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Removal of sulfur dioxide by fly ash/CaO/$CaSO_4$ sorbents

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Abstract

This study presents findings from an experimental investigation of the influences of several factors on the desulfurization activity of sorbents synthesized from coal fly ash, CaO, and $CaSO_4$. Specifically, the effects of specific surface area (16.1–133.3 m^2/g), reaction temperature (60–300 °C), feed concentration of SO_2 (500–2500 ppm), and feed concentration of NO (0–750 ppm) were elucidated using a fixed bed reactor. In general, the sorbent desulfurization activity increased with increasing specific surface area, reaction temperature, and NO concentration but with decreasing SO_2 concentration. The physical and chemical properties of sorbent before and after SO_2 capture were characterized through scanning electron microscopy, X-ray diffraction, and Fourier transform infrared analyses.

Keywords: Desulfurization; Fixed bed reactor; Flue gas; Fly ash; Sorbent; Sulfur dioxide

1. Introduction

Sulfur in coal is converted to sulfur dioxide (SO_2) during combustion. SO_2 is a precursor to acid rain which is one of the most widespread forms of pollution worldwide. In addition, SO_2 causes the formation of secondary particles in the atmosphere that impair visibility. To minimize the adverse impacts of SO_2 emissions on the environment, much effort has been put into developing flue gas desulfurization (FGD) technologies over the past few decades for the control and abatement of SO_2 emissions by coal-fired power plants and boilers of industrial processes. For example, dry FGD processes use calcium-based sorbents, usually hydrated lime ($Ca(OH)_2$), as a reagent to remove SO_2 from flue gas.

Recent research in this area has focused on synthesizing different types of calcium-based sorbent from mixtures of coal fly ash/$Ca(OH)_2$/CaO/$CaSO_4$. The use of coal fly ash as the base material in sorbent synthesis is attractive both economically and environmentally, as it is the most voluminous by-product of coal-fired power plants. A number of studies have shown that mixing coal fly ash with $Ca(OH)_2$ or CaO in a hydration process produces sorbents with SO_2 capture capacity higher than that of hydrated lime [1–11]. In addition, it has been shown that addition of $CaSO_4$ to the preparation mixture has a positive or negative effect on the sorbent desulfurization activity, depending on the specific hydration conditions being used [12–14]. These coal fly ash-based sorbents have been successfully used in a dry-type FGD system to treat 644 000 m^3/h of flue gas [4].

The extent of SO_2 capture varies significantly for different types of sorbent synthesized from coal fly ash/$Ca(OH)_2$/CaO/$CaSO_4$. The structural properties of these sorbents (e.g., specific surface area and porosity) are believed to play an important role in SO_2 capture. In general, it has been shown that higher desulfurization activity correlates with higher specific surface area [2,11], although some studies have produced inconclusive results [8,9]. These previous results suggest that further study on the role of specific surface area in SO_2 capture is warranted. In this work, we report an experimental investigation of SO_2 removal by sorbents having a range of specific surface areas prepared from coal fly ash, CaO, and $CaSO_4$. The other key areas of interest are the effects of reactor operating conditions such as temperature and feed concentrations of SO_2 and NO on the extent of SO_2 removal and characterization of sorbent before and after SO_2 capture through scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) analyses to gain insight into the mechanism of SO_2 removal.

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Table 1
BET specific surface areas of the starting materials

Starting material	Specific surface area (m^2/g)
Coal fly ash	1.46
CaO	5.62
$CaSO_4$	4.89

2. Materials and methods

2.1. Sorbent preparation

The raw materials used to prepare the sorbents were coal fly ash, CaO, and $CaSO_4$. The coal fly ash was provided by a coal-fired power plant of Tenaga Nasional Berhad, Malaysia. The chemical composition of the fly ash was 60% SiO_2, 20% Al_2O_3, 4.7% Fe_2O_3, 3.0% CaO, 1.1% K_2O, 1.0% MgO, 7.5% C, 2.4% others, and 0.3% ignition loss. The CaO and $CaSO_4$ were obtained from BDH Laboratories, England. The BET surface area of these raw materials was analyzed using an Autosorb 1C Quantachrome analyzer and the results are listed in Table 1.

To evaluate the effect of specific surface area on SO_2 capture, sorbents having a range of specific surface area were prepared by varying some of the preparation conditions. Specifically, a full factorial design was used to synthesize sorbents of different surface areas by varying three experimental variables: hydration period, amount of coal fly ash, and amount of $CaSO_4$. The amount of CaO used was kept constant. Table 2 displays the matrix for the 3^3 factorial design. The procedure used to prepare the sorbents comprised the following steps. A fixed amount of CaO (5 g) was added to 100 ml of water at 65 °C. Different amounts of coal fly ash and $CaSO_4$ were added to the slurry simultaneously, according to the design matrix shown in Table 2. The slurry was then maintained at 95 °C for a period of time for the hydration process to occur. The hydration period for different runs was varied according to the design matrix shown in Table 2. The resulting slurry was filtered and dried at 200 °C for 2 h. The BET surface area of the resulting sorbents was analyzed as described above and the results are tabulated in Table 2.

To study the effects of reactor operating conditions such as temperature, SO_2 concentration, and NO concentration on the extent of SO_2 capture, a reference sorbent having a fixed specific surface area was prepared. The reference sorbent was synthesized by mixing 5 g CaO, 13.7 g fly ash, and 7.4 g $CaSO_4$ for a hydration period of 10 h. The resulting sorbent had a specific surface area of 64.5 m^2/g.

2.2. Desulfurization experiments

Desulfurization experiments were performed using a fixed bed test rig, as shown in Fig. 1. The reaction zone was contained in a 0.13 m diameter stainless steel tube fitted in a furnace for isothermal operation. The sorbent (0.7 g) was packed in the center of the reactor supported by glass wool. A N_2 stream passed through a humidification system consisting of two 250 ml conical flasks immersed in a water bath at constant temperature. After humidification, the N_2 stream was mixed with a gas stream consisting of SO_2, NO, O_2, and CO_2. The combined feed gas flowed through the reactor at a flow rate of 150 ml/min. The SO_2 concentration of the effluent gas was continuously monitored by an Enerac 2000E flue gas analyzer. Two or three replicate measurements were made for each sorbent activity test and the relative standard deviation was found to be less than 3%. For clarity, only the average values are presented in this paper. The desulfurization activity is expressed in three different ways: maximum utilization of CaO (mg captured SO_2/g CaO) in the sorbent when

Table 2
Full factorial design matrix and specific surface areas of sorbents

Experimental variables			Specific surface area (m^2/g)
Hydration period (h)	Amount of fly ash (g)	Amount of $CaSO_4$ (g)	
4	5	0	28.7
18	5	0	42.7
32	5	0	41.8
4	10	0	24.2
18	10	0	29.2
32	10	0	34.5
4	15	0	18.1
18	15	0	29.8
32	15	0	44.6
4	5	6	16.8
18	5	6	45.3
32	5	6	55.3
4	10	6	22.5
18	10	6	92.8
32	10	6	133.3
4	15	6	23.2
18	15	6	102.0
32	15	6	105.5
4	5	12	16.1
18	5	12	42.2
32	5	12	49.1
4	10	12	23.4
18	10	12	71.0
32	10	12	80.9
4	15	12	26.6
18	15	12	64.6
32	15	12	97.2

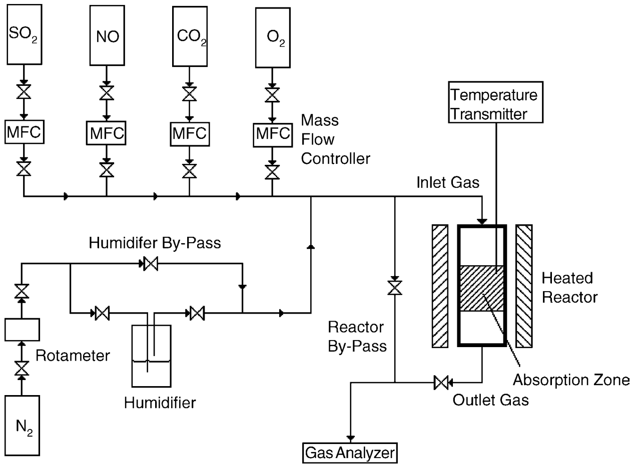


Fig. 1. Schematic diagram showing the experimental set-up for fixed bed desulfurization.

it is completely exhausted (i.e., percent removal of $SO_2 = 0$) [13]; duration the sorbent could maintain above 80% removal of SO_2 per gram CaO (min/g CaO) [5]; percent removal of SO_2.

To evaluate the effect of specific surface area on SO_2 capture, a range of sorbents having different surface areas were selected from Table 2 for the activity test. The feed gas composition at 100 °C was maintained at 1000 ppm SO_2, 500 ppm NO, 5% O_2, 12% CO_2, and the balance N_2. To study the effects of reactor operating conditions on SO_2 capture, the fixed bed reactor packed with the reference sorbent was subjected to a feed gas consisting of 500–2500 ppm SO_2, 0–750 ppm NO, 5% O_2, 12% CO_2, and the balance N_2. The range of reaction temperature tested was 60–300 °C. Additional desulfurization experiments were carried out at 150 °C using the fixed bed reactor packed with each of the raw materials (coal fly ash, CaO, or $CaSO_4$) and a feed gas consisting of 1000 ppm SO_2, 500 ppm NO, 5% O_2, 12% CO_2, and the balance N_2.

2.3. Physical and chemical analyses

The specific surface area and pore volume distribution of sorbents were determined using the BET and BJH methods, respectively, on an Autosorb 1C Quantachrome analyzer. A Leica Cambridge S360 scanning electron microscope with 15 kV of accelerating voltage was used to examine the sorbent surface morphologies. The CaO content of sorbent was determined using a Rigaku RIX 3000 X-ray spectrometer. XRD analysis was carried out using a Philips PW 1820 X-ray diffractometer with Cu Kα radiation in the diffraction angle (2θ) range of 5–90° at a sweep rate of 3°/min. FTIR spectra were recorded on a Perkin-Elmer FTIR 2000 spectrophotometer. The amount of sample used in the XRD and FTIR analyses was kept constant so that the peaks obtained in the spectra can be used to represent the relative concentrations of a chemical species.

3. Results and discussion

3.1. Effect of specific surface area

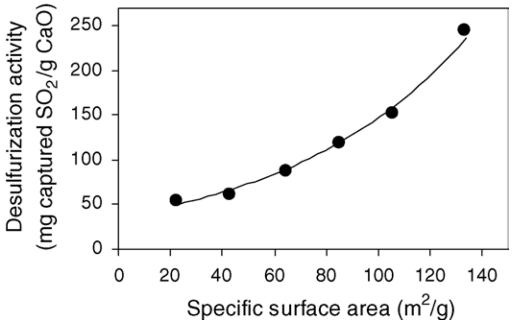


Fig. 2. Effect of specific surface area on the desulfurization activity of fly ash/CaO/$CaSO_4$ sorbents. Feed gas composition at 100 °C: 1000 ppm SO_2, 500 ppm NO, 5% O_2, 12% CO_2, and the balance N_2. The solid line is calculated from Eq. (1).

A number of previous studies have produced inconclusive results with regard to the influence of specific surface area on the desulfurization activity of sorbents derived from fly ash/$Ca(OH)_2$/CaO/$CaSO_4$. Some studies reported that desulfurization activity increased with increasing specific surface area [2,11] while others did not find a direct relationship between these two parameters [8,9]. To elucidate the role of specific surface area in SO_2 capture, sorbents having surface areas in the range of 16.1–133.3 m^2/g were synthesized from coal fly ash/CaO/$CaSO_4$ by varying some of the preparation conditions according to a full factorial design, as shown in Table 2. Selected sorbents were tested for their desulfurization activity which is defined as the maximum utilization of CaO (mg captured SO_2/g CaO) in the sorbent when it is completely exhausted (i.e., percent removal of $SO_2 = 0$). Fig. 2 shows the desulfurization activity of sorbents versus their specific surface area. The desulfurization activity is seen to increase exponentially from 53.6 to 244.7 mg captured SO_2/g CaO as the specific surface area was increased from 22.5 to 133.3 m^2/g. Within this specific surface area range, the exponential trend can be described quantitatively by the following empirical equation with a correlation coefficient of 0.991:

$$\text{Desulfurization activity} = 36.4\ \exp(0.014 \times \text{specific surface area}) \qquad (1)$$

Although Eq. (1) is useful for predicting the effect of specific surface area on sorbent desulfurization activity, it is obvious that it should not be used for extrapolation purposes due to the empirical nature of the expression. This observation corroborates the finding of Lin et al. [11] which showed that SO_2 capture by sorbents prepared from fly ash/$Ca(OH)_2$ increased with increasing specific surface area. However, they found a linear correlation between desulfurization activity and specific surface area. It may be concluded that specific surface area plays a key role in enhancing the desulfurization capacity of sorbents derived from either fly ash/CaO/$CaSO_4$ or fly ash/$Ca(OH)_2$. Having established the influence of specific surface area on SO_2 capture, a reference sorbent prepared from fly ash/CaO/$CaSO_4$ with a specific surface area of 64.5 m^2/g was used in all desulfurization experiments reported below.

3.2. Comparison of fly ash/CaO/$CaSO_4$ sorbent and starting materials

SO_2 removal by the reference sorbent and the three starting materials is shown in Fig. 3. The fixed bed reactor was subjected to a feed gas consisting of 1000 ppm SO_2, 500 ppm NO, 5% O_2, 12% CO_2, and the balance N_2 at 150 °C. As can be seen in Fig. 3, the reference sorbent easily outperformed its base components in removing SO_2. The sorbent removed 100% of the SO_2 in the feed gas during the first 30 min of reaction. The SO_2 started to breakthrough at reaction time > 30 min, resulting in a gradual decrease in the percent removal of SO_2 with increasing reaction time. The percent removal of SO_2 eventually reached zero after 150 min of reaction. In contrast, each of the three starting materials; coal fly ash, CaO, and $CaSO_4$, did not exhibit any significant desulfurization activity. These results most likely reflect the fact that the specific surface area of the reference sorbent (64.5 m^2/g) was much larger than those of the starting materials (Table 1, 1.5–5.6 m^2/g).

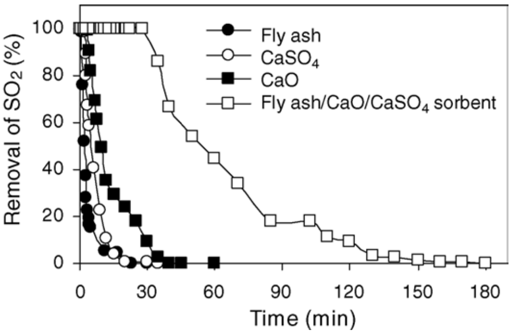
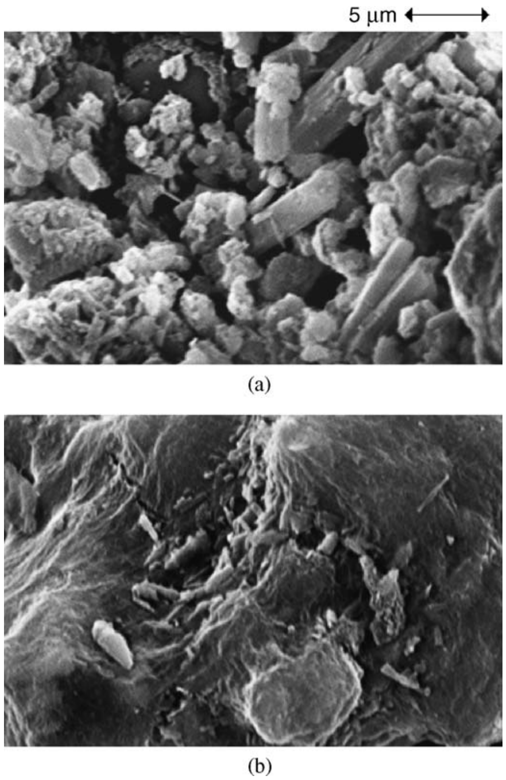


Fig. 3. Comparison of the desulfurization activity of the reference sorbent and its base components. Feed gas composition at 150 °C: 1000 ppm SO_2, 500 ppm NO, 5% O_2, 12% CO_2, and the balance N_2.

The surface morphology of the reference sorbent before and after SO_2 capture was studied through SEM. As shown in Fig. 4a, the hydration process produced a sorbent with a highly porous surface. After reacting with SO_2, Fig. 4b shows that the porous surface of the sorbent was no longer discernible. The pore volume distributions of the reference sorbent before and after desulfurization are shown in Fig. 5. For the fresh sorbent, mesopores with an average pore size of 41.8 nm appeared to be the major contributor to the total pore volume. After desulfurization, a large portion of the pore volume had disappeared and the average pore size dropped to 28.6 nm, indicating significant pore filling by the reaction product. It may be concluded that the surface of the spent sorbent was covered by a layer of the reaction product $CaSO_4$, reducing its porosity.



(a)

(b)

Fig. 4. SEM micrographs of the reference sorbent (a) before and (b) after SO_2 capture.

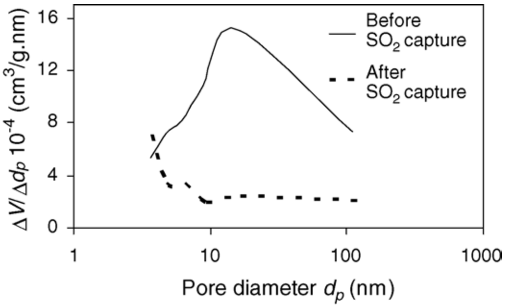


Fig. 5. Pore volume distributions of the reference sorbent before and after SO_2 capture.

The chemical composition of the reference sorbent before and after desulfurization was studied through XRD analysis. The XRD spectra are shown in Fig. 6. The peaks in the spectra can be assigned as follows: peaks a = calcium aluminate silicate hydrate compound ($Ca_2(Si_9Al_3)O_{24}{\cdot}8H_2O$), peaks b = calcium carbonate ($CaCO_3$), and peaks d = calcium sulfate ($CaSO_4$). $Ca_2(Si_9Al_3)O_{24}{\cdot}8H_2O$ and $CaCO_3$ are the products of the hydration process while the $CaSO_4$ detected in the fresh sorbent is the unreacted base material. The absence of silica (SiO_2) and alumina (Al_2O_3) in Fig. 6a, the two main components of coal fly ash, suggests that they have reacted completely with $CaO/CaSO_4$ to form $Ca_2(Si_9Al_3)O_{24}{\cdot}8H_2O$ which reacts with SO_2. After desulfurization, Fig. 6b shows noticeable changes in the spectrum of the sorbent. It can be seen that peaks a and b became weaker, indicating that $Ca_2(Si_9Al_3)O_{24}{\cdot}8H_2O$ and $CaCO_3$ were converted to other chemical forms. Since the intensity of peaks d for $CaSO_4$

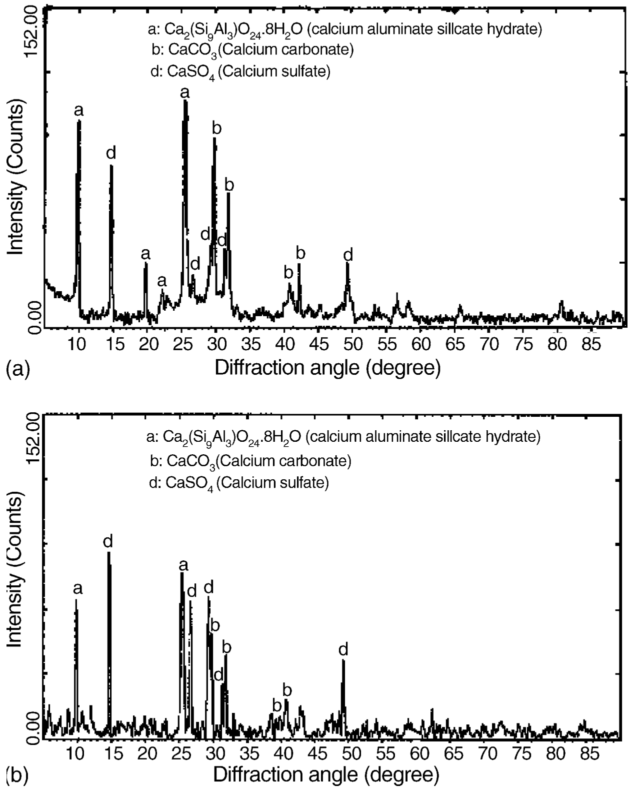


Fig. 6. XRD spectra of the reference sorbent (a) before and (b) after SO_2 capture.

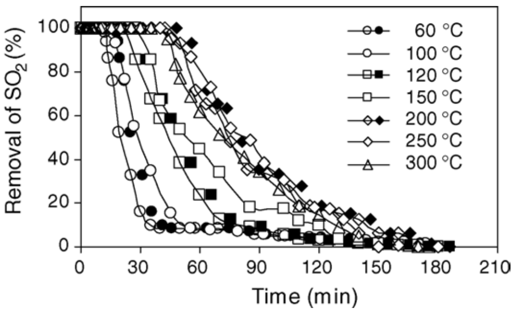


Fig. 7. Effect of reaction temperature on the percent removal of SO_2 by the reference sorbent. Feed gas composition: 1000 ppm SO_2, 500 ppm NO, 5% O_2, 12% CO_2, and the balance N_2.

increased, it may be concluded that the two compounds reacted with SO_2 to produce $CaSO_4$. As already mentioned, the formation of $CaSO_4$ led to a loss of sorbent porosity through $CaSO_4$ deposit in the sorbent pores, as can be seen in the SEM image of Fig. 4b.

3.3. Effect of reaction temperature

Fixed bed experiments were performed to examine the effects of reaction temperature, SO_2 concentration, and NO concentration on the desulfurization activity of the reference sorbent. Fig. 7 shows the effect of reaction temperature (60–300 °C) on the percent removal of SO_2 from a feed gas containing 1000 ppm SO_2. As can be seen in Fig. 7, the desulfurization activity increased when the temperature was raised from 60 to 200 °C but further increases in temperature beyond 200 °C did not seem to enhance the desulfurization activity. A possible explanation for this observation is that the hydrated water contained within the sorbent was released upon exposure to the hot gas stream, creating new pores which increased the surface area of the sorbent [15]. As already mentioned, desulfurization activity increases with increasing specific surface area.

When the temperature was raised by 40 °C from 60 to 100 °C, the breakthrough time increased from 12 to 16 min, a rather modest increase in the sorbent's ability to maintain 100% SO_2 removal. This observation suggests that not much of the hydrated water trapped within the sorbent could be released at temperatures below the boiling point of water to create additional surface area. The weak effect of reaction temperature below 100 °C on the desulfurization activity of fly ash/$Ca(OH)_2$ sorbent has also been reported by Liu et al. [16]. By contrast, raising the temperature by 50 °C from 100 to 150 °C increased the breakthrough time from 16 to about 30 min; the sorbent could maintain 100% removal of SO_2 for a much longer period of time. Similar enhancement in desulfurization activity was observed when the temperature was raised from 150 to 200 °C. This implies that the temperature range of 100–200 °C was able to cause significant release of the hydrated water of the sorbent which led to creation of additional pore volume and hence specific surface area for desulfurization. However, the breakthrough time remained somewhat constant when the temperature was increased from 200 to 300 °C. Two possible reasons may account for this observation. First, at temperatures > 200 °C, surface coverage of the sorbent by the resulting reaction product $CaSO_4$ prevented further release of hydrated water. Second, all the hydrated water of the sorbent had already been released when the temperature reached 200 °C.

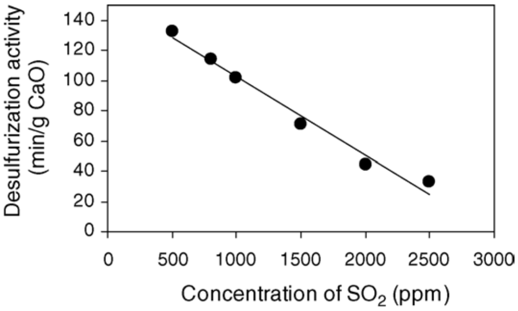


Fig. 8. Effect of SO_2 concentration on the desulfurization activity of the reference sorbent. Feed gas composition at 100 °C: 500–2500 ppm SO_2, 500 ppm NO, 5% O_2, 12% CO_2, and the balance N_2.

3.4. Effect of SO_2 concentration

The effect of SO_2 concentration on the desulfurization activity of the reference sorbent is shown in Fig. 8. The desulfurization activity decreased linearly when the SO_2 concentration was increased from 500 to 2500 ppm. The slope of the line in Fig. 8 estimated by a linear regression with a correlation coefficient of 0.979 was −0.052 min/(g CaO ppm SO_2). The drop in the desulfurization activity is a direct consequence of exposing a fixed amount of sorbent to increasing SO_2 concentration in the feed gas.

3.5. Effect of NO concentration

Fig. 9 shows the effect of NO concentration on the extent of SO_2 removal by the reference sorbent. The presence of NO in the feed gas had a beneficial effect on the desulfurization activity. In the absence of NO the time that the sorbent could maintain 100% removal of SO_2 was only about 9 min; however, when 250 ppm NO was included in the feed gas the breakthrough time increased to about 20 min. Further enhancement of the breakthrough time was observed using a feed gas containing 500 ppm NO. It has been postulated that the presence of NO in the feed

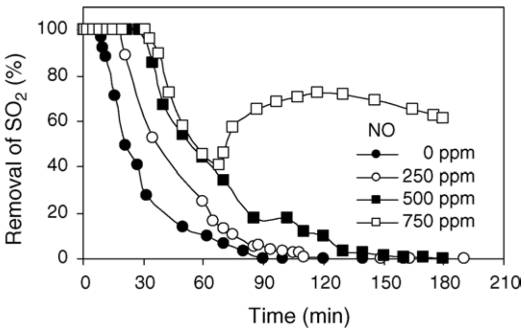


Fig. 9. Effect of NO concentration on the percent removal of SO_2 by the reference sorbent. Feed gas composition at 100 °C: 1000 ppm SO_2, 0–750 ppm NO, 5% O_2, 12% CO_2, and the balance N_2.

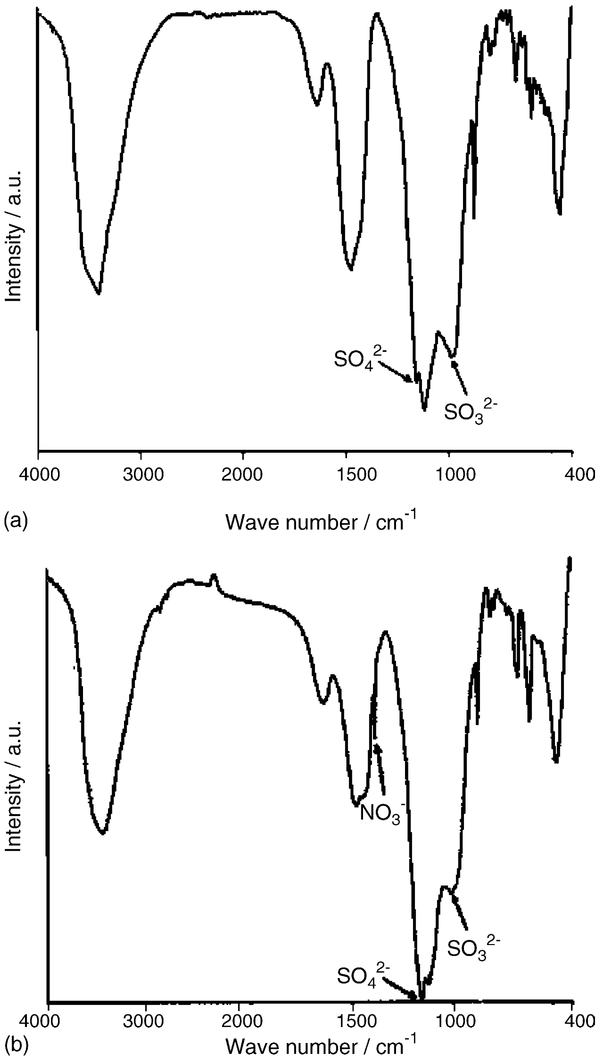


Fig. 10. FTIR spectra of spent sorbent (a) in the absence of NO and (b) in the presence of 500 ppm NO.

gas resulted in the formation of NO_2 which oxidizes SO_2 to SO_3. The resulting SO_3 can react with calcium compounds in the sorbent several times faster than SO_2 to form sulfate salts. However, an unexpected phenomenon occurred when the feed NO concentration was increased to 750 ppm. As can be seen in Fig. 9, the breakthrough behavior at 750 ppm NO was similar to that at 500 ppm NO up to a reaction time of 70 min. After 70 min, the percent removal of SO_2 began to increase with time, reaching a maximum before declining slowly. This unexpected behavior has also been observed in a previous study using slaked lime sorbent and a feed gas containing 800 ppm SO_2 and 800 ppm NO [17]. The reason for this behavior is not known and further research is needed in order to shed light on this phenomenon.

The role of NO in SO_2 removal was studied through FTIR analysis. The FTIR spectra of spent sorbent in the absence of NO and in the presence of 500 ppm NO are shown in Fig. 10. In the absence of NO, Fig. 10a shows that the vibration absorption peaks ascribed to SO_3^{2-} (sulfite) and SO_4^{2-} (sulfate) were detected in the spent sorbent. The peak for SO_3^{2-} is probably due to the absorption of SO_2 in the form of sulfite salts, while the SO_4^{2-} peak is due to the unreacted base material used in synthesizing the sorbent or it could also be due to the absorption of SO_2 in the form of sulfate salts. In the presence of 500 ppm NO, the vibration absorption peaks ascribed to SO_3^{2-} and SO_4^{2-} were still detected in the spent sorbent, as shown in Fig. 10b. Comparison of the two spectra indicates that the peak for SO_4^{2-} in Fig. 10b became more intense while the peak for SO_3^{2-} was weaker. The increase in the intensity of the SO_4^{2-} peak and decrease in the intensity of the SO_3^{2-} peak may be attributed to the oxidizing effect of NO. Most of the SO_2 was absorbed in the form of sulfate salts instead of sulfite salts in the presence of NO. Further, a weak vibration absorption peak ascribed to NO_3^- (nitrate) was also detected, as shown in Fig. 10b, indicating that a small amount of NO was absorbed in the form of nitrate salts.

4. Conclusions

The desulfurization activity of sorbents synthesized from coal fly ash/CaO/$CaSO_4$ was observed to increase exponentially with increasing specific surface area. The extent of SO_2 capture by a reference sorbent with a specific surface area of 64.5 m^2/g was much higher than those of its starting materials. Enhancement of desulfurization activity by reaction temperature and inclusion of NO in the feed gas was also observed. SEM showed that SO_2 capture resulted in a reduction of sorbent porosity through surface coverage by the reaction product $CaSO_4$. XRD and FTIR analyses confirmed that SO_2 was absorbed in the form of sulfate salts.

Acknowledgements

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