Enhancement mechanism of SO₂ removal with calcium hydroxide in the presence of NO₂

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Abstract–The enhancement mechanism of SO₂ removal by the presence of NO₂ under low temperature and humid conditions was studied in a fixed bed reactor system. The presence of NO₂ in the flue gas can enhance SO₂ removal. The interaction between SO₂ and NO₂ in gas phase could not explain the effect of NO₂ on SO₂ removal under low-temperature and humid conditions. When $Ca(NO_3)_2$ and $Ca(NO_2)_2$ as additive were added on the surface of sorbent, the desulfurization activity of sorbent decreased. However, the sorbent pretreated by NO₂ for a moment has higher SO₂ removal. The oxidization of SO_3^{2-} to SO_4^{2-} and the evolution of sorbent surface structure in the presence of NO₂ can explain the enhancement of SO₂ removal by the presence of NO₂. HSO_3^- and SO_3^- reacted with NO₂ to form sulfate, which can accelerate the hydrolysis of SO₂. The reaction between NO₂ and $Ca(OH)_2$ can make the unreacted sorbent under the SO₂ removal product exposed to the reactant gas.

Key words: SO₂ and NO₂, Desulfurization, Denitrification, Flue Gas, Calcium Hydroxide

INTRODUCTION

Considering the high proportion of SO₂ removal processes with Ca-based sorbents in old existing power plants, developing an economical and effective technology for simultaneous removal of SO₂ and NO_x in the conventional FGD reaction cell has attracted many researchers' attention. Many studies have shown that oxidizing NO to more soluble NO₂ is a promising method for enhancing NO removal in conventional FGD processes. NO is first oxidized to NO₂ by the addition of an oxidant such as KMnO₄ [1,2], O₃ and methanol into the flue gas duct at an optimum temperature [3-5], then it reacts with the conventional alkaline sorbent. Compared with the conventional desulfurization reaction process, the presence of NO₂ in the flue gas not only makes the sorbent surface reactions more complicated, but also affects the reaction path of SO₂ removal. Therefore, understanding the effect mechanism of NO₂ on SO₂ removal under conventional semi-dry and dry FGD processes conditions is important for retrofitting the conventional FGD processes to achieve simultaneous removal of SO₂ and NO_x.

Concerning the effect of NO_x on SO₂ removal, there have been reports by many researchers. Chu et al. revealed that the presence of NO in the gas phase has a negligible effect on the reaction between $Ca(OH)_2$ and SO₂, and even had a negative effect on SO₂ removal at a high level of NO concentration [6]. Lee et al. [7] found that the sulfation of Ca-based sorbent was not affected by the presence of NO alone. However, the coexistence of NO and O₂ in the flue gas enhances desulfurization reaction. Ishizuka et al. reported that NO_x barely affects SO₂ removal in the wet and semidry FGD processes; a promotive effect of NO_x is evident at the high temper-

ature dry FGD process [8]. Tsuchiai et al. pointed out that the desulfurization activity of the sorbent synthesized from the coal ash and calcium oxide markedly increased with NO concentration, and remained constant above 500 ppm [9]. The preceding studies mentioned above suggested that NO itself has no impact on SO₂ removal, because of its low activity with the alkaline material and low solubility in aqueous solutions. However, the studies surveyed in the literature all agree with the great impact of NO₂ derived from the oxidization of NO on SO₂ removal. This issue has captured many researchers' attention, and various influence mechanisms have been proposed.

O'Dowd et al. investigated the characterization of NO₂ and SO₂ removals in a spray dryer/baghouse system, and found that SO₂ removal in the spray dryer is not influenced by the presence of NO₂ [10]. However, the presence of NO₂ seems to enhance the baghouse SO₂ removal. They did not point out the enhancement mechanism. Liu et al. maintained that the great enhancement effect exerted by the presence of NO_x/O_2 resulted from the rise in the NO₂ concentration, which enhanced the oxidation of HSO_3^- and SO_3^{2-} to SO_4^{2-} in the water layer and the formation of deliquescent salts calcium nitrite and nitrate [12]. However, Bausach et al. maintained that the conversion of sulfite to sulfate cannot account for the positive effect of NO₂ on SO₂ removal [11], and ascribed higher SO₂ removal in the presence of NO₂ to a greater amount of water adsorbed on the surface of sorbent due to the presence of highly hygroscopic species calcium nitrite and nitrate. Tsuchiai et al. assumed that NO plays a catalytic role in the oxidation of SO₂ to SO₃. NO₂ derived from the oxidization of NO in the presence of O₂ was assumed to oxidize SO₂ to SO₃ [9]. Lee et al. also postulated O₂ and NO as an oxidizing agent to oxidize SO₂ to SO₃, which has a higher reaction activity with alkaline solids than SO₂ [7]. However, Li et al. pointed out that the reaction products $Ca(NO_3)_2$ could react with SO₂ to form gyp-

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sum and NO, which was deemed as the reason for explaining NO_x enhancement [13].

Although the influences of NO_x in the flue gas on SO_2 removal have been investigated by many researchers with various apparatus, almost no consistent enhancement mechanism of SO_2 removal by NO_x were obtained. Concerning the role of NO_x removal products in SO_2 removal, the report has not yet been found. Therefore, it is worthwhile to investigate this subject further. The aim of this paper is to study the effect of NO_2 absorption on SO_2 removal by calcium hydroxide particles under low temperature and humid circumstance in detail. The SO_2 absorption characteristic of calcium hydroxide was obtained in a widespread concentration range of NO_2. The interaction between SO_2 and NO_2 in the gas phase in and without presence of H_2O was investigated by using CHEMKIN software. The effects of NO_2 removal products $Ca(NO_3)_2$ and $Ca(NO_2)_2$ on SO_2 removal are discussed by the step experiments and pretreatment experiments. Finally, the possible effect mechanism of NO_2 on SO_2 removal with calcium hydroxide particle under low temperature and humid circumstance is discussed.

EXPERIMENTAL SECTION

The raw material used to prepare the sorbent is calcium oxide, which is of reagent grade. The raw calcium oxide was first milled and sieved to ensure that almost all calcium oxide particles were in the size range 60-80 μm. The powder-type calcium oxide was then added into de-ionized water at an H_2O/CaO weight ratio of 5 at a temperature of 70 °C. The slurry was heated to 90 °C and maintained for 3 h with continuous stirring. After stirring, the resulting slurry was dried at 110 °C until there was no weight change to produce the dry absorbent. The dry absorbent was then crushed and sieved into the required particle size range of 250-500 μm with a specific BET surface area 7.39 m^2/g.

The experiments for the reaction of absorbent with SO_2 and NO_2 were carried out by a fixed bed reactor system. The details of the experimental setup and procedure are described in our previous report [14]. In this study about 1.2 g absorbent was used for each run, except for the runs specially pointed out. To prevent channeling and absorbent agglomeration in the reactor, about 14 g of silicon dioxide with particle size range of 125-250 μm mixed with absorbent was packed in the reactor. The total flow rate of the simulated flue gas was controlled at 1,500 mL/min (STP). The concentration of SO_2, NO, NO_2 and H_2O was continuously monitored by an online Fourier transform infrared (FTIR) gas analyzer (GASMET-DX4000, Finland), with the measurement error of ±2%. A flue gas analyzer (Testo350, Germany) was used to measure the concentrations of O_2, with the measurement errors of ±0.8 vol%. Fourier transform infrared (FTIR) spectroscopy (Thermo Nicolet 5700, USA) was employed to identify the presence of specific functional groups in the spent absorbents and to gain insight into the effect mechanism of NO_2 on SO_2 removal. The surface morphologies of the spent absorbents were observed by scanning electron microscopy (SEM) (Hitachi, S-4700, Japan). The removal efficiency of SO_2 was defined as follows:

$$SO_2 \text{ removal: } \eta_{SO_2} = \frac{C_{SO_2,in} - C_{SO_2,out}}{C_{SO_2,in}} \times 100\% \qquad (1)$$
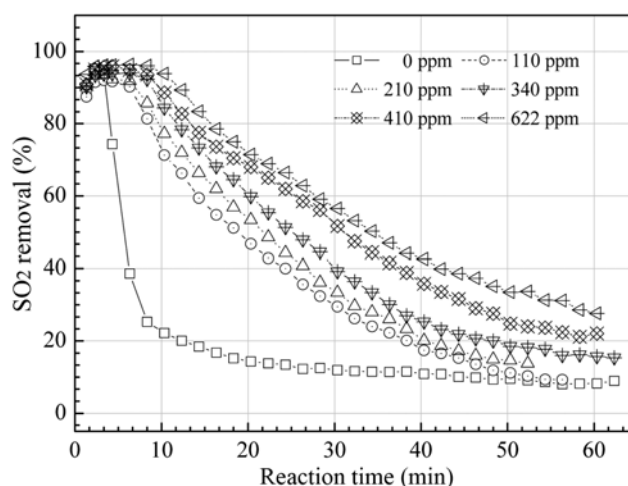
Fig. 1. Effects of NO_2 on SO_2 removal. Reaction conditions: SO_2= 1,500 ppm, NO_2=0-650 ppm, O_2=6%, H_2O=18%, reaction temperature=70 °C, sorbent: 1.2 g.

Where $C_{SO_2,in}$, $C_{SO_2,out}$ represent the concentration of SO_2 in the flue gas at the inlet and outlet of the reactor, respectively.

RESULTS AND DISCUSSION

1. Effects of NO_2 on SO_2 Removal

The evolution of SO_2 removal with time exposure at 70 °C, 1,500 ppm SO_2 and 60% RH for different NO_2 concentrations in the range of 0-650 ppm is shown in Fig. 1. By comparing with the case in the absence of NO_2, it can be seen that the presence of NO_2 in the flue gas can markedly enhance SO_2 removal. SO_2 removal increases with an increase in NO_2 concentration. This finding is good agreement with that reported by Bausach [11] and Siddiqi [16]. This indicates that there is no competition between SO_2 and NO_2 absorption on the surface of calcium hydroxide particle, although both SO_2 and NO_2 are acid gases and can react with calcium hydroxide.

Under low temperature and humid conditions, SO_2 absorption on the surface of calcium based sorbent particle can be summarized as follows. Water vapor molecules were first adsorbed on the wall of wide pore and the exterior surface of the sorbent to form a thin water layer. SO_2 molecules diffuse through the gas film and reach the sorbent surface to react with adsorbed water molecules to form $SO_2 \cdot nH_2O$, which subsequently reacts with $Ca(OH)_2$. The reaction product layer formed under the water layer not only covers the sorbent surface, but also increases the reactant gas diffusion resistance. The gas diffusion in the product layer becomes the rate limiting step. Therefore, SO_2 removal rapidly decreases with reaction time in Fig. 1.

When NO_2 is fed into the gas phase, some NO_2 molecules are also absorbed by sorbent in the same way as SO_2. There are many possible reactions between SO_2 and NO_2 occurring in SO_2 removal process. On the basis of the previous investigation and the absorption processes of SO_2 and NO_2 in the fixed reactor, the possible reaction sites in which NO_2 enhancing SO_2 removal occurs are depicted in Fig. 2. In gas phase, SO_2 can react with NO_2 to form SO_3 and NO. In the water layer, SO_3^{2-} ion derived from the hydrolysis of SO_2 can be oxidized to SO_4^{2-} by NO_2. Moreover, the presence of NO_2 removal products on the surface of sorbent may also affect SO_2
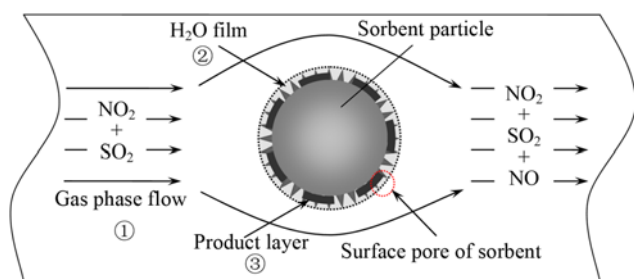
Fig. 2. The possible reaction sites for NO$_2$ enhancing SO$_2$ removal.

removal. To better understand the role of NO$_2$ in SO$_2$ removal reaction and obtain the effect mechanism of NO$_2$ on desulfurization process, the interaction between SO$_2$ and NO$_2$ in gas phase and the influences of NO$_2$ and NO$_2$ removal products were studied in detail.

2. Interaction between NO$_2$ and SO$_2$ in Gas Phase

When SO$_2$ and NO$_2$ coexist in the gas phase, SO$_2$ can be oxidized to SO$_3$ by the following reaction:

$$SO_2 + NO_2 = SO_3 + NO \qquad (2)$$

Besides reaction (2), many other main reactions occurring in the presence of H$_2$O are summarized in Table 1. Some reactions were negligible in terms of rate constants. The concentrations of relevant components were calculated by using CHEMKIN software (version 4.1). The reaction rate constants of the reactions listed in Table 1 were obtained from the National Institute for Standards and Technology (NIST) chemical reactions database.

Fig. 3(a) and (b) show the evolution of SO$_2$ concentration with time for different reaction temperature in and without the presence of H$_2$O. As can be seen, the reaction rate between SO$_2$ and NO$_2$ increases with reaction temperature increasing in the absence of H$_2$O. However, the interaction between SO$_2$ and NO$_2$ is negligible at a temperature lower than 603 K. The addition of H$_2$O into the gas phase did not enhance the reaction between SO$_2$ and NO$_2$ under low temperature condition (see Fig. 3(b)), although the presence of H$_2$O in the gas phase makes the homogeneous reaction more complicated. Therefore, the interaction between SO$_2$ and NO$_2$ in gas phase could not explain the effect of NO$_2$ on SO$_2$ removal under low-temperature and humid conditions.

3. Effects of NO$_2$ Removal Products on SO$_2$ Removal

To elucidate the roles of NO$_2$ removal products in SO$_2$ removal by Ca(OH)$_2$, experiments for the reactions between the modified
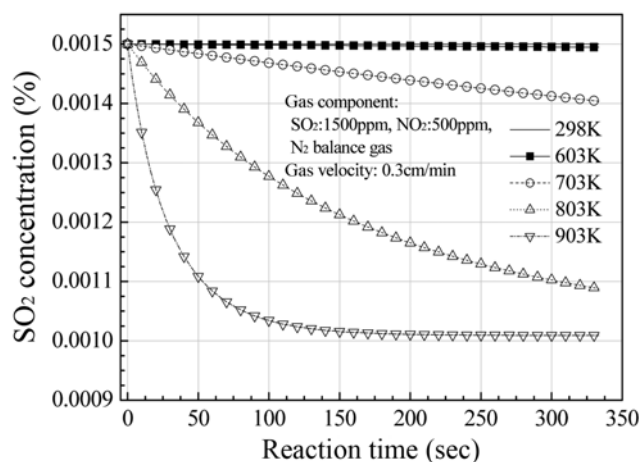
(a) Without presence of H$_2$O in the gas phase
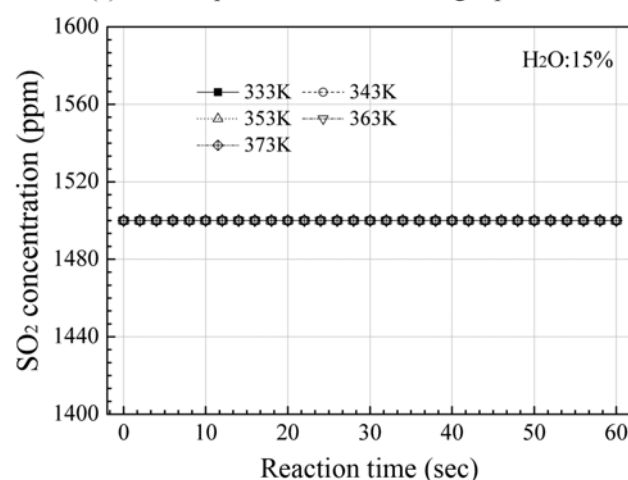
(b) 15% H$_2$O added into the gas phase

Fig. 3. Evolution of SO$_2$ concentration calculated by CHEMKIN software under the conditions: NO$_2$=450 ppm, SO$_2$=1,500 ppm, H$_2$O=0 or 15%, O$_2$=6%.

sorbent and SO$_2$ were carried out at 70 °C and 60% relative humidity. The modified sorbent was prepared from calcium hydroxide and the different amount of additives (Ca(NO$_3$)$_2$ and Ca(NO$_2$)$_2$). The calcium nitrite and calcium nitrate used were reagent-grade solution. In the modified process, the calcium nitrite and calcium nitrate solutions were equably dispersed on the surface of the cal-

Table 1. Main reactions in SO$_2$, NO$_2$ and H$_2$O gas phase system

Reactions	Rate constant (cm^3/mol-s)	
NO(g)+O$_2$(g)=NO$_2$(g)	$k_2 = 1.2 \times 10^9 \exp(4.407/RT)$	R-2
2NO$_2$(g)=N$_2$O$_4$(g)	$k_3 = 5.0 \times 10^{11}(T/298)^{-1.10}$	R-3
NO(g)+NO$_2$(g)=N$_2$O$_3$(g)	$k_4 = 4.71 \times 10^{12}(T/298\ K)^{1.40}$	R-4
N$_2$O(g)+N$_2$O$_3$(g)=2HNO$_2$(g)	$k_5 = 3.79 \times 10^{13} \exp(-37.17/RT)$	R-5
N$_2$O$_4$(g)+H$_2$O(g)=HNO$_2$(g)+HNO$_3$(g)	$k_6 = 2.52 \times 10^{14} \exp(-48.47/RT)$	R-6
NO$_2$(g)+NO$_2$(g)=NO(g)+NO$_3$(g)	$k_7 = 6.17 \times 10^{11}(T/298\ K)^{0.73} \exp(-87.30/RT)$	R-7
NO$_2$(g)+NO$_3$(g)=NO(g)+NO$_2$(g)+O$_2$(g)	$k_8 = 5.73 \times 10^{10} \exp(-11.72/RT)$	R-8
NO$_2$(g)+NO$_3$(g)=N2O$_5$(g)	$k_9 = 3.86 \times 10^{11}T^{0.2}$	R-9
N$_2$O$_5$(g)+H$_2$O(g)=HNO$_3$(g)+HNO$_3$(g)	$k_{10} = 1.21 \times 10^2$	R-10

(a) Effect of Ca(NO$_2$)$_2$

(b) Effect of Ca(NO$_3$)$_2$
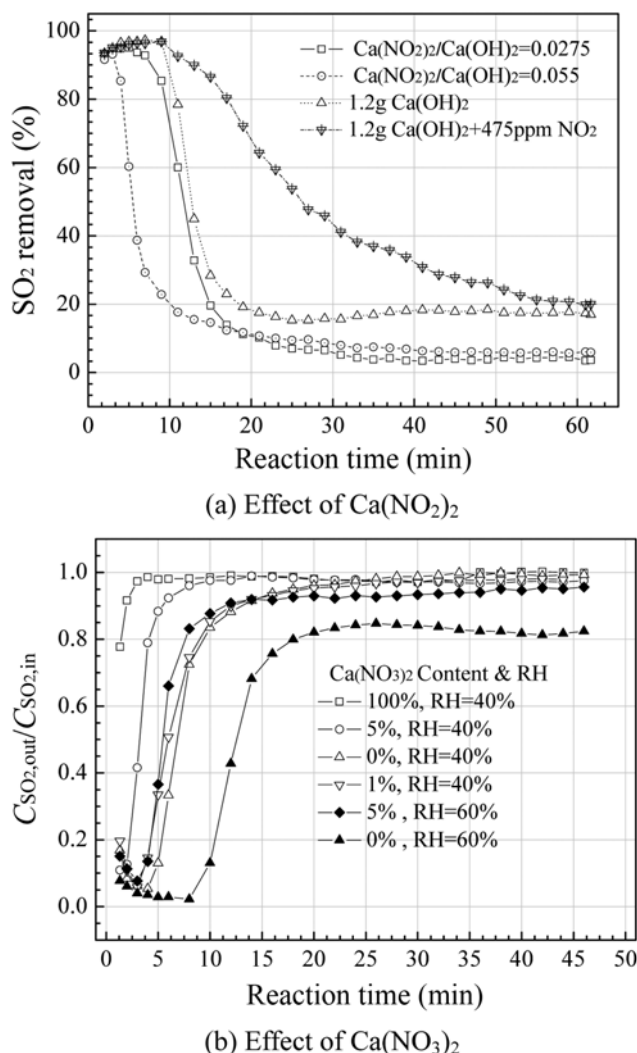
Fig. 4. Effects of NO$_2$ removal products on SO$_2$ removal. Reaction conditions: SO$_2$=1,200 ppm, O$_2$=6%, Relative humidity= 40% or 60%, reaction temperature=70 °C.

cium hydroxide particle by using a sprayer, then dried at 105 °C with N$_2$ purging to restrain calcium nitrite oxidization.

Fig. 4(a) shows SO$_2$ removal by the modified sorbent with different amount of Ca(NO$_2$)$_2$ as additive. As can be seen, SO$_2$ removal decreases with an increase in the amount of additive Ca(NO$_2$)$_2$. Compared with the sorbent without being modified by Ca(NO$_2$)$_2$, the presence of Ca(NO$_2$)$_2$ on the surface of sorbent lowers the desulfurization activity of Ca(OH)$_2$. Therefore, the presence of Ca(NO$_2$)$_2$ on the surface of sorbent cannot be used to explain the enhancement of SO$_2$ removal by the presence of NO$_2$. The evolution of the ratio of SO$_2$ concentrations at reactor outlet ($C_{SO_2,out}$) to inlet ($C_{SO_2,in}$) for the modified sorbents with different amount of Ca(NO$_3$)$_2$ as additive is given in Fig. 4(b). It can be found that Ca(NO$_3$)$_2$ shows no reactivity toward SO$_2$. The presence of Ca(NO$_3$)$_2$ on the surface of sorbent also restrains SO$_2$ removal.

Prior to this study, concerning the effect of NO$_x$ removal products on the reaction between SO$_2$ and Ca(OH)$_2$, only Bausach et al. performed some relevant work [11]. They maintained that the presence of nitrite and nitrate species on the surface of sorbent caused
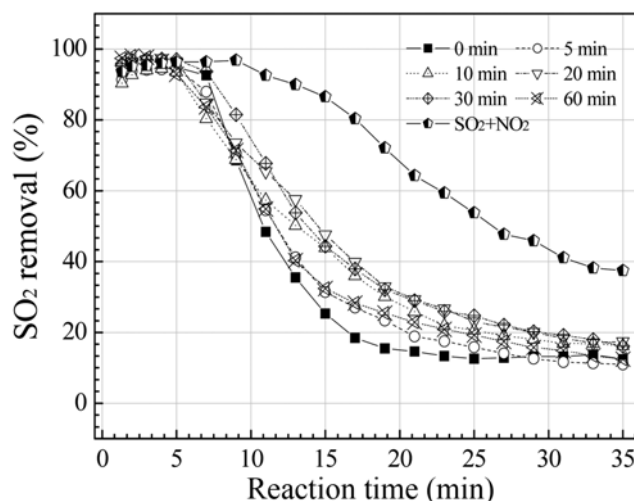
Fig. 5. Effects of NO$_2$ pretreatment on SO$_2$ removal. Reaction conditions: SO$_2$=1,200 ppm, O$_2$=6%, H$_2$O=18%, Ca(OH)$_2$=1.2 g, reaction temperature: 70 °C.

an effect similar to an increase of the relative humidity in the gas flow. The hydrophilic character of nitrite and nitrate species can collect a great amount of water on the sorbent surface, and thus greatly enhance the reaction between SO$_2$ and Ca(OH)$_2$. However, we cannot reach the conclusion that nitrite and nitrate species can enhance SO$_2$ removal from the results in Fig. 4(a) and (b).

For the purpose of further elucidating the effect of NO$_2$ removal products on SO$_2$ removal, NO$_2$ pretreatment experiments were performed. In the experiment process, the sorbent was first pretreated by 500 ppm NO$_2$ at 70 °C and 60% relative humidity for different times to obtain the pretreated sorbent containing different amount of NO$_2$ removal products, and then the pretreated sorbent was exposed to SO$_2$. The evolution of SO$_2$ removal is plotted against time in Fig. 5. With increasing pretreatment time from 0 to 20 min, SO$_2$ removal obviously increases, which indicates that the sorbent reacting with NO$_2$ for a moment will have a higher desulfurization activity. If the enhancement of SO$_2$ removal by the presence of NO$_2$ can be explained by the presence of NO$_2$ removal products, the more NO$_2$ removal products formed on the surface of sorbent, the higher SO$_2$ removal should be obtained. However, it can be found that a declining trend is obtained as the pretreatment time above 20 min. This result further confirms that the presence of NO$_2$ removal products cannot explain the enhancement of SO$_2$ removal by the presence of NO$_2$. Thus, it can be deduced that the NO$_2$ pretreatment must change the surface structure characteristic, which is in favor of the reaction between SO$_2$ and Ca(OH)$_2$. Moreover, compared with the case in which both SO$_2$ and NO$_2$ are present in flue gas, SO$_2$ removal by the sobent pretreated for 20 min is still lower. This indicates that NO$_2$ may take part in the desulfurization reaction.

To confirm this presumption, a step experiment was performed at 70 °C and 60% relative humidity. During the experiment, SO$_2$ and NO$_2$ were fed into the reactor separately. The sorbent was first exposed to a gas stream involving 1,200 ppm SO$_2$ without the presence of NO$_2$, then the gas stream was switched to the bypass and NO$_2$ was added into the gas stream. After SO$_2$ and NO$_2$ concentration was stable, the gas stream was quickly switched into the reactor.
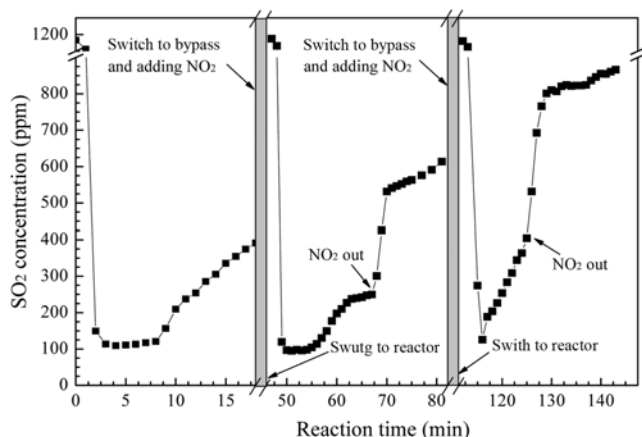
Fig. 6. Results of the step experiment. Reaction conditions: SO₂= 1,200 ppm. NO₂=470 ppm, relative humidity=60%, sorbent =1.2 g.

Fig. 7. FTIR spectrum of the spent sorbent. (a) Simultaneous removal of SO₂ and NO₂; (b) NO₂ single removal; (c) SO₂ single removal.

Then, NO₂ was excluded from the gas stream after 20 min reaction. The reduplicate process was performed again. The result of step experiment is shown in Fig. 6. The SO₂ concentration remains at 100 ppm for the first 8 min, and then increases with reaction time. After 20 min reaction, SO₂ concentration at the reactor outlet is about 400 ppm. When 480 ppm NO₂ was fed into the gas stream, SO₂ concentration rapidly decreased, and also remained at 100 ppm. When NO₂ was excluded from the gas stream, SO₂ concentration rapidly increased, and was higher than 400 ppm. The reduplicate experiment also got the same result. This result confirms the inference that the presence of NO₂ gas in the flue gas must take part in the SO₂ absorption reaction.

4. Solid Products Analysis and Enhancement Mechanisms of SO₂ Removal by the Presence of NO₂

From the above-mentioned analysis, the effects of NO₂ on SO₂ removal may be explained from the following two aspects. On the one hand, the reaction between NO₂ and Ca(OH)₂ changes the surface structure of the sorbent. On the other hand, NO₂ takes part in the desulfurization reaction. For the purpose of finding the effect mechanism of NO₂ on SO₂ removal, solid products analyses were performed by using FTIR and SEM.
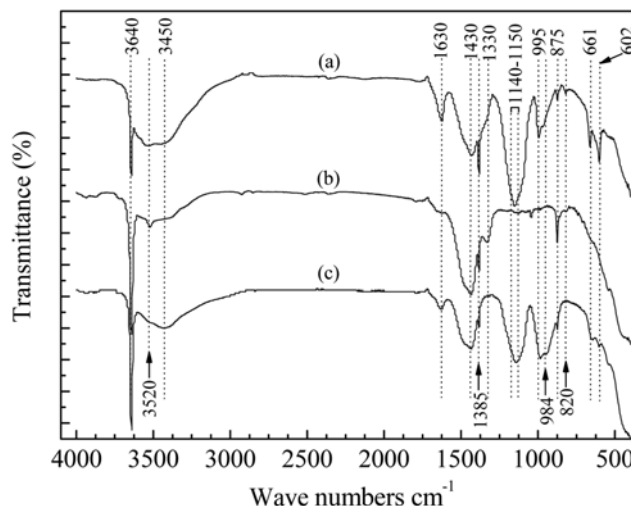
Fig. 7 shows the FTIR spectra of the spent sorbent. The sharp vibration band approximately at 3,640 cm⁻¹ can be attributed to the stretching of CaO-H [17]. The band at 3,450 cm⁻¹ is typically caused by hydroxyl groups [18]. A single peak close 1,630 cm⁻¹ related to O-H bending was also observed. Due to the effect of CO₂ in air, the obvious bands at 1,430 and 874 cm⁻¹ were detected for the carbonate species. Apart from the above species, sulfite (SO₃²⁻) was also detected on the surface of the sorbent being treated with SO₂ due to the band at around 984 cm⁻¹. In addition, the band around 1,140-1,150 cm⁻¹ can be attributed to sulfate (SO₄²⁻). When NO₂ was fed into the gas stream, the nitrite and nitrate species were detected at bands around 1,330 and 1,385 cm⁻¹. The relative intensity of the sulfate species (at 1,140-1,150 cm⁻¹) displayed an obvious increase; moreover, the bands at near 602 cm⁻¹ and 661 cm⁻¹, which can characterize the sulfate species, were also detected [19]. However, the relative intensity of the sulfite (at around 984 cm⁻¹) displays an obvious decrease. This indicates the desulfurization products were mainly composed of sulfate species in the presence of NO₂. Sulfite could be converted to sulfate in the presence of NO₂, which
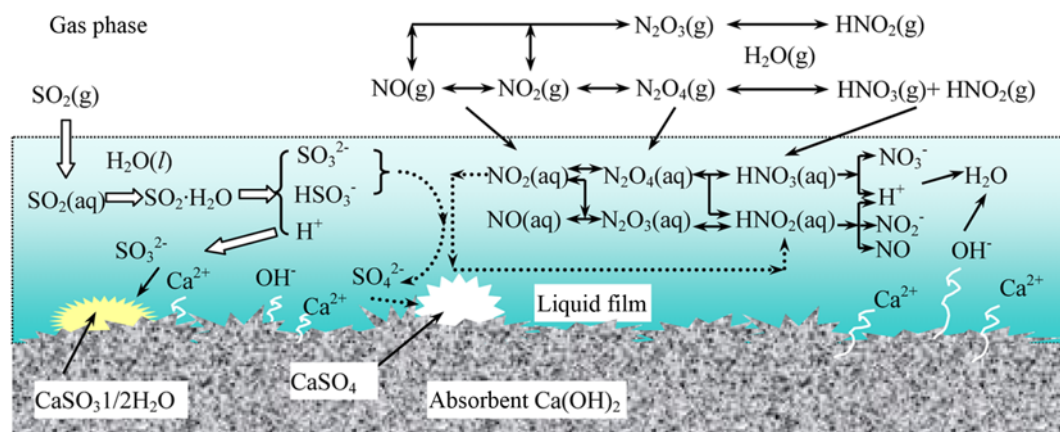

Fig. 8. Reaction paths for simultaneous removal of SO₂ and NO₂ on the surface of sorbent.

confirms the existence of the reaction between sulfite and NO_2 on the sorbent surface.

On the basis of the mechanisms of SO_2 removal by $Ca(OH)_2$ and NO_2 absorption in water and sulfite solution, the possible reaction paths are shown in Fig. 8. Water molecules are first adsorbed on the surface and the inner pore of the sorbent to form a water layer. The hydrolysis of SO_2 occurs in the water layer and forms SO_3^{2-} in the presence of OH^-. Some SO_3^{2-} combines with Ca^{2+} to form the sparingly soluble $CaSO_3$. When NO_2 is fed into the gas stream, the hydrolysis of NO_2 also takes place and forms HNO_2 and HNO_3, which subsequently react with OH^- to form H_2O and NO_3^- and NO_2^-. Meanwhile, NO_2 also reacts with SO_3^{2-} and HSO_3^- derived from the hydrolysis of SO_2 in the following manner:

$$SO_3^{2-}+2NO_2+H_2O \rightarrow SO_4^{2-}+2NO_2^-+2H^+$$
$$HSO_3^-+2NO_2+H_2O \rightarrow SO_4^{2-}+2NO_2^-+3H^+$$
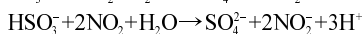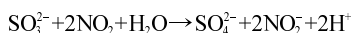
The conversion of SO_3^{2-} to SO_4^{2-} can enhance the hydrolysis of SO_2, which favors SO_2 removal.

Fig. 9 shows the surface morphologies of the spent sorbent. It is obvious that the surface morphology of the sorbent in simultaneous removal of SO_2 and NO_2 is very different from those in SO_2 and NO_2 single removal. The samples solely exposed to SO_2 were covered with the compact product layer. The pores formed by the agglomeration of the small particles on the surface of sorbent were filled by the reaction products. However, the surface of the samples simultaneously exposed to SO_2 and NO_2 appear much rougher and more complex. Some new pores were formed on the surface of spent sorbent in Fig. 9(b).

As we all know, SO_2 removal products $CaSO_3$ and $CaSO_4$ are sparingly soluble. When they are formed in the water film, some of them will deposit on the surface of sorbent and cover the unreacted sorbent surface. Therefore, the product layer is very compact. The evolution of sorbent surface can be depicted in Fig. 10(a). However, NO_2 removal products $Ca(NO_2)_2$ and $Ca(NO_3)_2$ readily dissolve in the water, and canot deposit on the surface of sorbent to form the product layer. When the exterior $Ca(OH)_2$ reacts with HNO_2 and HNO_3 to form H_2O, Ca^{2+}, NO_3^- and NO_2^-, the inner unreacted $Ca(OH)_2$ can be exposed to HNO_3 and HNO_2. The evolution of sor-
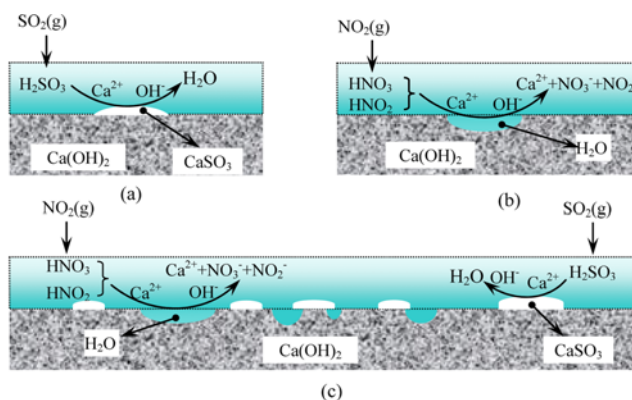

Fig. 10. Schematic diagram of the reaction product formation on the surface of sorbent. (a) SO_2 single removal; (b) NO_2 single removal; (c) simultaneous removal of SO_2 and NO_2.

bent surface is depicted in Fig. 10(b). When both SO_2 and NO_2 are present in the flue gas, the surface structure has a great change. Our previous works reveal that the interaction of SO_2 and NO_2 has great effect of the change of sorbent surface structure [15]. Although unreacted sorbent can be covered by SO_2 removal product, the presence of NO_2 can make the covered sorbent exposed to the hydrolysis products of SO_2 and NO_2. The evolution of sorbent surface is shown in Fig. 10(c). The exposure of the unreacted sorbent under the SO_2 removal products layer favors SO_2 removal.

CONCLUSIONS

The presence of NO_2 in the flue gas can enhance SO_2 removal under low temperature and humid conditions. The interaction between SO_2 and NO_2 in the gas phase was very weak at low temperature, which could not explain the promotive effect of NO_2 on SO_2 removal. The sorbent modified by the addition of $Ca(NO_2)_2$ and $Ca(NO_3)_2$ has lower desulfurization activity, by comparing with the desulfurization activity of the unmodified sorbent. This indicates that the presence of NO_2 removal products on the surface of sorbent cannot enhance SO_2 removal, but the sorbent after being treated by NO_2

(a) SO_2 single removal

(b) SO_2 and NO_2 simultaneous removal
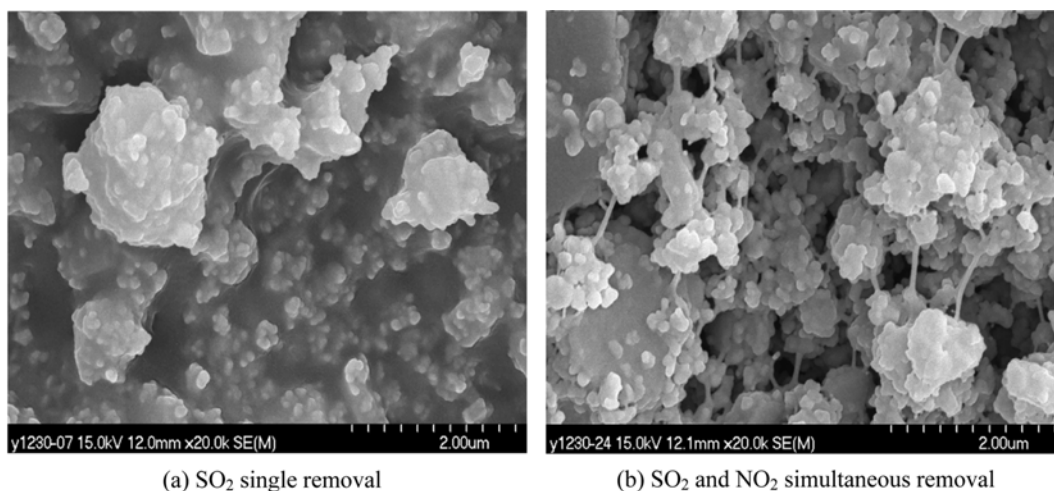
Fig. 9. SEM images of the spent sorbents.

for moment will have higher SO$_2$ removal. From the SEM images of the spent sorbents, the reaction between NO$_2$ and Ca(OH)$_2$ can make the unreacted sorbet component under the SO$_2$ removal product exposed to the reactant gas. Moreover, the oxidization of sulfite to sulfate by the presence of NO$_2$ was also detected in the FTIR analysis spectrum, which is in favor of the hydrolysis of SO$_2$ in the water film on the surface of sorbent.

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