Korean J. Chem. Eng., **24**(6), 1113-1117 (2007)

Simultaneous removal of SO_2 and NO by low cost sorbent-catalysts prepared by lime, fly ash and industrial waste materials

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(*Received 23 August 2006 • accepted 9 March 2007*)

Abstract−The potential of the sorbent-catalysts prepared from three low cost materials, i.e., the lime, fly ash and some industrial waste material containing iron oxide, have been investigated for simultaneous removal of SO_2 and NO_x from flue gas in the temperature range 700-850 °C. NH_3 was chosen as the reducing agent for NO reduction in this study. Experimental results showed that SO_2 and NO could be simultaneously removed efficiently in the absence of O_2 at the temperature window of 700-800 °C. The effect of product layer generated from SO_2 removal on NO removal was not obvious. NO removal efficiency was strongly inhibited by O_2, which was attributed to the partial oxidation of NH_3 to NO over the sorbent-catalysts in the presence of oxygen. Neither NO_2 nor N_2O by-product was detected both in the absence and presence of O_2. Three routes were suggested to overcome the negative effect of O_2.

Key words: Multi-pollutant Control, Desulphurization, Denitrification, Flue Gas, Calcium Oxide

INTRODUCTION

Most of the energy consumed in China, now and in the near future, will still be coal, since the estimated coal reserve is very large. Removal of SO_2 and NO_x from coal combustion has received much attention, since SO_2 and NO_x emissions cause many problems, such as acid rain and effect on human health [1].

Wet and semi-dry scrubbing flue gas desulfurization (FGD) techniques have been found to be very effective for SO_2 removal [2]. However, wet scrubbing method requires a large amount of water and high initial investment and operating expense. Semi-dry FGD needs less water than the wet-FGD, but it still needs large amounts of water to achieve high desulfurization efficiency. In many regions, water resource shortage is becoming a significant problem. These drawbacks of wet and semi-dry methods limit their application in some developing countries and the area lack of water resource. Therefore, a dry-FGD technique with the characteristics of low initial investment and operating expense, low water consumption, is necessary to be developed.

$Ca(OH)_2$ sorbents has been widely studied at low (in-duct injection, <150 °C) and medium temperatures (economizer injection, 300-450 °C) for dry-FGD [3]. In order to promote the activity of the calcium-based sorbent, Li Y. and co-workers [4-6] have done much work for SO_2 removal by dry-FGD using $Ca(OH)_2$/fly ash sorbent at medium temperatures (320-380 °C) in the laboratory scale circulating fluidized bed (CFB). Previous work [7] done in our institute in the similar temperature range 250-400 °C at a pilot scale CFB-FGD apparatus obtained similar results, 70% SO_2 removal efficiency at Ca/S molar ratio of 2.2. To some extent, this dry-FGD technique meets the need for low cost and low water consumption. But the calcium utility efficiency is about 30%, which is relatively low and not satisfactory.

In order to achieve a more satisfactory calcium utility efficiency, the medium temperature window investigated for dry-FGD was extended to 400-800 °C in our institute, by using a highly active sorbent prepared from lime and fly ash [8-10]. The TGA experiment results showed that high calcium utility efficiency (above 90%) could be achieved at the temperature window of 700-800 °C. In this temperature range, CaO is the effective composition in the sorbent for SO_2 removal, since the decomposition temperature of $Ca(OH)_2$ is usually below 450 °C. The reaction stoichiometry is reaction (1) with $CaSO_4$ as the main desulfurization product. The negative effect of carbonate reaction (reaction (2)) is negligible in this temperature range. The pilot scale CFB-FGD experiment results [11] showed that SO_2 removal efficiency reached 85-95% at Ca/S molar ratio of 2 in the temperature range 700-770 °C. The best temperature window around 750 °C was suggested for dry-FGD in the medium temperature window. There were two advantages for the dry CFB-FGD operating in the higher medium temperature window (700-800 °C), compared to the lower medium temperature window (near 350 °C). One was the higher calcium utility efficiency. The other was the higher SO_2 removal efficiency, with the same operation conditions except the reaction temperature. These investigations above showed that dry FGD technology, with the features of low initial investment, low operating expense, low water consumption, and high desulphurization efficiency, have been achieved in our institute in the temperature range 700-800 °C for the flue gas desulphurization process.

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \qquad (1)$$

$$CaO + CO_2 \rightarrow CaCO_3 \qquad (2)$$

Simultaneous removal of SO_2 and NO_x in the same temperature window in a single reactor is more attractive than alternative tech-

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[‡] This work was presented at the 6th Korea-China Workshop on Clean Energy Technology held at Busan, Korea, July 4-7, 2006.

niques which remove SO_2 and NO_x separately.

The current technology for reducing NO emissions from the flue gas is the well-known Selective Catalytic Reduction (SCR) by NH_3 in the presence of O_2. The commercial catalysts used today are vanadium-based [12]. Although the commercial vanadium-based catalysts are highly active, they have the problems of being poisoned by SO_2, high activity for the oxidation of SO_2 to SO_3, and significant product selectivity for forming N_2O, which is a non-CO_2 greenhouse gas. Hence, continuing efforts are being made for developing new catalysts. It has been found that transition metallic oxides, such as Fe, Cu, Ni and Co oxides also have high activities for the SCR reaction [13]. Iron-based catalysts are particularly preferred because of their low-cost, abundance and nontoxicity as compared to commercial vanadium catalysts. Long and Yang [14] reported that Fe-ZSM-5 catalysts prepared by specific ion-exchange procedures have shown remarkably high activities (above 90% NO_x conversion) within a wide temperature window (400-600 °C) for SCR of NO by NH_3 in the presence of O_2. Schwidder et al. [15] reported similar experiment results in the SCR of NO with low Fe content Fe-ZSM-5 catalysts. When Fe content was 0.6 wt%, NO conversion reached 85% at 600 °C.

In the optimum temperature window (700-800 °C) for dry-FGD process developed in our previous work [11], NO reduction performance is unknown. In this study, the potential of the sorbent-catalysts prepared from three low-cost materials including lime, fly ash, and the industrial waste material containing iron oxides, has been investigated for the simultaneous removal of SO_2 and NO at temperatures of 700-850 °C. NH_3 was chosen as the reducing agent for NO reduction.

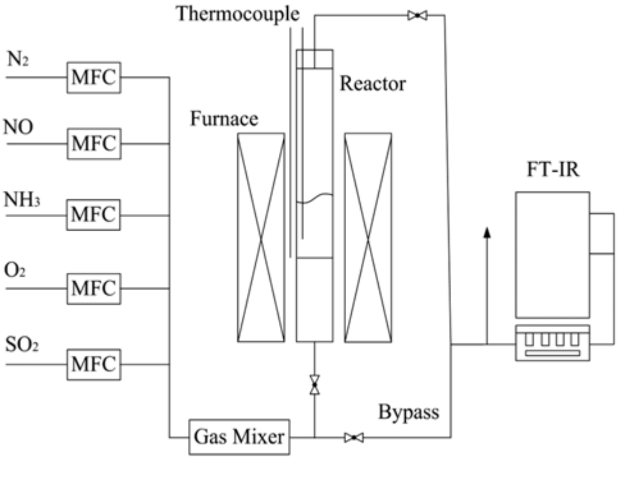

Fig. 1. Schematic diagram of experimental apparatus.

EXPERIMENTAL

1. Apparatus

Fig. 1 shows a schematic diagram of the experimental apparatus. The apparatus consists of three parts: the gas injection system, a bubbling fluidized bed reactor, and the gas analyzing system. The reactor with an inner diameter of 27 mm and a height of 0.8 m was made of quartz and could be placed inside the furnace. The flow rate of the premixed gas was controlled by the Mass Flow Controller (MFC). At the beginning of the experiment, the inlet gas was inducted only to the bypass. When the reaction temperature was increased to near the designed experiment temperature, the quartz reactor filled with the sorbent-catalysts was placed into the furnace. The feed gas was changed into the main stream route from the bypass when the temperature was almost stabilized at the desired value. The concentrations of SO_2, NO, NO_2 and N_2O were continuously monitored by an FT-IR spectrometer (Nicolet Corporation, NEXUS670) which was equipped with a liquid N_2-cooled MCT detector. The FT-IR was calibrated beforehand.

2. Sorbent-Catalysts Preparation and Characterization

Three low cost materials, fly ash, lime and some industrial waste material containing iron oxides, were used as the raw materials for the preparation of the sorbent-catalysts. The coal fly ash was collected from the electrostatic precipitator (ESP) of a coal-fired power plant, and was sieved to 74-125 μm. The lime used in the study was commercial lime. The industrial waste materials containing iron oxide were from a chemical plant in China. The raw lime was ground and calcined in air at 450 °C for 3 h in order to convert $Ca(OH)_2$ to CaO. The sorbent-catalysts used in our experiments were prepared by specific procedures that were similar to the processes in our previous work [7,9-11]. Two types of sorbent-catalysts were prepared, which are named as Sample-A and Sample-B hereinafter. The difference of Sample-A and Sample-B was the percentage of the industrial waste materials used for the preparation of the two samples.

Table 1 shows the chemical composition of the three raw materials and Sample-A and B. The sum of SiO_2 and Al_2O_3 content in this fly ash was above 80%, with some Fe_2O_3, CaO and TiO_2. CaO was the main composition of the raw lime, with some SiO_2 and MgO. The main composition of the industrial waste material was SiO_2 and Al_2O_3, with some Fe_2O_3, P_2O_5, La_2O_3 and CeO_2. The main composition of Sample-A and B was SiO_2, Al_2O_3 and CaO, with some Fe_2O_3 and TiO_2. No La_2O_3 or CeO_2 was detected in both Sample-A and B, since the proportion of the industrial waste material used in the preparation of the sorbent-catalysts was small.

The surface area of the sorbent-catalysts was measured by nitrogen adsorption based on the BET method (Micromeritics ASAP2010). Table 2 gives the results of the BET specific surface area of fly ash,

Table 1. Chemical composition of three raw materials and Sample-A and B (wt%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	TiO_2	La_2O_3	CeO_2
Fly ash	48.64	38.10	4.30	2.93	0.64	0.76	0.43	0.39	1.39	-	-
Lime	3.64	0.34	0.44	86.45	3.51	0.05	-	0.11	0.01	-	-
Waste materials	45.42	45.89	1.67	0.49	0.19	0.23	0.47	1.36	0.18	1.20	1.18
Sample-A	41.97	31.47	3.90	19.43	0.63	0.72	0.09	0.16	1.19	-	-
Sample-B	39.82	30.57	4.41	22.00	0.74	0.53	0.08	0.24	1.17	-	-

Table 2. BET surface area of fly ash, calcined lime, and the sorbent-catalysts (m^2/g)

Fly ash	Calcined lime	Sample-A	Sample-B
1.3	6.6	8.7	13.3

calcined lime and the sorbent-catalysts. It can be seen that the surface area of the raw fly ash used in this work is small. The specific area of Sample-B is about 1.5 times of that of Sample-A.

3. Activity Measurement

The activity test experiments were carried out in the bubbling fluidized bed quartz reactor. Prior to reaction, the sorbent-catalysts were calcined in air at 450 °C for 3 h to reduce the influence of H_2O that generated from the samples. The pretreated sorbent-catalysts were sealed and stored in a desiccator. For each experiment, 30 g samples were placed into the reactor. The total gas flow rate was 1,000 ml/min (under ambient conditions). The flue gas was simulated by blending different gaseous reactants. The typical reactant gas composition used for simultaneous removal of SO_2 and NO in the absence of oxygen was as follows: 1,500 ppm SO_2, 1,000 ppm NO, 667 ppm NH_3, and balanced by N_2.

NO and SO_2 conversions were defined as follows:

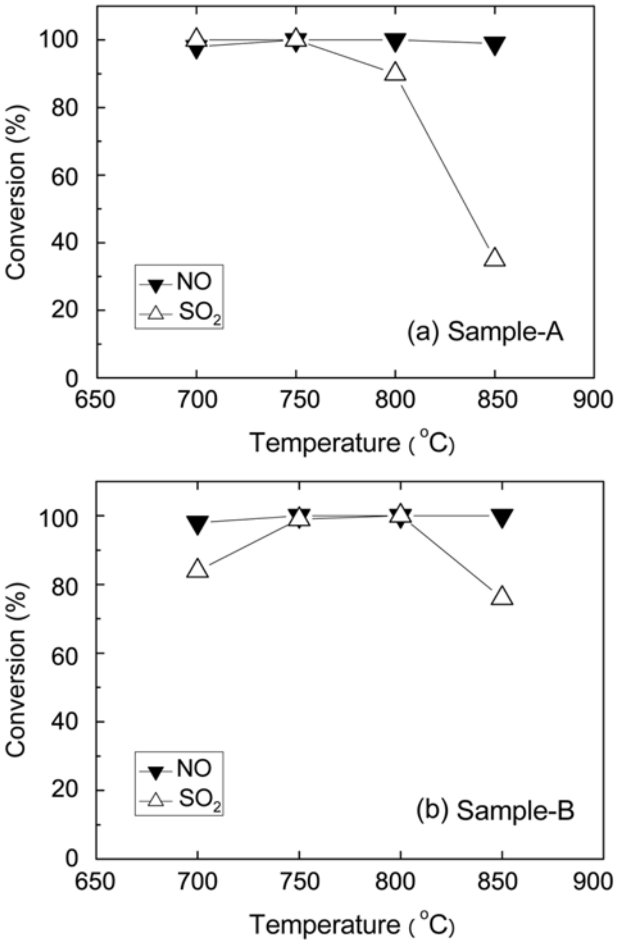

Fig. 2. The effect of temperature on simultaneous removal of SO_2 and NO in the absence of oxygen using Sample-A and Sample-B.

$$\eta_{NO}(\%) = \left(1 - \frac{C_{NO}^{out}}{C_{NO}^{in}}\right) \times 100 \tag{3}$$

$$\eta_{SO_2}(\%) = \left(1 - \frac{C_{SO_2}^{out}}{C_{SO_2}^{in}}\right) \times 100 \tag{4}$$

where C_{NO}^{in}, C_{NO}^{out}, $C_{SO_2}^{in}$ and $C_{SO_2}^{out}$ were the NO and SO_2 concentrations (in the units of ppm) measured at the inlet and outlet of the quartz reactor, respectively.

RESULTS AND DISCUSSIONS

1. Simultaneous Removal of SO_2 and NO

Fig. 2 shows the effect of temperature on the simultaneous removal of SO_2 and NO in the absence of oxygen by using Sample-A and Sample-B. Ammonia was used as the reducing agent for NO reduction under stoichiometric conditions. The reaction temperature was increased stepwise from 700 to 850 °C. Conversion data was taken by averaging the conversion rate within 20 minutes after the reaction temperature had been reached. The results showed that SO_2 and NO could be simultaneously removed efficiently at the temperature window of 700-800 °C on both samples. NO conversions were similar for the two samples, above 95% in the wide temperature range from 700 to 850 °C. No by-product N_2O or NO_2 was detected in the outlet gas stream during the experiment. Repeated experimentation was done and the same result was obtained. This indicated a high catalytic activity and product selectivity of the samples for the removal of NO by NH_3 in the reductive atmosphere at the temperature range of 700-850 °C.

In the absence of O_2, the reaction stoichiometry of NO and NH_3 is reaction (5). This reaction might be accelerated at the relatively high temperature window of 700-850 °C by some active components contained in the samples, such as the iron oxide or calcium oxide.

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \tag{5}$$

The desulphurization characteristics of the two samples were quite different. High conversion of SO_2 was maintained at the temperature range 700-800 °C on both samples. SO_2 conversion of Sam-

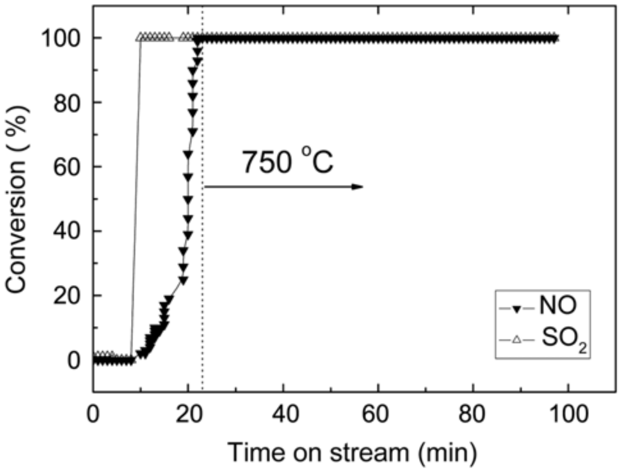

Fig. 3. Time-on-stream conversion of SO_2 and NO in the absence of oxygen over Sample-B at 750 °C.

ple-A decreased considerably at 850 °C, while a lesser decrease was observed for Sample-B. This might be attributed to the specific area of Sample-B, which is about 1.5 times that of Sample-A. A big specific surface area makes for improving the desulphurization activity of the calcium-based sorbent [16].

Fig. 3 shows the history of simultaneous removal of SO_2 and NO of Sample-B in the absence of oxygen at 750 °C. The gas mixtures were changed into the reactor from the by-pass route at 8 minutes when the flow rate stabilized. Then the temperature of the reactor was increased from the ambient temperature. The temperature became stable at 750 °C at 23 min. It can be seen that SO_2 and NO are effectively removed simultaneously for a long time by the sorbent-catalysts prepared from the three low cost raw materials. Also no by-product N_2O or NO_2 was detected in the outlet gas stream during the experiment. The effect of the product layer generated from SO_2 removal on NO removal was not obvious, since the active site for NO removal seemed to remain and the conversion rate of NO remained at almost 100% after the temperature stabilized at 750 °C. The reason for this phenomenon is still unclear. A possible explanation of this phenomenon is that some calcium based materials, i.e., $CaSO_4$ and CaO, may also catalyze the removal of NO at a temperature around 750 °C in a reductive atmosphere when NH_3 is chosen as the reducing agent.

2. Effect of O_2

Fig. 4 shows the influence of oxygen on the simultaneous removal of SO_2 and NO over Sample-A at 750 °C. The reactor was preheated to about 500 °C. Then the gas mixtures were changed into the reactor from the by-pass route at 13 minutes. The temperature stabilized at 750 °C 9 min later. It can be seen from Fig. 4 that NO conversion was restrained seriously by oxygen, while SO_2 conversion was not changed during the variation of O_2 concentration. Also, no by-product N_2O or NO_2 was detected in the outlet gas stream during the experiment. In the absence of oxygen, SO_2 and NO could be simultaneously removed efficiently for Sample-A at 750 °C. When 0.3% (v/v) O_2 was added into the system, NO conversion dropped rapidly from 100% to around 16%. When O_2 concentration was changed to 2%, NO conversion dropped even further. When O_2 concentration was adjusted to 0% again, NO conversion was recovered to 100% gradually. These indicated that the high selectivity of ammonia to NO in the presence of oxygen, which was an important characteristic of the traditional SCR reaction (reaction (6)), seemed to be no longer maintained at a temperature around 750 °C. On one hand, partial NH_3 was oxidized by oxygen to form the undesired product NO through reaction (7). On the other hand, NH_3 was consumed as the reducing agent to reduce NO to N_2 through reaction (6). Some active materials contained in the samples might accelerate reactions (7) and (6). A steady dynamic equilibrium might be built between the two reactions. The net NO conversion was dependent on the competition between the catalytic oxidation of ammonia (reaction (7)) and the catalytic reduction of NO by NH_3 (reaction (6)).

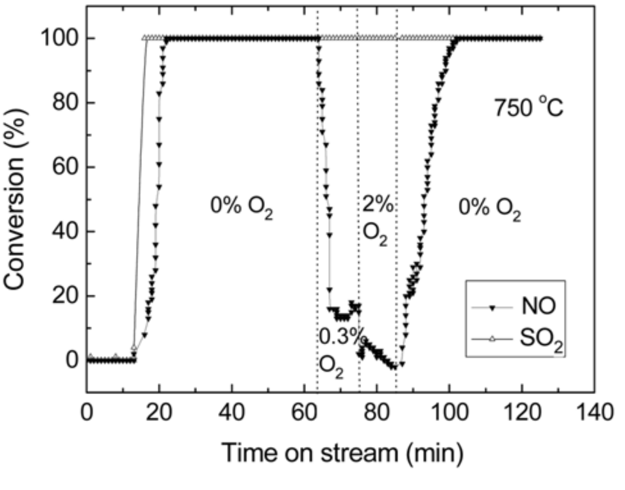

Fig. 4. Time-on-stream profile of the simultaneous removal of SO_2 and NO at 750 °C and different concentration of oxygen over Sample-A. Reaction conditions: 30 g samples; total flow rate 1,000 ml/min (under ambient conditions); SO_2=1,500 ppm, NO=1,000 ppm, NH_3=667 ppm, N_2 as gas balance.

$$4NO+4NH_3+O_2 \rightarrow 4N_2+6H_2O \tag{6}$$

$$4NH_3+5O_2 \rightarrow 4NO+6H_2O \tag{7}$$

On the same sorbent-catalysts, NO conversion was much higher when the concentration of oxygen was 0.3% than 2%. This indicated that except for the active materials contained in the samples, the content of O_2 also played an important role during the competition between the two reactions. Compared with high O_2 concentration, low O_2 concentration was able to constrain the undesired oxidization of NH_3 to NO to some extent.

Since there is always some amount of O_2 in the practical flue gas from the ordinary coal-fired power plant, it seems difficult for the immediate application of the low cost sorbent-catalysts prepared in this study for simultaneous removal SO_2 and NO in one reactor due to the negative effect of O_2. Three possible routes are suggested to overcome the negative effect of O_2. The first one is to remove O_2 before the flue gas is injected into the reactor, i.e., injecting a small amount of natural gas at the reburning zone of the boiler to work out O_2. The injected natural gas will be used as the fuel, and the energy generated by natural gas combustion could be utilized in the boiler systems. The second is to change the reducing agent to those which can reduce NO in the presence of O_2. Hydrocarbons might be an attractive alternative reducing agent, since it is reported by some researchers that NO can be reduced by hydrocarbons even in the presence of excess O_2 [17,18]. The third is to improve the characteristics of the sorbent-catalysts.

CONCLUSIONS

SO_2 and NO can be simultaneously removed efficiently in one reactor by sorbent-catalysts prepared from three low cost raw materials: lime, fly ash, and some industrial waste material containing iron oxide, in the absence of oxygen at the temperature window of 700-800 °C. No by-product N_2O or NO_2 was detected in the outlet gas stream both in the absence and presence of oxygen. The effect of product layer generated from SO_2 removal on NO removal was not obvious. The effect of the concentration of oxygen on NO removal was great over the sorbent-catalysts. NO conversion decreased rapidly from 100% to 16% after 0.3% O_2 was added into the feed gas. When 2% O_2 was added into the feed gas, there was almost no net NO reduction but the oxidation of NH_3 to NO. The high selectivity of ammonia to NO in the presence of oxygen, which was an important characteristic of the traditional SCR reaction, seemed to be no longer maintained at a temperature around 750 °C. Equilibrium might be established between the oxidization of NH_3 by O_2 to form NO and the reduction of NO by NH_3 in the presence of O_2. The net NO conversion was dependent on the competition between the two reactions. Immediate application of the low cost sorbent-catalysts prepared in this study for simultaneous removal SO_2 and NO in a single reactor seems difficult due to the negative effect of O_2. Three possible routes are proposed to overcome the negative effect of O_2. Further work is needed in order to gain more information on simultaneous removal of SO_2 and NO with the low cost sorbent-catalysts.

ACKNOWLEDGMENT

The financial support by the National Key Basic Research and Development Program of China (2006CB200301) for this study is gratefully acknowledged.

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