intensity however, was observed for the bands at 1445 cm^{-1} and 1635 – 1850 cm^{-1} suggesting that the thermal treatment led to a loss of Brønsted acid sites on the material. This was likely due to the decomposition of $\text{Fe}_2(\text{SO}_4)_3$, as the presence of SO_4^{2-} and HSO_4^- on the surface formed Brønsted acid sites according to previous reports [20]. Brønsted acid sites play a key role in NH_3 -SCR reactions for sulfate catalysts [42,53]. For NH_3 -SCR reaction, NH_3 is first absorbed on surface Brønsted acid sites and then reacted with NO and O_2 to form N_2 and H_2O . The thermal treatment caused the decomposition of $\text{Fe}_2(\text{SO}_4)_3$ on $\text{Fe}_2(\text{SO}_4)_3/\text{TiO}_2$ catalysts and thus most of the Brønsted acid sites disappeared, which hindered the adsorption and activation of NH_3 on the surface of the catalyst, as shown in Scheme 1a. The loss of Brønsted acid sites were likely to be the main reason why such a significant loss in activity was observed after the thermal deactivation. The bands

associated with chemisorbed NH_4^+ onto Brønsted acid sites reemerged on FeTi-S material, providing further evidence that the activity re-recovery procedure in the presence of SO_2 assisted with the reformation of some of the Brønsted acid sites.

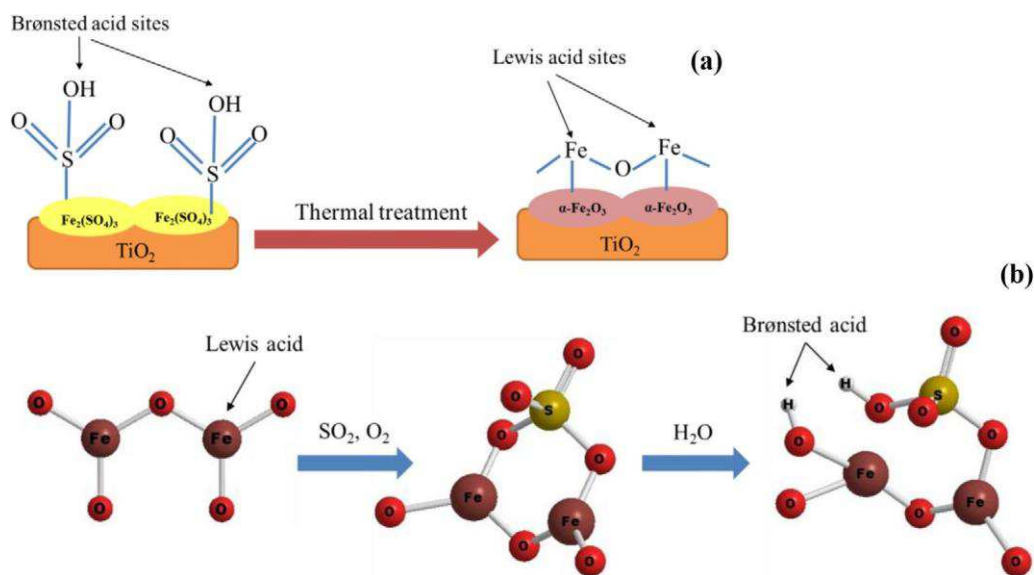
The adsorption of NO was also detected by in situ DRIFTS and the results can be found in Fig. 6. It can be found that NO was hardly adsorbed on the surface of prepared materials at $350\text{ }^\circ\text{C}$. The influence of SO_2 on the adsorption of NH_3 over FeTi-T material was also investigated and the corresponding results are displayed in Fig. S3. It is clear that the intensity of both the band at 1445 cm^{-1} and the broad band from 1635 to 1850 cm^{-1} increased with the exposure time, suggesting that Brønsted acid sites are formed in situ on the surface of the material in the presence of SO_2 .

The interaction between NO/O_2 and NH_3 pre-adsorbed on FeTi and FeTi-S materials was investigated at $350\text{ }^\circ\text{C}$ and the results can be found in Figs. S4 and S5. After NO and O_2 were introduced, bands assigned to NH_3 adsorbed on FeTi material decreased significantly and almost disappeared after 2 min. A new band at 1624 cm^{-1} indicative of a bridging nitrate species and a small band at 1345 cm^{-1} indicative of a surface NO_3^- species appeared [54,55]. However, both these bands almost disappeared after purging with N_2 for 15 min, implying that the bridging nitrate and surface NO_3^- species were unstable at $350\text{ }^\circ\text{C}$. It is likely that the surface reaction mechanism on $\text{Fe}_2(\text{SO}_4)_3/\text{TiO}_2$ catalysts proceeds via an Eley-Rideal surface mechanism- NH_3 was absorbed onto the surface of catalyst and then reacted with NO and O_2 , forming N_2 and H_2O . To investigate whether the same surface mechanism occurred on FeTi-S material, a same in situ DRIFTS experiment was conducted. The in situ DRIFTS experiment conducted over FeTi-S material yielded very similar results, suggesting that the newly formed Brønsted acid sites participate in the reaction in the same way as the Brønsted acid sites in the fresh FeTi catalyst. It was therefore highly likely that the surface mechanism that took place on both FeTi-S and FeTi materials was the same. As such, we can conclude that the new Brønsted acid sites formed from exposing FeTi-T material to SO_2 are likely to be the main reason why the recovery of catalytic activity is observed.

3.2.3. In situ DRIFTS of FeTi-T material under $\text{SO}_2 + \text{O}_2$

The co-adsorption of SO_2 and O_2 on FeTi-T was also investigated by in situ DRIFTS. The results from this investigation are displayed in Fig. 7a. After exposure to SO_2 and O_2 for 30 min, bands at 1370 , 1298 and 1170 cm^{-1} were observed. The bands at 1370 and 1298 cm^{-1} were indicative of the asymmetric vibrations of surface sulfate species with covalent O]S]O [11,56]. The band at 1170 cm^{-1} was indicative of bulk sulfate species [11], suggesting that both surface and bulk sulfate species were formed in the presence of SO_2 and O_2 . The sample was subsequently purged by N_2 for another 15 min and then exposed to NH_3 (Fig. 7b). Interestingly, the peaks associated with surface and bulk sulfate species were still detected after purged by N_2 , suggesting that most of the newly formed sulfate species was stable. According to previous research, SO_2 can be adsorbed on TiO_2 as $(\text{Ti}-\text{O})_3\text{S]O}$ and would give two peaks of roughly equal intensity at 1367 – 1381 and 1386 – 1408 cm^{-1} , respectively [57]. However, we can only find one peak at 1370 cm^{-1} from Fig. 7a. F. Liu et al. [29] studied the adsorption of SO_2/O_2 on Fe_2O_3 and they found a peak at 1372 cm^{-1} from in situ DRIFTS and the peak was indicative of the sulfate species formed on iron sites in a chelating bidentate conformation. It can be concluded that the bidentate sulfate on Fe atoms should be formed in the thermal deactivated $\text{Fe}_2(\text{SO}_4)_3/\text{TiO}_2$ catalyst after treated by SO_2 and O_2 .

After pretreated by SO_2/O_2 and purged by N_2 , NH_3 was introduced and the bands at 1445 cm^{-1} and the broad band at 1635 – 1850 cm^{-1} were detected (Fig. 7b), providing evidence for the existence of Brønsted acid sites on the material after the treatment with SO_2 and O_2 . As such, we can conclude that the exposure of FeTi-T material to SO_2 reforms sulfate species on the surface of materials which ultimately leads to the regeneration of Brønsted acid sites. The proposed pathway for formation of Brønsted acid sites on FeTi-S material can be found in



Scheme 1. (a) The influence of thermal treatment on the Brønsted acid site over $\text{Fe}_2(\text{SO}_4)_3/\text{TiO}_2$ catalyst; (b) The proposed pathway for formation of Brønsted acid sites on FeTi-S material.

Scheme 1. Due to the electron-withdrawing oxygen groups, the partial positive charge created on Fe atom formed Lewis acid sites. After sul-fated by SO_2 and O_2 , the bidentate sulfates were formed on Fe atoms. Then the Brønsted acid sites were generated by interaction of water with surface bidentate sulfates.

3.3. DFT calculations

According to previous researches, the stability of (0 0 1) surfaces of anatase TiO_2 was the lowest and should play an important role in catalytic reaction [30], thus the model of TiO_2 (0 0 1) surfaces has been used by many researchers in DFT calculations. The optimized model of Fe_2O_3 bonded to TiO_2 (0 0 1) surface was calculated firstly and can be found in Fig. 8a. The bond length of Fe-O was 1.700 Å and the bond length of O-Fe-O was range from 1.721 to 1.759 Å. Then the adsorption of SO_2 on the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ model was calculated (Fig. 8b). It could be found that SO_2 was preferential adsorbed on Fe_2O_3 via Fe-S (the bond length was 2.129 Å) and S-O (the bond length was 2.429 Å). The ad-sorption of SO_2 also affected the configuration parameter of Fe_2O_3 . The bond length of Fe-O increased to 1.711 Å and the bond length of O-Fe-O decreased to 1.708 Å. The electron density difference (EDD) map can characterize the electron accumulation and loss of atoms and EDD map

of SO_2 adsorption can be found in Fig. 8c. In the EDD map, electron accumulation was showed by the red and yellow regions and electrons loss was showed by blue and green regions. The color between S and Fe atoms was red, suggesting that the electron accumulation between S and Fe atoms was very high, thus S atom was easy to form chemical bond with Fe atom, further proving that SO_2 was preferential adsorbed on Fe_2O_3 of FeTi-T material. The S atom would loss electron after the adsorption of SO_2 on Fe_2O_3 , which could lead to the increase of chemical valence of S atom, in consistent with the results of XPS. As Fig. 3 showed, the highest valence of S (S^{6+} from HSO_4^- and SO_4^{2-}) was the main S species. It can be concluded that the sulfate on FeTi-S material should mainly unite with Fe species from the results of DFT calculations, in accordance with the results of in situ DRIFTS.

The adsorption of NH_3 on each model was then calculated and the results are shown in Fig. 9. For the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ model, it can be found NH_3 should be adsorbed on Fe_2O_3 via Fe-N and the adsorption energy was -2.12 eV. When NH_3 was adsorbed on sulfated $\text{Fe}_2\text{O}_3/\text{TiO}_2$ model, it can be found that the adsorption of NH_3 had a large influence on the SO_2 adsorption: the S-Fe bond was broken and SO_2 adsorbed on Fe_2O_3 via S-O bond- NH_3 was adsorbed on the top of SO_2 via N-S bond and the adsorption energy was -1.11 eV. Thus, it can be concluded that the

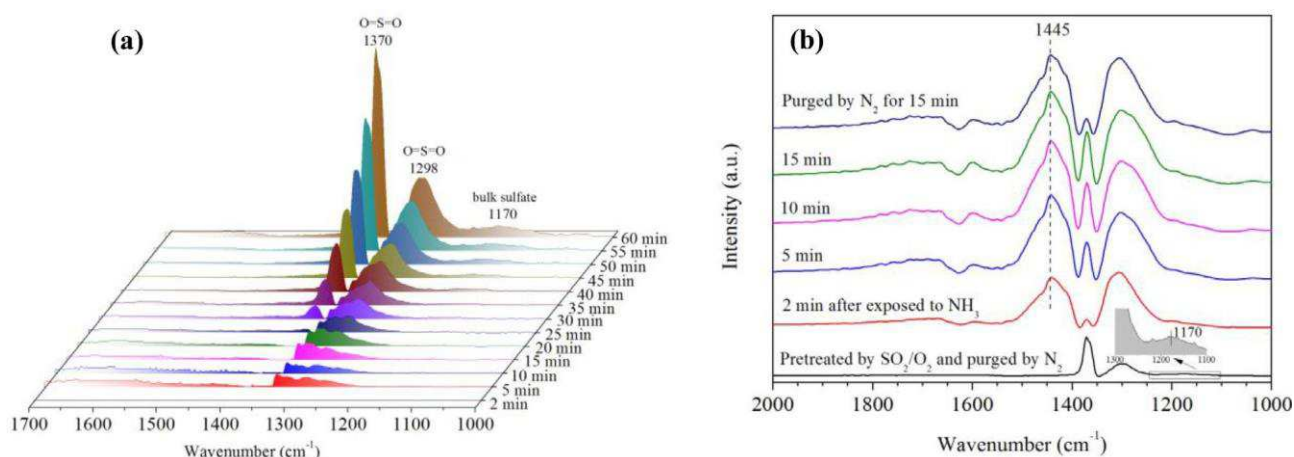


Fig. 7. DRIFTS spectra corresponding to (a) the co-adsorption of SO_2 and O_2 on the FeTi-T material and (b) the adsorption of NH_3 on the FeTi-T material pretreated by SO_2 and O_2 . All spectra were collected at 350 °C.

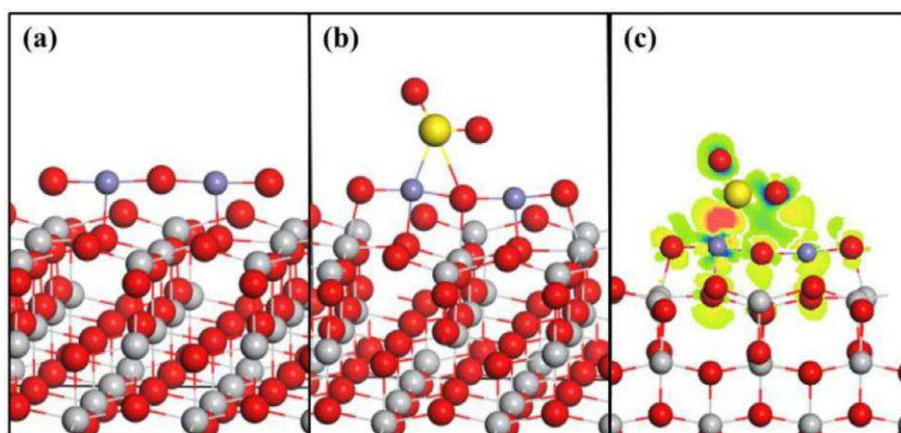


Fig. 8. Optimized structures of (a) $\text{Fe}_2\text{O}_3/\text{TiO}_2$, (b) SO_2 adsorbed on $\text{Fe}_2\text{O}_3/\text{TiO}_2$ and (c) EDD map of SO_2 adsorbed on $\text{Fe}_2\text{O}_3/\text{TiO}_2$ (Red ball: O atom; Gray ball: Ti atom; Light blue ball: Fe; atom; Yellow ball: S atom).

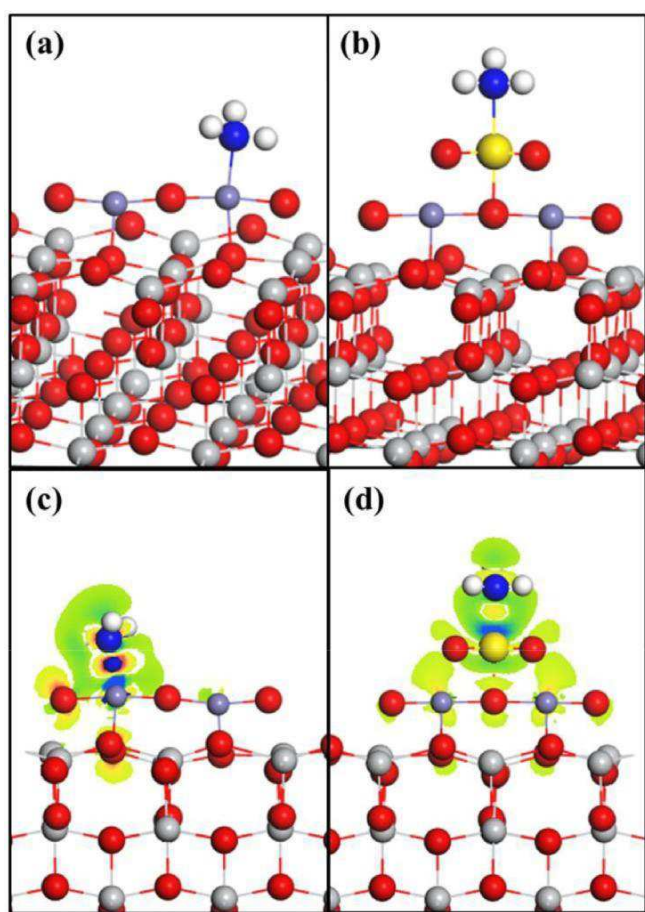


Fig. 9. Optimized structures for NH_3 adsorption on (a) $\text{Fe}_2\text{O}_3/\text{TiO}_2$, (b) Sulfated $\text{Fe}_2\text{O}_3/\text{TiO}_2$ and (c, d) corresponding EDD maps (Red ball: O atom; Gray ball: Ti atom; Light blue ball: Fe; atom; Yellow ball: S atom; Dark blue ball: N atom; White ball: H atom).

newly formed sulfate should be the main sites for NH_3 adsorption, in accordance with the results of in situ DRIFTS.

Projected density of states (PDOS) analysis can be used to understand the interaction and nature bonding between SO_2 and surface atoms [58,59]. The total PDOS of the system could be found in Fig. S6, it could be found that the total PDOS was mainly composed of p- and d-orbitals in the energy level range. Following this, the PDOS results of S and Fe atoms were further analyzed (Fig. 10). The degree of over-

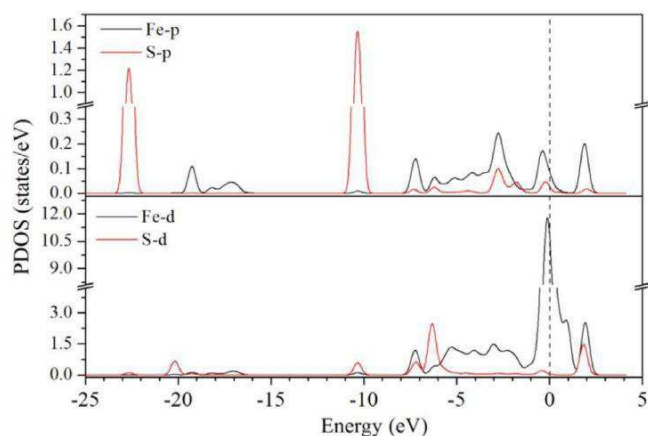


Fig. 10. PDOS analysis of Fe and S orbitals of sulfated $\text{Fe}_2\text{O}_3/\text{TiO}_2$.

lapping between the density peaks and their position with respect the Fermi level (0 eV) was usually used to analyze the bonding strength between adsorbate and surface atoms [58,59]. As Fig. 10 showed, the degree of overlapping in p orbitals for S and Fe atoms was very high, indicating that the orbital hybridization between O and Fe atoms occurred and there was a strong interaction between S and Fe atoms. S-p orbital presented the same peak positions at -2.9 , -6.1 , -7.1 and -10.4 eV below the Fermi level as Fe-p orbital. Compared with p orbital, the over-lapping in d orbital showed a lower degree and the over-lapping position was further from the Fermi level, suggesting that S-Fe bond should mainly formed by electrons from p orbitals of S and Fe atoms.

4. Conclusions

The exposure of $\text{Fe}_2(\text{SO}_4)_3/\text{TiO}_2$ catalyst to high temperatures leads to decomposition of $\text{Fe}_2(\text{SO}_4)_3$, thus causes a significant reduction of Brønsted acid sites on the surface of the material. This reduction in Brønsted acidity correlates with a reduction in the NO_x conversion, indicating that the Brønsted acid sites play an important role in the catalytic conversion of NO_x . Interestingly, exposing this thermally-de-activated catalyst to SO_2 under the standard reaction conditions leads to the recovery of most $\text{Fe}_2(\text{SO}_4)_3$ and the regeneration of some of the Brønsted acid sites on the material surface and ultimately increases the catalytic performance to the level observed with the fresh catalyst. Given that many industrial flue gas streams contain SO_2 , sulfate catalysts such as the one used in this study offer a stable and highly active alternative to conventional vanadium-based catalysts for industrial

NH₃-SCR applications. We hope that this work will provide a foundation for further investigations into sulfate vanadium-free SCR catalysts.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2018.12.149>.

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