1 Study on the performance of simultaneous desulfurization and 2 denitrification of Fe₃O₄-TiO₂ composites

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8 **Abstract:** With Fe₃O₄ as the carrier, tetrabutyl titanate as precursor, the TiO₂ was
9 wrapped on the surface of Fe₃O₄ by hydrothermal method to synthesize the
10 Fe₃O₄-TiO₂ composite. X-ray powder diffraction(XRD), Transmission electron
11 microscopy (TEM) and Fourier transform infrared (FTIR) analysis showed that the
12 nano TiO₂ formed a better coating layer on the surface of Fe₃O₄ particles. In the
13 experiment, the simulation of the SO₂ and NO of the industrial coal-fired flue gas was
14 tested respectively by Fe₃O₄, TiO₂ and x%Fe₃O₄-TiO₂ (x% represents the mass
15 fraction of Fe₃O₄ of the total material). The results showed that the activities of TiO₂
16 and Fe₃O₄-TiO₂ were good, and both of them had good removal effect on SO₂ and
17 NO_x. TiO₂ was wrapped on Fe₃O₄, which formed a special package structure, the
18 surface layer of nano TiO₂ and Fe₃O₄ carrier can promote each other, the performance
19 of simultaneous desulfurization and denitrification can be further improved.
20 Fe₃O₄-TiO₂ composites with different ratio were tested at 100°C; 10% Fe₃O₄-TiO₂ had
21 high reaction performance; the removal effect gradually decreased with the increase
22 of Fe₃O₄ content. The performance of 10%Fe₃O₄-TiO₂ composite on simultaneous
23 desulfurization and denitrification at 100°C,150°C,200°C was in descending order. At
24 the temperature of 100°C, the removal effect of 10%Fe₃O₄-TiO₂ on SO₂ and NO_x can
25 be maintained at 100% and 50% respectively, and it was not until after 64 min the
26 NO_x was close to penetrate. The addition of H₂O enhanced the SO₂ adsorption; and
27 the NO adsorption capacity decreased with the increase of the H₂O content. NO_x and
28 SO₂ were adsorbed on the surface of the composite material by physical and chemical

adsorption, the products were sulfate and nitrate according to the results of the characterization.

Keywords: Fe₃O₄; TiO₂; Fe₃O₄-TiO₂; simultaneous desulfurization and denitrification

1 Introduction

Emissions from coal-fired flue gas of sulfur dioxide (SO₂) and oxides of nitrogen (NO_x) are not only important precursors of haze in the main pollutant PM_{2.5}, but also cause acid rain, smog, ozone layer destruction and other serious pollution problems of important factors, having a serious impact on the environment and human health^[1-2]. At present, countries around the world have invested a lot of manpower and material resources to develop a series of flue gas purification technology competing in desulfurization and denitrification aspects, such as wet, dry, semi-dry desulfurization, denitrification selective catalytic reduction(SCR), and activated carbon adsorption, electron beam radiation, corona, wet desulfurization denitration technology, etc^[3]. Among them, for the control of SO₂ in flue gas, the most mature and widely used technique is wet limestone/ gypsum flue gas desulfurization(FGD); For the NO_x, selective catalytic reduction process denitration(SCR) is mainly used^[4]. While there are still some defects in aspects of technology and economy in the dry flue gas simultaneous desulfurization denitration process, it remains to be a researched flue gas purification technology^[5] due to the advantages of low water consumption, low operation cost, simple equipment, lower land consumption, ease of sulfur recovery, etc.

In recent years, the research on the degradation of wastewater and gaseous pollutants by TiO₂ has received extensive attention and has achieved good results in basic research and applied research. TiO₂, with excellent catalytic performance, is not only a kind of new catalytic material that has wide application prospects in the field of environmental protection, but also one of the worldwide research hotspots in the field of new catalytic materials. Nano TiO₂ has the advantages of no toxicity, low cost, mild reaction conditions, stable chemical properties and so on[6]; and with the small particle size, high surface activity, a unique surface effect and quantum effect, it has

1 been widely used in wastewater treatment, air purification and other fields[7].
2 However, due to the aggregation of TiO_2 nanoparticles in the reaction system, the
3 effective specific surface area of the catalyst subsequently decreases, which leads to
4 the rapid decrease of the activity. In addition, the use of such ultrafine particles will
5 also cause a lot of separation problems[8]. In order to solve the problems of TiO_2
6 powder, such as easy to gather, difficult to recycle, to make full use of the
7 characteristics of nano TiO_2 and to enhance its activity, the TiO_2 composite material
8 was studied[9-11]. People tried to fix the TiO_2 powder on the magnetic carrier to
9 prepare a magnetically recyclable TiO_2 composite particle catalyst. The material can
10 be recovered and reused under the external magnetic field[12-13]. This magnetic
11 catalyst has high catalytic performance and is easy for magnetic separation and
12 recovery, and magnetic carrier Fe_3O_4 magnetic particle is commonly used by people.
13 As Chen research group also synthesize flower-like Fe_3O_4 - TiO_2 core shell nano
14 particles[14].

15 However, the research on simultaneous desulfurization and denitrification of
16 Fe_3O_4 - TiO_2 composites is less, and the principle of flue gas simultaneous
17 desulfurization and denitrification based on the Fe_3O_4 - TiO_2 is less reported. Therefore,
18 this paper used hydrothermal method to prepare Fe_3O_4 - TiO_2 composite that TiO_2 layer
19 was wrapped on the surface of Fe_3O_4 . Simulated flue gas flow rate and temperature
20 and studied the effects on reaction activity of different proportions of adsorbent under
21 different reaction temperatures to research desulfurization and denitration
22 performance of the material. The catalysts were characterized by FTIR and TEM, and
23 the results were correlated with the activity of the materials in the reaction.

24 **2. Experimental section**

25 **2.1 Experimental reagents and instruments**

26 Laboratory reagent: tetrabutyl titanate (TBOT), anhydrous ethanol, triethylamine
27 (TEA), iron oxide(Fe_3O_4) were of analytical grade, purchased from Sinopharm
28 Chemical Reagent Co., Ltd.

29 Instruments used in the experiments include: JEM-2010 type HRTEM analyzer,
30 Japan Jeol company; Magna-750 Fourier transform infrared spectrometer, US Nicolet

company; 101-3AB type blast electric dryer, Experimental instrument Co., Ltd. of North China in Tianjin; KM9106 flue gas analyzer, British Kane company.

2.2 Preparation for Fe₃O₄-TiO₂ Composites

Fe₃O₄-TiO₂ was synthesized by hydrothermal method with tetrabutyl titanate as titanium source: According to the mass ratio to weigh the corresponding purchased Fe₃O₄ in four beakers, respectively added 30mL of anhydrous ethanol, 10mL tetrabutyl titanate, and added suitable amount of deionized water, ultrasonic dispersion for 15min. The reaction solution was then transferred into a high pressure reaction kettle with a 250mL lined PTFE(in which a small amount of deionized water is added). The reaction kettle was then placed in an oven at 150°C for 4 h, cooled to room temperature naturally. Products were washed several times with anhydrous ethanol and deionized water, then placed in a vacuum drying oven at 110°C for 12h, set aside. The material was recorded as x% Fe₃O₄-TiO₂, where x% was the mass fraction of Fe₃O₄. At the same time, pure TiO₂ nano materials were prepared by the same method.

2.3 Characterization of materials

2.3.1XRD

X-ray powder diffraction (XRD) was performed in a Multi-functional X-ray diffractometer 20 by using Cu K α radiation (λ =0.15406nm) at a rate of 10° /min from 2 θ = 10° to 90°

2.3.2 Transmission electron microscopy (TEM)

The product was finely powdered in a mortar, ultrasonic dispersed in deionized water and prepared into homogeneous suspension. The suspension was sprayed on the copper net coated with carbon film, then used for TEM analysis after air-dried under normal temperature. Measured in JEM-2010 transmission electron microscope (JEOL Co.), the acceleration voltage is 200kV.

2.3.3 FTIR

The sample was mixed with KBr, Powder, then material was tableted quickly after drying. The wavenumber measurement range is 400~4000cm⁻¹.

2.4 Sample testing

The experimental simulation of NO/SO₂/O₂/N₂ was generated by the control of the dynamic air distribution system, and the experimental device was shown in Figure 1. The inner diameter of the quartz tube fixed-bed reactor was 7mm, the gas flow rate 200mL/min, the loading capacity 0.35g, space velocity 24000h⁻¹. The import feed gas mixture contained 500 ppm SO₂, 300 ppm NO, 5% O₂, N₂ as the balance gas and the reaction temperature was controlled by the program temperature control device. When the outlet NO gas concentration reached 80% of imports on the adsorption bed, which was defined to reach the point of penetration. The concentrations of SO₂, NO_x (NO and NO₂) in flue gas were measured by KM9106 portable integrated flue gas analyzer (Kane). The removal rate and adsorption capacity of SO₂ and NO_x were calculated according to the concentration of SO₂, NO and NO₂ of the product. The removal rate was defined as:

$$\eta = \frac{C_{inlet} - C_{outlet}}{C_{inlet}} \times 100\%$$

Where C_{inlet} was the air intake concentration (ppm), C_{outle} was the outlet concentration.

The formula for calculating the adsorption capacity was:

$$S = \frac{\int_0^t (C_0 - C_i) Q dt}{G}$$

Where S was the saturated adsorption capacity (mmol·g⁻¹), t was the adsorption time (min), C₀ was the air intake concentration (ppm), C_i was the outlet concentration (ppm), Q was the feed flow (mL·min⁻¹), and G was the mass of adsorbent.

Fig.1 Flow chart of experimental system

3. Results and discussion

3.1 Comparison of the performance of Fe₃O₄-TiO₂, Fe₃O₄ and TiO₂ on simultaneous desulfurization and denitrification

The samples of the prepared TiO₂, the purchased of raw materials Fe₃O₄, 10%Fe₃O₄-TiO₂ were used as adsorbent at 100°C in the simultaneous desulfurization and denitrification experiment. In order to compare the difference in performance between the composite material and the components mixed physically, the samples of the same quality of the prepared TiO₂ and the purchased raw materials Fe₃O₄ mixed physically were tested under the same conditions. The results were shown in Figure 2, in which showed the activity of Fe₃O₄ on simultaneous desulfurization and denitrification was poor and SO₂ and NO_x were very quick to penetrate; The activity of TiO₂ on simultaneous desulfurization and denitrification was better: there was no outlet of SO₂ within the measured time, and NO_x removal rate was reduced to 20% after 56min; In contrast, the activity of 10%Fe₃O₄-TiO₂ was higher, in which SO₂ was not detected in the export until 64min, while NO_x decreased to 20%, the overall effect of 10%Fe₃O₄-TiO₂ was higher than TiO₂. The desulfurization effect of Fe₃O₄-TiO₂, Fe₃O₄ and TiO₂ mixed physically were basically the same, can achieve 100% removal

1 efficiency in the test of time. But the difference on denitrification was large, physical
2 mixture of adsorbent was close to penetrate around 32 min, while the removal rate of
3 $\text{Fe}_3\text{O}_4\text{-TiO}_2$ composite material was reduced to 20% around 64 min. In order to
4 compare the adsorption effect of different materials, the adsorption capacity of each
5 material was calculated. When the outlet NO gas concentration reached 80% of
6 imports on the adsorption bed, it was deemed to reach the breakthrough point that
7 corresponding to the absorption time. The adsorption capacity of each material was
8 summarized in Table 1. According to the table 1, $\text{Fe}_3\text{O}_4\text{-TiO}_2$ material had the
9 strongest adsorption capacity. The adsorption capacity of NO and SO_2 respectively
10 were $0.2031\text{mmol}\cdot\text{g}^{-1}$ and $0.8152\text{mmol}\cdot\text{g}^{-1}$.

11 In the case of the same amount, the activity of $\text{Fe}_3\text{O}_4\text{-TiO}_2$ material was higher
12 than that of Fe_3O_4 and pure TiO_2 . It indicates $\text{Fe}_3\text{O}_4\text{-TiO}_2$ is a kind of special
13 composite structure, $\text{Fe}_3\text{O}_4\text{-TiO}_2$ has good dispersibility and stability with the
14 capability of improving the material of simultaneous desulfurization and
15 denitrification activity. By the comparison of $\text{Fe}_3\text{O}_4\text{-TiO}_2$ with the physical mixture of
16 Fe_3O_4 and TiO_2 , it also can be seen that $\text{Fe}_3\text{O}_4\text{-TiO}_2$ is not a simple physical mixture,
17 because it may form a special package structure. The surface layer of nano TiO_2 and
18 Fe_3O_4 carrier promote each other, improving the material simultaneous desulfurization
19 and denitrification activity. The Fe_3O_4 itself does not have a high catalytic activity, but
20 only acts as the role of a promoter. It can promote the NO to be better effected with
21 the material's surface to strengthen its chemical adsorption process[15], then cause
22 more of the SO_2 and NO_x to be adsorbed on the surface of TiO_2 . The addition of
23 metal oxides can significantly improve the catalytic activity of the catalyst for the
24 catalytic activity of NO is researched more. These metal oxides include Fe_3O_4 , Al_2O_3 ,
25 CaO , MgO , etc[16-17].

Fig. 2 Comparison of the performance of Fe₃O₄-TiO₂, Fe₃O₄ and TiO₂ on simultaneous desulfurization and denitrification

Table 1 Adsorption capacity of NO_x and SO₂ on different adsorbents

Adsorption capacities(mmol·g ⁻¹)	Fe ₃ O ₄	TiO ₂	Fe ₃ O ₄ -TiO ₂	Fe ₃ O ₄ +TiO ₂
S(NO)	0.014	0.1556	0.2031	0.0457
S(SO ₂)	0.0629	0.7092	0.8152	0.3041

The infrared spectrum diagram of Fe₃O₄-TiO₂ materials with Fe₃O₄, TiO₂ components as well as the physical mixture was shown in figure 3. As shown in Figure 3, the -OH bending vibration band on Fe₃O₄ was at 3439cm⁻¹, while the -OH bending vibration band on Fe₃O₄-TiO₂ shifted to 3373cm⁻¹, same as the -OH bending vibration band position on pure TiO₂. This suggests that the TiO₂ was wrapped up by the surface of Fe₃O₄. In addition, the band at 580cm⁻¹ corresponded to the Fe-O stretching vibration[18], which is the characteristic absorption band of Fe₃O₄. The band at 580cm⁻¹ on the Fe₃O₄-TiO₂ spectrum obviously disappears, suggesting that the TiO₂ was wrapped on the Fe₃O₄ surface, so that the groups on the Fe₃O₄ surface could not be displayed in the infrared spectrum.

Compared the two spectra of Fe₃O₄-TiO₂ material and Fe₃O₄, TiO₂ that physically mixed, although the two spectrum were very similar, there were some differences of the mark in the spectrum. It should be the Fe-O vibration absorption band of the Ti-O-Fe oxygen bridge structure at 449cm⁻¹, we can see the Fe³⁺ of

1 composite adsorbent partially replaced of Ti^{4+} in the Ti-O-Ti network, forming a
 2 Ti-O-Fe bridging oxygen structure[19]. Not only exists the absorption bands of TiO_2
 3 and Fe_3O_4 , but also appears a new absorption peak by the effect of them in the sample
 4 of $\text{TiO}_2\text{-Fe}_3\text{O}_4$. It can be concluded that the Fe_3O_4 carrier was wrapped by TiO_2
 5 successfully, and between TiO_2 and Fe_3O_4 is not a simple mixture, it formed the new
 6 structure of the adsorbent through the effect of the two generation by new chemical
 7 bonds.

8
 9 Fig. 3 Infrared spectra of Fe_3O_4 , TiO_2 and $\text{Fe}_3\text{O}_4\text{-TiO}_2$

10 3.2 Structure and Morphology analysis of $\text{Fe}_3\text{O}_4\text{-TiO}_2$

11 3.2.1 XRD analysis

12 In order to determine the crystal structure and the composition of the as-prepared
 13 samples, an X-ray power diffraction experiment was carried out. Figure 4 respectively
 14 showed the XRD patterns of the Fe_3O_4 , TiO_2 and 10% $\text{Fe}_3\text{O}_4\text{-TiO}_2$ samples. Curve a in
 15 Figure 4 showed that the characteristic peaks of Fe_3O_4 was very obvious, and in
 16 contrast with Fe_3O_4 standard XRD pattern (JCPDS), the main characteristic peaks of
 17 Fe_3O_4 presentation on the spectra (17.5° , 30.1° , 35.5° , 42.9° , 57.2° , 62.8°) were
 18 consistent with the Fe_3O_4 standard XRD pattern[20]. By the comparison of all peaks
 19 in curve b and TiO_2 standard XRD pattern(JCPDS: NO.21-1272)[21], the
 20 corresponding $2\theta = 25.5^\circ$, 37.9° , 48.1° , 54.2° and 62.8° were all at its typical
 21 characteristic diffraction peaks. The curves c in Figure 4 was the XRD patterns of

1 Fe_3O_4 - TiO_2 composites, and curve 4b and 4c were very similar. From the spectrum,
2 each peak corresponded substantially with the standard card(JCPDS: NO.21-1272).
3 But compared with the curve a, the characteristic peak of Fe_3O_4 at $2\theta = 30.1^\circ$, 35.5° ,
4 42.9° and 57.2° weakened; Characteristic peaks at $2\theta = 62.8^\circ$ may be Fe_3O_4
5 characteristic peaks or characteristic peaks of TiO_2 , the characteristic peaks of the
6 other places almost disappeared. This shows that the characteristic peak of Fe_3O_4 has
7 been weakened or covered by the characteristic peak of TiO_2 , indicating that TiO_2
8 formed a layer of coating on the surface of Fe_3O_4 , and the Fe_3O_4 - TiO_2 composite
9 material was synthesized.

Fig.4 XRD patterns of Fe_3O_4 (a), TiO_2 (b) and 10% Fe_3O_4 - TiO_2 nanoparticles(c)

3.2.2 TEM analysis

In order to further verify the structure of the composites, the structure of the composites was characterized by transmission electron microscopy. The TEM images of the Fe_3O_4 - TiO_2 composite were shown in Figure 5. As can be observed from Figure 5 (a), (b), the shape of Fe_3O_4 crystallite was mainly spherical. From figure 5 (c), (e) we can see that nano TiO_2 crystallite was small, and Fe_3O_4 - TiO_2 crystallite size distribution was not uniform, an average crystallite diameter was about 20nm-50nm. But there was also a part of the TiO_2 that was not wrapped up by the Fe_3O_4 surface, as well as part of the Fe_3O_4 - TiO_2 connected together to form a reunion. Figure 5 (d)

showed inside the deeper place was the Fe_3O_4 , the edge of the shallower was the TiO_2 [22], and Fe_3O_4 nanoparticles most were in the form of adhesion with a single particle or a few particles or a number of particles that was wrapped by TiO_2 . A high-magnification HRTEM was used to further investigate the structure of the Fe_3O_4 - TiO_2 sample in Figure 5(f). This revealed that the prepared samples were well crystallized, as evidenced by well-defined lattice fringes. The small crystallite size and the well crystallized structure contributed to the efficient photocatalytic property of adsorbent[23], which was confirmed by the previous experiments on simultaneous desulfurization and denitrification of the Fe_3O_4 - TiO_2 nano composites.

Fig. 5 TEM micrographs of 10% Fe_3O_4 - TiO_2 composites

3.3 Study on simultaneous desulfurization and denitration of Fe_3O_4 - TiO_2 composites with different proportions

Simulated coal-fired power plant flue gas conditions, the performance of each material on simultaneous desulfurization and denitration was tested at 100°C with different ratio of the Fe_3O_4 - TiO_2 composite (mass ratio respectively was 10%, 20%, 30% and 40%) as adsorbent, the results were shown in Figure 6. By figure 6 (a) it can

1 be seen that in terms of desulfurization, the material removal effect was good: with
 2 the increase of reaction time, the desulfurization effect of each material can reach
 3 100%. Figure 6 (b) showed that in terms of the denitration, the removal efficiency of
 4 each material decreased with the increase of ratio, the removal effect of
 5 10%Fe₃O₄-TiO₂ on NO_x was the best, it was not until after 64 min the removal rate
 6 was reduced to 20% at the temperature of 100°C. The adsorption capacity of NO and
 7 SO₂ with different ratio of Fe₃O₄-TiO₂ materials were shown in table 2. This is mainly
 8 due to the surface effect and quantum size effect of nano TiO₂ and larger specific
 9 surface area ,which have a strong adsorption capacity to SO₂, NO and other small
 10 molecules. In addition, there are a lot of oxygen vacancies on the surface of TiO₂ in
 11 the preparation process of Fe₃O₄-TiO₂[24]; Oxygen defects on TiO₂ (110) surface
 12 provides important adsorption sites and further contributes to the occurrence of some
 13 surface reactions. And the NO_x removal efficiency decreased with the increase of
 14 ratio, which may be when the Fe₃O₄ content is less in the composite, the TiO₂
 15 nanoparticles uniformly dispersed on the surface of the carrier to improve the surface
 16 area and is conducive for gas removal; When the Fe₃O₄ content increases, part of
 17 Fe₃O₄ was not wrapped, and the presence of particle agglomeration and other
 18 phenomena can cause the specific surface area of adsorbent decrease and active sites
 19 reduced[25], so that the performance of simultaneous desulfurization and
 20 denitrification was decreased.

(a)

(b)

Fig. 6 Different ratio of Fe₃O₄-TiO₂ on simultaneous desulfurization and

1 denitrification experiment

2

3 Table 2 Adsorption capacity of NO_x and SO₂ of Fe₃O₄-TiO₂ under different ratio

Adsorption	10%Fe ₃ O ₄ -TiO ₂	20%Fe ₃ O ₄ -TiO ₂	30%Fe ₃ O ₄ -TiO ₂	40%Fe ₃ O ₄ -TiO ₂
capacities (mmol·g ⁻¹)				
S(NO)	0.2031	0.1448	0.1266	0.0778
S(SO ₂)	0.8152	0.6090	0.4332	0.3061

4

5 **3.4 Study on simultaneous desulfurization and denitration of Fe₃O₄-TiO₂**
6 **composites at different reaction temperatures**

7 Choose the 10%Fe₃O₄-TiO₂ to do the simultaneous desulfurization and
8 denitrification experiments at different reaction temperatures. The results were shown
9 in Figure 7 and the adsorption capacity was listed in Table 3. As can be observed from
10 Figure 7(a) and table 3, there was a slight gap in the first few minutes at each
11 temperature in terms of desulfurization; with the increase of reaction time, the
12 desulfurization efficiency of two kinds materials under various temperature both can
13 reach 100%. Figure 7 (b) showed two kinds of materials had certain removal effect for
14 NO_x under various temperature, the denitration effect was better under the 100°C, and
15 it was not until after 64 min the removal rate was reduced to 20%. While the
16 denitrification effect decreased particularly with the rise of temperature. This could be
17 explained that the NO_x is reacting on the surface of the Fe₃O₄-TiO₂ adsorbent,
18 including both physical adsorption and chemical adsorption. The physical adsorption
19 process is caused by the van der Waals forces between NO_x molecules and the surface
20 of the TiO₂ particles; while the physical process is reversible and can cause the
21 phenomenon that the heated molecular escaping from the surface of the adsorbent.
22 Due to the presence of SO₂ in the experiment, the reactant particle diffusion rate and
23 the collision frequency are improved with the increase of temperature, and the
24 reaction rate is accelerated; which leads to increase the chances of the molecule to

spread on the surface of the adsorbent particles and to occupy more adsorption holes[26]; so that on a certain amount of load catalyst, it reduces the adsorption of the $\text{Fe}_3\text{O}_4\text{-TiO}_2$ particles on NO_x molecular.

Comparing Figure 7 (a) and Figure 7 (b), it can be concluded that two kinds of materials on the removal efficiency of SO_2 were better than NO_x . This may be due to the relevant theory of adsorption[27], it is a selective process of the adsorbent on a material. Based on the selective adsorption of molecular polarity, degree of unsaturation and the rate of polarizability, the molecular polarization is induced by electrostatic induction. So the polarity is stronger or easier to be polarized that the molecules are more likely to be adsorbed. Adsorbents such as $\text{Fe}_3\text{O}_4\text{-TiO}_2$ have high adsorption capacity for both polar molecules and unsaturated molecules, and in nonpolar molecules, there is also a high selective adsorption capacity for the large polar molecules. Therefore, there is a strong affinity of higher polarity such as H_2O , SO_2 molecules. And especially for water, it has a high adsorption capacity even in low ambient conditions of pressure or low concentration and high temperature condition. While NO_x is not highly polar gas[28], the physical adsorption that occurs on the solid particles is relatively weak. People in the study on simultaneous desulfurization and denitration also found the similar phenomenon. It may be due to the difference of molecular polarity and the adsorption dynamics of the two molecules, resulting in some differences in the absorption level of them. Generally speaking the SO_2 removal is prior to the removal of NO_x [29].

(a)

(b)

Fig. 7 Simultaneous desulfurization and denitrification experiment of 10% Fe₃O₄ - TiO₂ at different temperatures

Table 3 Adsorption capacity of NO_x and SO₂ of Fe₃O₄-TiO₂ under different temperature

Adsorption capacities (mmol·g ⁻¹)	100℃	150℃	200℃
S(NO)	0.2031	0.1049	0.0267
S(SO ₂)	0.8152	0.6626	0.3566

3.5 Effect of H₂O content on the simultaneous adsorption of SO₂ and NO

In the actual flue gas, there is a certain concentration of moisture. Considering the experimental need and industrial condition, the effect of moisture on the simultaneous adsorption of SO₂ and NO was worthy of studying. The moisture content in the actual flue gas is typically 4%-10%. And the moisture content was adjusted to 0%, 5% and 10%, which was added to the flue gas by evaporator. Select the best performing 10% Fe₃O₄-TiO₂ composite to do the test, the experimental results were shown in Figure 8. And the NO and SO₂ adsorption capacities were summarized in Table 4.

As shown in the Figure 8, in terms of SO₂, the removal effect was already very good with the absence of moisture, so with the addition of moisture, the removal efficiency had no significant change compared with the absence of moisture; For NO_x, the removal efficiency decreased with the increase of water content. According to the literature, the presence of a small amount of H₂O in flue gas is beneficial to desulfurization. The reason may be that the SO₂ dissolved in water itself, reacted with the H₂O to form H₂SO₄ and promoted the SO₂ chemical adsorption[30]. Increasing the H₂O concentration, the NO removal efficiency decreased obviously. The water molecules may occupy the active position[31], compete with the NO_x adsorption and is easy to generate nitric acid with NO₂ to cover adsorption sites[32], which resulted in the inhibition of NO adsorption.

(a)

(b)

Fig. 8 Simultaneous desulfurization and denitrification experiment of 10% Fe₃O₄ - TiO₂ at different moisture content

Table 4 Adsorption capacity of NO_x and SO₂ of 10%Fe₃O₄-TiO₂ with different H₂O content

Adsorption capacities (mmol·g ⁻¹)	0% H ₂ O	5% H ₂ O	10% H ₂ O
S(NO)	0.2031	0.1469	0.1006
S(SO ₂)	0.8152	0.7647	0.4592

3.6 Analysis of desulfurization and denitrification products of Fe₃O₄-TiO₂ Composites

Choosing 10%Fe₃O₄-TiO₂ that had better desulfurization and denitration effect to make infrared spectrogram before and after the reaction, the results were shown in Figure 9. As can be observed from Figure 9, the differences of FTIR were large between the fresh and used sample, the large and broad band at 3387cm⁻¹ was attributed to the -OH stretching vibration on material surface, while the band at 1631cm⁻¹ was attributed to the -OH bending vibration band of H₂O. Compared with the unused adsorption materials, the band at 1047cm⁻¹ and 1129cm⁻¹ corresponded to the S-O vibration band of SO₄²⁻[33], which confirmed that the formation of SO₄²⁻ in the reaction to achieve the removal of SO₂. Besides, the vibration peak in spectra of

1 experiments with water was greater here, which indicated that the addition of water
 2 can promote the formation of SO_4^{2-} [30]. A very sharp absorption peak was appeared
 3 at 1386cm^{-1} of the used sample, which is the characteristic infrared absorption of
 4 nitrate[34-35]. After adding the 5% water, the vibration peak was even more shape,
 5 which showed that the formation of nitrate increased. It could be that the nitric acid
 6 was generated by the product of NO_2 after reacting with water[32]. This result
 7 indicated that NO_2 was formed by catalytic oxidation of NO and was adsorbed,
 8 further was reacted with metal oxide on the carrier to form nitrate[36], so as to
 9 achieve the removal of NO . Dalton etc[37] after testing the surface reaction between
 10 the nitrogen oxide and surface of the TiO_2 by XPS and Raman spectrometer, also
 11 shows that there is a good lattice defects on TiO_2 surface that have a good catalytic
 12 activity and can effectively convert nitrogen into nitrates.

13
 14 Fig.9 FI-IR spectra of 10% $\text{Fe}_3\text{O}_4\text{-TiO}_2$ composites before and after tests

15 **4. Conclusions**

16 (1)In this paper, $\text{Fe}_3\text{O}_4\text{-TiO}_2$ composites with stable structure were prepared by
 17 hydrothermal synthesis method. By the comparison of simultaneous desulfurization
 18 and denitration performance of $\text{Fe}_3\text{O}_4\text{-TiO}_2$, each single components and the
 19 physically mixture of both, it indicates the formation of a composite material, and the
 20 mutual promotion between the composite material attributes to the best performance
 21 of simultaneous desulfurization and denitrification. TiO_2 was wrapped uniformly on

the Fe_3O_4 surface by the characterization of XRD and TEM. The average size of the composite material was in the range of 35~50nm, the surface is the nanoparticles TiO_2 crystallite with the size of nm 20~50nm.

(2) Simulated coal-fired power plant flue gas conditions, the performance on simultaneous desulfurization and denitration of $\text{Fe}_3\text{O}_4\text{-TiO}_2$ with different ratio was tested at 100°C. 10% $\text{Fe}_3\text{O}_4\text{-TiO}_2$ has higher response performance, and the NO_x removal efficiency gradually declined with the increase of Fe_3O_4 content.

(3) The performance of 10% $\text{Fe}_3\text{O}_4\text{-TiO}_2$ composite on simultaneous desulfurization and denitrification was tested at 100°C, 150°C, 200°C three different temperatures. The performance of the composite was decreased gradually, and it had higher performance at the lower temperature (100 °C). The removal efficiency of 10% $\text{Fe}_3\text{O}_4\text{-TiO}_2$ composite on simultaneous desulfurization and denitrification was significantly higher than that of Fe_3O_4 and pure nano TiO_2 . The H_2O content of the simulated flue gas had significant effect on the adsorption of NO and SO_2 . The addition of H_2O enhanced the SO_2 adsorption; and the NO adsorption capacity decreased with the increase of the H_2O content.

(4) Through the Fourier transform infrared (FTIR) characterization of $\text{Fe}_3\text{O}_4\text{-TiO}_2$ composite before and after reaction, it can be concluded that there are both physical adsorption and chemical adsorption in the reaction, however the chemical adsorption is the main. SO_2 and NO_x are converted into sulfates and nitrates so as to achieve the removal of gas.

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