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Effects of water vapor, CO_2 and SO_2 on the NO reduction by NH_3 over sulfated CaO

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Abstract−Gas effects on NO reduction by NH_3 over sulfated CaO have been investigated in the presence of O_2 at 700-850 °C. CO_2 and SO_2 have reversible negative effects on the catalytic activity of sulfated CaO. Although H_2O alone has no obvious effect, it can depress the negative effects of CO_2 and SO_2. In the flue gas with CO_2, SO_2 and H_2O co-existing, the sulfated CaO still catalyzed the NO reduction by NH_3. The in situ DRTFTS of H_2O adsorption over sulfated CaO indicated that H_2O generated Brønsted acid sites at high temperature, suggesting that CO_2 and SO_2 competed for only the molecularly adsorbed NH_3 over Lewis acid sites with NO, without influencing the ammonia ions adsorbed over Brønsted acid sites. Lewis acid sites shifting to Brønsted acid sites by H_2O adsorption at high temperature may explain the depression of the negative effect on NO reduction by CO_2 and SO_2.

Key words: Sulfated CaO, NO, CO_2, SO_2, H_2O

INTRODUCTION

The nitric oxide (NO) reduction by ammonia (NH_3) over sulfated CaO has been investigated extensively because of its potential application in the simultaneous removal of SO_2 and NO_x in circulating fluidized bed by flue gas desulphurization technique (CFB-FGD) [1-3]. Previous pilot-scale CFB-FGD results have indicated that the SO_2 removal efficiency could be as high as 85-95% at the Ca/S molar ratio of 2 in the temperature range of 700-800 °C [4]. For NO_x removal, the previous investigation indicated that sulfated CaO has a catalytic effect on NO reduction by NH_3 [1-2,5] in NH_3+NO+O_2+N_2 atmosphere. However, little investigation has been done on the effects of flue gas components, such as CO_2, SO_2, and H_2O, which may have significant influences on the catalyst activity [6-10]. Previous study has already found that CaO has high catalytic effect on NH_3 oxidation to NO [11-13], but greatly suppressed by H_2O [14-16] and SO_2 [5,17]. CO_2 can also affect the catalytic activity of CaO in NH_3 oxidation [14,18]. The effects of the major gas components on the catalytic activity of sulfated CaO in NO reduction are of great interest. For a catalyst to be used in the post-combustion process, it must have satisfactory activity in the presence of high concentration of CO_2 and H_2O, and sufficient resistance to the poisonous effect of SO_2. For the coal-fired electrical utility plant, the typical flue gas might contain 150-1,000 ppm NO, 5% O_2, 13% CO_2, 8% H_2O, and 200-2,000 ppm SO_2 [19]. Hence, 14% CO_2, 8% H_2O and 2,000 ppm SO_2 were selected in this study to investigate the flue gas effect. In situ analytical techniques, such as in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), were used to determine the intermediates over the catalyst surface to analyze the flue gas affecting mechanisms. Previous study has indicated that the surface-species over sulfated CaO produce acidic sites and favor ammonia adsorption [2]. The acidic gas of SO_2 and CO_2 may not directly affect the surface acid sites, whilst the adsorbed H_2O over sulfates can generate Brønsted acid sites [20] or modifying the site structure [21-23]. Therefore, the influence of water vapor, SO_2 and CO_2 on the catalytic activity of sulfated CaO were comprehensively investigated in this study to understand their affecting mechanism under different atmospheres.

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EXPERIMENTAL SECTION

1. Activity Measurement

The effect of flue gas species on the catalytic activity of sulfated CaO (prepared by CaO sulfation in 2,000 ppm SO_2+5%O_2+N_2 at 850 °C, CaO sulfation extent (X_{Ca}) was 36.5%) has been tested in a quartz fixed-bed reactor system, as shown in Fig. 1. The quartz fixed-

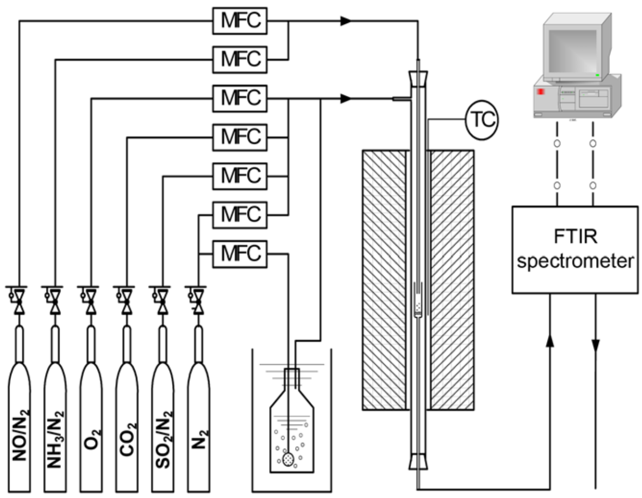

Fig. 1. Schematic of the reaction system.

bed reactor is the main body of the reaction system, with an inner diameter of 20 mm. The reactor is placed in an electrically heated furnace capable of maintaining the reaction zone at a constant temperature. The bed material is placed on a sintered porous quartz disc located in the middle section of inner reactor. Blank tests without bed materials were conducted at 800 and 850 °C to determine the effect of SNCR (selective non-catalytic reduction). The results indicated that SNCR contributed less than 4% of NO reduction at 800 °C and about 30% of NO reduction at 850 °C.

The CaO sulfation extent (X_{Ca}) was calculated from the mass increase of the solid sample defined as (1):

$$X_{Ca}(\%) = \frac{n_S}{n_{Ca}} \times 100 \qquad (1)$$

where n_S was the molar of sulfur element in the sulfated CaO, and n_{Ca} was the molar of calcium element in the sulfated CaO. The catalytic activity of the sulfated CaO in the presence/absence of H_2O, SO_2 and CO_2 was mainly measured over 4.0 g sulfated CaO. The inlet flow gas was carefully controlled by mass flow controllers to obtain the desired gas concentration and flow rate. The total flow rate was set at 1,000 ml/min (273.15 K, standard atmospheric pressure), then the gas velocity was 83,000 h^{-1} at 800 °C, and 87,000 h^{-1} at 850 °C over the 4.0 g sulfated CaO. The gas mixture at inlet was 500 ppm NO+500 ppm NH_3+5% O_2+N_2 (as balanced gas), and 2,000 ppm SO_2, 14% CO_2, 8% H_2O would be added when their effects were investigated. The concentration of H_2O vapor was controlled by regulating the flow rate of the N_2 through a 55 °C water tank (constant temperature, atmospheric pressure). The NO, NH_3, NO_2, N_2O and SO_2 concentrations in the exhaust at reactor out were continuously monitored by a pre-calibrated FTIR spectrometer (Nicolet Corporation, NEXUS 670) aided by a liquid N_2-cooled MCT detector and a 2 m gas cell, collecting 32 scans at a resolution of 0.5 cm^{-1}. The gas cell temperature was maintained at 150 °C. The pipeline between the reactor and the gas analyzer was heated to 90 °C to prevent the water vapor condensation and the potential secondary reactions in gas mixtures. The measurement accuracy has been estimated to be ±2% for a single gas, and ±2% (NO), ±3% (NH_3), ±3% (SO_2) for simultaneous monitoring of multiple gas species, as tested by Li et al. [24]. During the catalyst activity test, the NO conversion (X_{NO}) and NH_3 conversion (X_{NH_3}) were calculated from their inlet and outlet concentration. These parameters were defined as Eqs. (2)-(3):

$$X_{NO}(\%) = \left(1 - \frac{C_{NO}^{out}}{C_{NO}^{in}}\right) \times 100 \qquad (2)$$

$$X_{NH_3}(\%) = \left(1 - \frac{C_{NH_3}^{out}}{C_{NH_3}^{in}}\right) \times 100 \qquad (3)$$

where C_{NO}^{in} was the NO concentration at the inlet of the quartz reactor, C_{NO}^{out} was the NO concentration at the outlet of the quartz reactor; $C_{NH_3}^{in}$ was the NH_3 concentration at the inlet of the quartz reactor, and $C_{NH_3}^{out}$ was the NH_3 concentration at the outlet of the quartz reactor.

2. In Situ DRIFTS Study

In situ DRIFTS was used to study the H_2O adsorption over sulfated CaO in this study. The in situ DRIFTS spectra were obtained using an FTIR (Thermo Nicolet Corporation, NEXUS670) equipped with an MCT detector and diffuse reflectance kit (HARRICK) including the Praying Mantis and a high temperature reaction chamber. The chamber was enclosed with a dome opened three windows, two ZnSe windows for spectrometer radiation, and one UV quartz window for sample inspection. The chamber was connected to the gas flow apparatus which passed gas over the solid samples, and to the water cooling system which controlled the chamber and window temperatures during high temperature operation. The spectra were obtained with the collecting parameter of 64 scans at a resolution of 8 cm^{-1}. Before H_2O adsorption, the catalysts were activated in N_2 under 700 °C for 30 min to remove impurities in the catalysts and then cooled within the chamber with N_2 purge to the desired experimental temperature 100 °C. During the cooling process of 700 °C to 100 °C, the spectra of the sample were collected at 500, 400, 300, 200 and 100 °C as the background spectra of corresponding temperature, which could be used later to generate H_2O adsorption spectra at different temperatures. For H_2O adsorption, the 100 °C was chosen to avoid water condensation in the reaction chamber; also, the connecting pipeline was heated to 100 °C.

RESULTS AND DISCUSSION

1. Effect of H_2O, SO_2 and CO_2 on SCR Activity

Fig. 2 shows NO conversion over 1.0 g sulfated CaO (particle diameter, 0.30-0.45 mm) in 1,000 ppm NH_3+1,000 ppm NO+5% O_2 with various SO_2 concentration at 800 °C. At first, the NO conversion was 15.1% without SO_2 in the inlet flue gas. Then the experiments were done with 2,000, 1,500, 1,000, 500, 250, 100 and 50 ppm SO_2 added successively, and the NO conversion was 4%, 4.4%, 4.8%, 5.5%, 6.5%, 7.4% and 8%, accordingly, which indicated the obvious restraining effect of SO_2, even when only 50 ppm SO_2 was added. Finally, the SO_2 was switched off, and the NO conversion increased to 13.5% immediately, which verified the restraining effect of SO_2 again. However, the little difference between the NO conversion of 13.5% (at last, without SO_2) and 15.1% (at first, without SO_2) was caused by the long term introducing of SO_2 over CaO sulfation products making the sulfation extent change, and the reason that the NO conversion decreased as the CaO sulfation increased

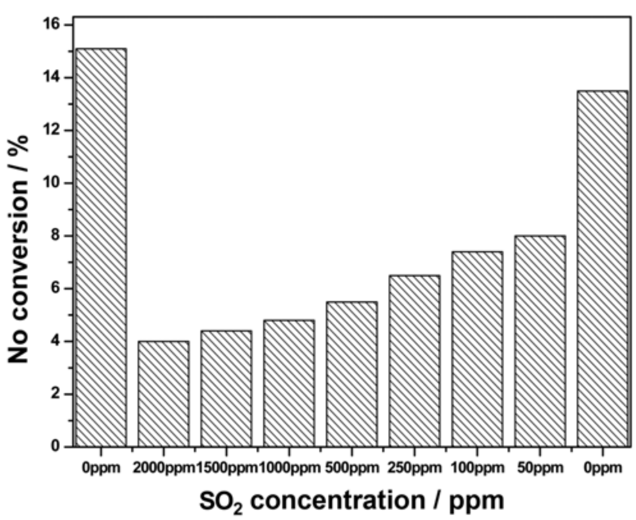

Fig. 2. The effect of SO_2 with different concentration on NO conversion at 800 °C.

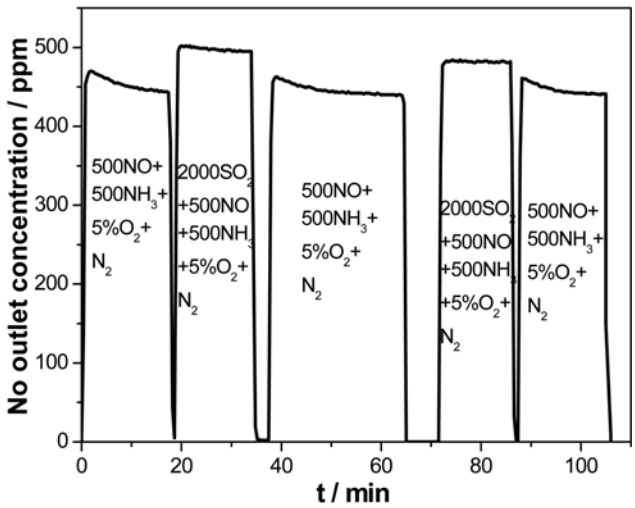

Fig. 3. NO conversion vs. time-on-stream at 800 °C (500 ppm NO+500 ppm NH_3+5% O_2+N_2 with SO_2 or without).

after a certain CaO conversion has been described and analyzed in detail in our previous work [1,2]. Besides, the increase of the No conversion to 13.5% at last time when SO_2 was 0 ppm also verified the gas restraining effect of SO_2 on the catalytic activity when SO_2 was added during the experiments, without considering the CaO sulfation effect.

Fig. 3 shows the NO conversion over 1.0 g sulfated CaO (particle diameter, 0.30-0.45 mm) in the atmosphere of 500 ppm NH_3+500 ppm NO+5% O_2+N_2 with or without 2,000 ppm SO_2 at 800 °C. The results revealed that the NO outlet concentration increased when 2,000 ppm SO_2 was added into the main gas stream (during the time of 20-37 and 72-87 min), which again indicated the restraining effect of SO_2 on the NO reduction by NH_3. However, when SO_2 was cut off after the 2,000 ppm (during the time of 38-64 min and 88-105 min), the NO outlet concentration recovered to about 440 ppm as appeared during 0-19 min. Since the introducing of SO_2 was not for a long time, and the CaO sulfation extent almost did not change, then the sulfation products catalytic activity for deNOx reaction did not change after SO_2 removal, which indicated that the gas effect of SO_2 was reversible for a certain CaO sulfation product.

The combined effects of H_2O, SO_2 and CO_2 on the SCR reaction were investigated at 800 °C (under which temperature the SNCR effect could be neglected) and 850 °C (under which temperature the SNCR effect was apparent) to see the effects of gas composition more obviously. In these tests, the sulfated CaO sample was 4.0 g.

The NO and NH_3 conversions of the reaction Sequence 1-5 over 4.0 g sulfated CaO at 850 °C are shown in Fig. 4. In Sequence 1, there were just NO, NH_3 and O_2, and the conversions of NO and NH_3 were 47% and 85.2%, respectively. When 14% CO_2, 8% H_2O and 2,000 ppm SO_2 were all presented in Sequence 2, the NO conversion decreased to 20.8%, while the NH_3 conversion decreased to 30%, indicating the overall effect of H_2O, SO_2 and CO_2 was to suppress the NO and NH_3 conversion, and consequently, the catalyst activity was reduced. In Sequence 3, only H_2O was added upon Sequence 1; the NO conversion was 48.2%, and NH_3 conversion was 59.8%. The NO conversion in Sequence 3 was almost the same with that in sequence 1, while the NH_3 conversion in Sequence 3 was lower than that in Sequence 1, which indicated that H_2O did not decrease the catalytic activity of sulfated CaO, but enhanced the selectivity of NH_3 for NO reduction. The combined effect of H_2O and SO_2 on the SCR reaction is shown in Sequence 4, and the individual effect of SO_2 is shown in Sequence 5. Comparing the NO and NH_3 conversions in Sequences 4 and 5, it could be found

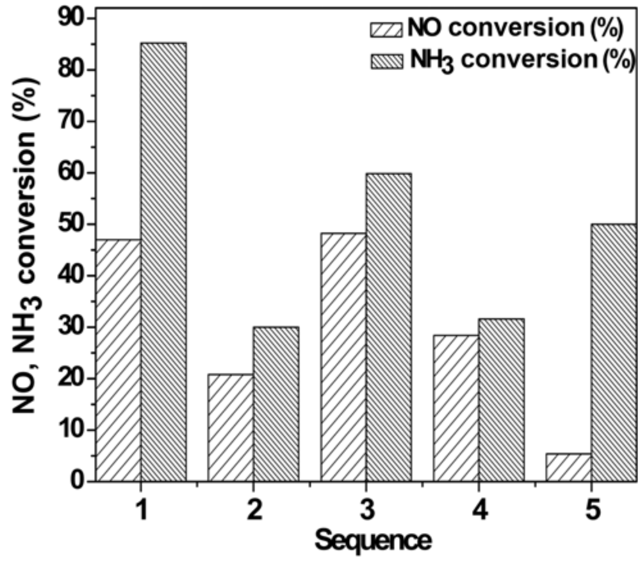

Fig. 4. NO, NH_3 conversion over 4.0 g sulfated CaO at different atmosphere at 850 °C (The inlet gas composition: Sequence 1, base gas: 500 ppm NO+500 ppm NH_3+5% O_2+N_2; Sequence 2, base gase+14% CO_2+2,000 ppm SO_2+8% H_2O; Sequence 3, base gas+8% H_2O; Sequence 4, base gas+8% H_2O+2,000 ppm SO_2; Sequence 5, base gas+2,000 ppm SO_2).

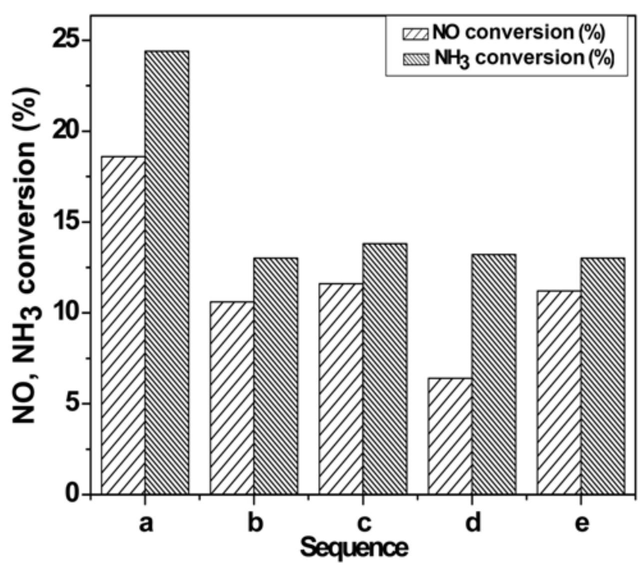

Fig. 5. NO, NH_3 conversion over 4.0 g sulfated CaO at different atmosphere at 800 °C (The inlet gas composition: Sequence a, base gas: 500 ppm NO+500 ppm NH_3+5% O_2+N_2; Sequence b, base gase+14% CO_2+2,000 ppm SO_2+8% H_2O; Sequence c, base gas+8% H_2O+2,000 ppm SO_2; Sequence d, base gas+2,000 ppm SO_2; Sequence e, base gas+8% H_2O +2,000 ppm SO_2).

that SO_2 had a strong inhibiting effect on NO conversion with the NO conversion decreased from 47% (in Sequence 1) to 5.4% (in Sequence 5), and H_2O could depress the inhibiting effect of SO_2 with the NO conversion increased from 5.4% (in Sequence 5) to 28.4% (in Sequence 4). The results in Sequence 2 and 4 suggested that CO_2 also had a negative effect on the SCR reaction. The results in Sequence 2 and 3 indicated that, when SO_2 and CO_2 were switched off, their negative effects disappeared, implying that the effects of CO_2 and SO_2 were both reversible.

The NO and NH_3 conversions of the reaction Sequence a-e over 4.0 g sulfated CaO at 800 °C are shown in Fig. 5. In Sequence a, NO conversion was 18.6% and NH_3 conversion was 24.4%. In Sequence b, CO_2, H_2O and SO_2 were simultaneously added, and the NO conversion decreased to 10.6% from 18.6%, while NH_3 conversion decreased to 13% from 24.4%, which agreed with the results of Sequence 1 and 2 at 850 °C in Fig. 4. Upon Sequence b, CO_2 was switched off in Sequence c, the NO conversion and NH_3 conversion both increased, which confirmed the negative effect of CO_2 on the catalyst activity. Upon Sequence c, H_2O was switched off and only SO_2 was added in Sequence d, and then the NO conversion significantly decreased. When H_2O was added again in Sequence e, NO conversion recovered to that in Sequence c. The results in Sequence c-e once again verified that H_2O depressed the negative effect of SO_2 on the catalytic activity.

The flue gas effect investigation at 800 and 850 °C both indicated that CO_2 and SO_2 had a negative effect on the catalyst activity, and their negative effect was reversible. H_2O can depress the negative effect of SO_2, and the catalyst still promotes NO reduction when CO_2, SO_2 and H_2O coexisted.

2. DRIFTS of H_2O Adsorption

To understand the improving mechanism of H_2O, H_2O adsorption over sulfated CaO was investigated. Fig. 6 shows the DRIFTS of H_2O adsorption with increasing temperature over sulfated CaO after passing N_2 with 8% H_2O over the sample at 100 °C. Many H_2O adsorption bands exist and the distinctive positive broad peak at 2,600-3,700 cm^{-1} has been assigned as the hydroxyl group from H_2O

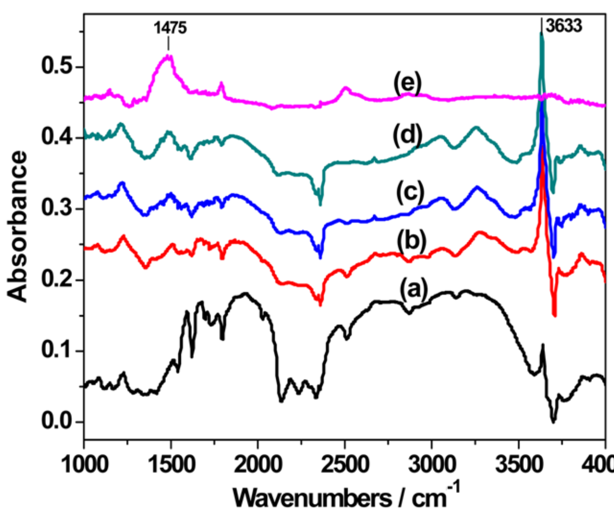

Fig. 6. DRIFTS of H_2O adsorption over sulfated CaO at different temperatures ((a) at 100°C; (b) at 200 °C; (c) at 300 °C; (d) at 400 °C; (e) at 500 °C).

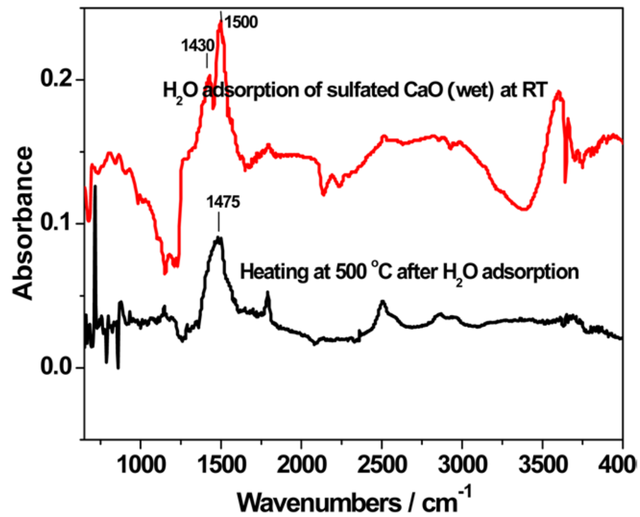

Fig. 7. Comparing of H_2O adsorption over sulfated CaO at RT and at 500 °C.

[25]. As the temperature increased from 100 to 400 °C, the peaks of the hydroxyl group from H_2O disappeared gradually, leaving two obvious peaks of freedom OH stretching band at 3,633 cm^{-1} and associated OH bending band at 1,475 cm^{-1} [26]. When the temperature increased to 500 °C, the obvious peak of the associated OH at 1,475 cm^{-1} still existed, and the OH associated to sulfate would be good for ammonia ions forming during the ammonia adsorption, which indicated the Brønsted acidity formed by water adsorption at high temperature over the active sites of sulfated CaO.

To verify the effect of the H_2O adsorption over the sulfated CaO catalyst, the 'wet' sulfated CaO was also prepared. The sulfated CaO was first put into a fixed bed reactor, passing N_2 with 8% H_2O through it at 650 °C for 30 min, and then removed from the reactor and cool to the room temperature (RT) for DRIFTS experiments. The spectra of sulfated CaO (wet) shown in Fig. 7 were collected using the spectra of the sulfated CaO without H_2O adsorption at RT as the background. The peaks around 1,430 and 1,500 cm^{-1} were the peaks of associated OH over sulfates [26], indicating the Brønsted acid sites formed at high temperature. The other curve in Fig. 7 is the spectra of the sample heated up to 500 °C after H_2O adsorption with the peak at 1,475 cm^{-1}. Comparing the two curves in Fig. 7, the peaks of 1,430, 1,475 and 1,500 cm^{-1} could all be the associated OH bands, presenting Brønsted acid sites formed at high temperature, and the shifts between them could be caused by the temperature difference. Hence, it once again indicates that the H_2O adsorption over sulfated CaO enhances Brønsted acidity at high temperature.

3. Influencing Mechanisms of Gas Species

The investigation of flue gas effect on the catalytic activity of sulfated CaO have indicated that CO_2 and SO_2 have a reversible negative effect on the catalytic activity, whereas H_2O can depress the negative effect from SO_2. Previous research has indicated that the SCR reaction over sulfated CaO could be the adsorbed NH_3 reacting with gaseous NO to form N_2 [2]. For NH_3 adsorption, previous study on V_2O_5-based catalysts and other metal oxide catalysts indicated that there are two kinds of ammonia adsorption patterns: (i) molecularly adsorbed ammonia through Lewis-type interaction on

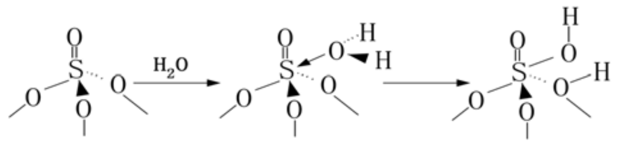

Fig. 8. Schemes of the generation of Brønsted acid sites over sulfated CaO from H_2O adsorption.

coordinatively unsaturated cations; and (ii) ammonium ions over Brønsted acidic -OH surface hydroxyl groups [27-29]. The in situ DRIFTS experiments of NH_3 adsorption over sulfated CaO in our previous study indicated that NH_3 adsorbed over both Lewis acid sites and Brønsted acid sites [30]. CO_2 and SO_2, as the acidic gas may influence the NH_3 molecule adsorbed over Lewis acid sites, and thus influence the SCR reaction. The DRIFTS of H_2O adsorption over sulfated CaO in Fig. 6 and 7 indicated that H_2O adsorption forms Brønsted acidity at high temperature. Yang et al. [31] suggested that H_2O molecules could provide OH group to adsorb ammonia and form ammonium ions required in SCR reaction. Furthermore, some investigations on H_2O adsorption over V_2O_5-based catalyst also indicated the formation of Brønsted acidity in the presence of H_2O [32-34]. Over sulfated CaO, the coordinate modes of SO_4^{2-} have been presented in previous study [2]. Combining the coordinate structure of SO_4^{2-} with the Brønsted acid sites generated from H_2O adsorption over vanadyl centers [29], the generation schemes of Brønsted acid sites over sulfated CaO are proposed in Fig. 8.

As the inhibiting effect of CO_2 and SO_2 on the catalytic activity of sulfated CaO was reversible, the affecting mechanism was inferred to be their competition for active sites. CO_2 and SO_2 are acidic gases; they may compete for the adsorbed NH_3 with NO over sulfated CaO, which would cause the decrease of NO reduction rate and NO conversion. However, the addition of H_2O can depress the inhibiting effect of SO_2. DRIFTS results have indicated that H_2O can generate Brønsted acid sites over sulfated CaO; hence, it could be deduced that CO_2 and SO_2 may not influence the NH_3 adsorbed over Brønsted acid sites, and just influence the molecularly adsorbed NH_3 over Lewis acid sites. When H_2O changed some Lewis acid sites to Brønsted acid sites, the effects of CO_2 and SO_2 were limited by H_2O. However, H_2O alone did not affect NO conversion obviously. This might be because NH_3 adsorbed over Lewis and Brønsted acid sites both could be activated to form NH_2 to reduce NO.

CONCLUSIONS

The experimental results and discussions show that:

1. CO_2 and SO_2 inhibit the catalytic activity of sulfated CaO for NO reduction by NH_3 in the presence of O_2, whereas H_2O alone has no obvious effect on the catalytic activity of the sulfated CaO. However, H_2O can depress the inhibiting effect of CO_2 and SO_2 on the catalytic activity of sulfated CaO. Sulfated CaO can still catalyze NO reduction by NH_3 when CO_2, SO_2, H_2O, and O_2 coexist in flue gas, which indicates the feasibility of using sulfated CaO as NO_x removal catalyst in post-combustion process;

2. In situ DRIFTS experiments of H_2O adsorption over sulfated CaO indicate that H_2O generates Brønsted acid sites over sulfated CaO at high temperature;

3. Combining the activity tests with and without CO_2, SO_2 and H_2O, the gas influencing mechanism was analyzed. CO_2 and SO_2 affect the catalytic activity of sulfated CaO by competing for the adsorbed NH_3 over Lewis acid sites against NO, and therefore decrease the NO reduction rate. CO_2 and SO_2 do not affect the ammonia ions over Brønsted acid sites. The addition of H_2O converts Lewis acid sites to Brønsted acid sites and suppresses the inhibiting effect of CO_2 and SO_2.

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REFERENCES

1. T. J. Li, Y. Q. Zhuo, Y. F. Zhao, C. H. Chen and X. C. Xu, *Energy Fuels*, **23**, 2010 (2009).
2. X. F. Yang, B. Zhao, Y. Q. Zhuo, C. H. Chen and X. C. Xu, *Asia-Pac. J. Chem. Eng.*, DOI:10.1002/apj.491 (2010).
3. T. J. Li, Y. Q. Zhuo, J. Y. Lei and X. C. Xu. *Korean J. Chem. Eng.*, **24**, 1113 (2007).
4. J. Zhang, S. W. Zhao, C. F. You, H. Y. Qi and C. H. Chen, *Ind. Eng. Chem. Res.*, **46**, 5340 (2007).
5. Y. Y. Lee, S. M. S. Soares and A. Sekthira, In *Proceedings of the 9th International Conference on Fluidized-Bed Combustion*, New York (1987).
6. M. D. Amiridis, I. E. Wachs, G. Deo, J. M. Jehng and D. S. Kim, *J. Catal.*, **161**, 247 (1996).
7. M. Stoll, J. Furrer, H. Seifert, G. Schaub and D. Unruh, *Waste Manage.*, **21**, 457 (2001).
8. T. J. Toops, A. B. Walters and M. A. Vannice, *Appl. Catal. B Environ.*, **38**, 183 (2002).
9. B. C. Michael, A. Donazzi and L. D. Schmidt, *J. Catal.*, **265**, 117 (2009).
10. W. Xu, H. L. Tong, C. H. Chen and X. C. Xu, *Korean J. Chem. Eng.*, **25**, 53 (2008).
11. T. Shimizu, Y. Tachiyama, D. Fujita and K. Kumazawa, *Energy Fuels*, **6**, 753 (1992).
12. G. J. Zijlma, A. D. Jensen, J. E. Johnsson and C. M. van den Bleek, *Fuel*, **81**, 1871 (2002).
13. T. J. Li, Y. Q. Zhuo, C. H. Chen and X. C. Xu, *Asia-Pac. J. Chem. Eng.*, **5**, 287 (2010).
14. G. J. Zijlma, A. Jensen, J. E. Johnsson and C. M. van den Bleek, *Fuel*, **79**, 1449 (2000).
15. T. Shimizu, M. Hasegawa and M. Inagaki, *Energy Fuels*, **14**, 104 (2000).
16. T. J. Li, Y. Q. Zhuo, C. H. Chen and X. C. Xu, *J. Eng. Thermophys.*, **30**, 1233 (2009).
17. G. J. Zijlma, A. D. Jensen, J. E. Johnsson and C. M. van den Bleek, *Fuel*, **83**, 237 (2004).
18. T. J. Li, Y. Q. Zhuo, C. H. Chen and X. C. Xu, In *Proceedings of the 33rd International Technical Conference on Coal Utilization & Fuel Systems*, Clearwater, Florida (2008).
19. B. Ramachandran, R. G. Herman, S. Choi, H. G. Stenger, C. E. Lyman and J. W. Sale, *Catal. Today*, **55**, 281 (2000).

20. W. Y. Su, Y. L. Chen, X. Z. Fu and K. M. Wei, *Chin. J. Catal.*, **22**, 175 (2001).
21. C. Cristiani, P. Forzatti and G. Busca, *J. Catal.*, **116**, 586 (1989).
22. G. Ramis, C. Cristiani, P. Forzatti and G. Busca, *J. Catal*., **124**, 574 (1990).
23. G. Deo and I. E. Wachs, *J. Catal.*, **146**, 323 (1994).
24. T. J. LI, Y. Q. Zhuo, C. H. Chen and X. C. Xu, *J. Tsinghua Univ. (Sci. Tech.)*, **48**, 1795 (2008).
25. C. H. Lin and H. Bai, *Ind. Eng. Chem. Res.*, **43**, 5983 (2004).
26. K. Nakanshi and P. H. Solomon, *Infrared absorption spectroscopy*, 2nd Edition, Holden-Day, San Francisco (1977).
27. L. Lietti, J. L. Alemany, P. Forzatti, G. Busca, G. Ramis, E. Giamello and F. Bregani, *Catal. Today*, **29**, 143 (1996).
28. G. Marbán, T. Valdés-Solís and A. B. Fuertes, *J. Catal.*, **226**, 138 (2004).
29. G. Busca, L. Lietti, G. Ramis and F. Berti, *Appl. Catal. B*, **18**, 1 (1998).
30. X. F. Yang, B. Zhao, Y. Q. Zhuo, Y. Gao, C. H. Chen and X. C. Xu, *Environ. Sci. Technol*., DOI: 10.1021/es103075p (2010).
31. J. P. Chen and R. T. Yang, *J. Catal*., **125**, 411 (1990).
32. G. Ramis, G. Busca, F. Bregani and P. Forzatti, *Appl. Catal.*, **64**, 259 (1990).
33. G. Ramis, G. Busca, V. Lorenzelli and P. Forzatti, *Appl. Catal.*, **64**, 243 (1990).
34. C. H. Lin and H. Bai, *Appl. Catal. B*, **42**, 279 (2003).