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Simultaneous SO_2/NO_x removal by a powder-particle fluidized bed

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Abstract

Simultaneous dry removal of SO_2 and NO_x from flue gas has been investigated using a powder-particle fluidized bed. In a process of flue gas desulfurization by use of solid sorbents such as FeO (dust from a steel plant) and CuO, the smaller the particle size of sorbents, the higher the expected SO_2 conversion. In a powder-particle fluidized bed (PPFB), fine particles less than 40 μm in diameter fed into the bed are fluidized with coarse particles. But only the fine particles are entrained from the bed, and their residence time in the bed is remarkably long.

The reduction of NO_x with NH_3 in the fluidized bed is catalyzed by coarse particles or both coarse and fine particles. In this study, PPFB was applied to simultaneous dry SO_2/NO_x removal process, and several kinds of sorbents or catalysts were evaluated in a PPFB. Using the selected sorbents and catalysts, kinetic measurements were made in the temperature range of 300 to 600°C. SO_2 removal efficiencies were affected by reaction temperature, sorbent/S ratio, and static bed height. NO_x removal efficiencies in excess of 95% were achieved at NH_3/NO_x mole ratio of 1.0. When FeO was used as sorbent, SO_2 conversion increased with increasing temperature and reached 80% at 600°C.

Keywords: Simultaneous SO_2/NO_x removal; Powder-particle fluidized bed; SO_2/NO_x removal

1. Introduction

There is a need to develop a simultaneous dry removal process of SO_2 and NO_x from flue gas which removes both SO_2 and NO_x in one step with no liquid waste byproducts. Various reactor configurations, such as fluidized bed, moving bed and gas-solid trickle flow reactors, using copper oxide and activated carbon as a sorbent-catalyst, have been developed or commercialized [1-5]. The process economics are greatly dependent on reactor configuration with lower sorbent feed rates. With the formation of surface sulfates, further reaction has to continue by diffusion through the sulfate product layer. This becomes a major resistance in the sulfation reaction. Thus, high capacity and reactivity of sorbent with SO_x is expected with fine particle sorbent.

Kato et al. have developed a new type of fluidized bed for utilization of fine particles as shown in Fig. 1: the powder-particle fluidized bed (PPFB) [6]. In the PPFB process, fine particles, ~ 40 μm in diameter, fed into the bed are

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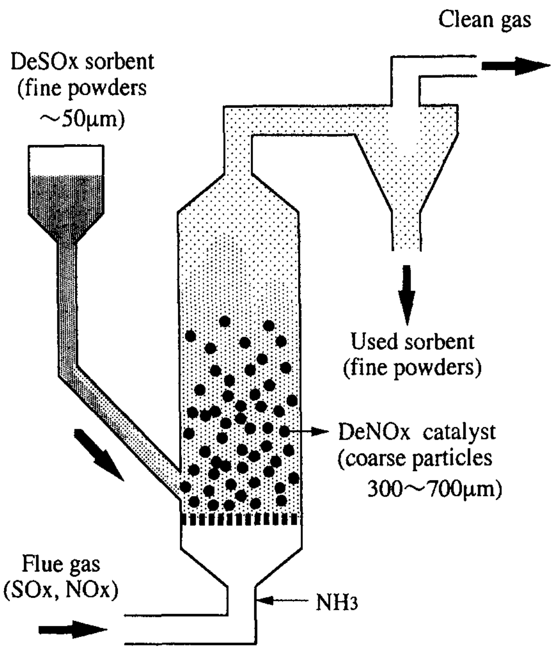

Powder-particle fluidized bed reactor

Fig. 1. Conceptual illustration of a powder-particle fluidized bed (simultaneous removal of SO_2 /NO_x process).

fluidized with coarse particles, and only the fine particles are entrained from the bed continuously. The fluidizing coarse particles prevent the fine particles from agglomerating, and the fines have a very long residence time in the bed, more than several hundred times longer than the residence time of the fluidizing gas. It has been considered that the fine particles in the bed adhere to the surface of the coarse particles. PPFB coupled with fine particle limestone has been applied to a de-SO_x process [7]. 100% of SO_2 conversion was obtained at Ca/S = 3 in the temperature range between 800 and 950°C because of the fine particles and sufficiently long residence time of limestone.

In this work, simultaneous dry removal of SO_2 and NO_x using a laboratory scale powder-particle fluidized bed with a combination of fine sorbents and coarse catalysts was carried out. Several kinds of sorbents or catalysts were evaluated in the PPFB. Using the selected sorbents and catalysts, the effects of operating factors on SO_2 and NO_x conversion were investigated.

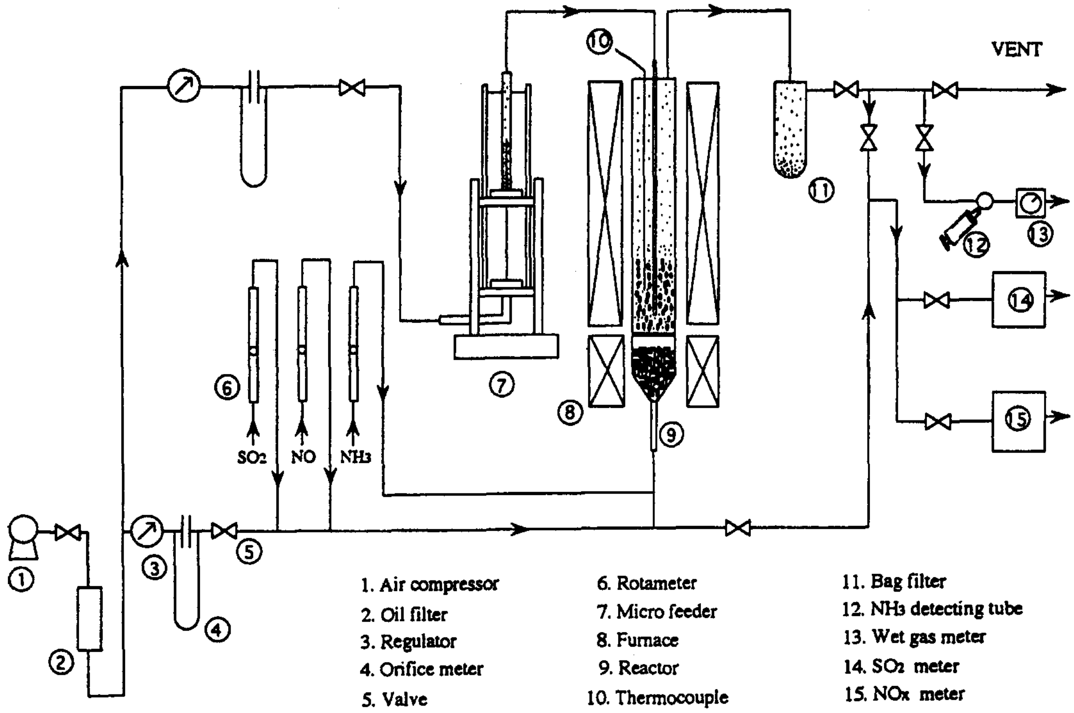

Fig. 2. Schematic diagram of experimental apparatus.

2. Experimental

Fig. 2 shows the experimental apparatus for the simultaneous dry removal of SO_2/NO_x. This apparatus consists of a micro-feeder of fine particles of sorbents, a powder-particle fluidized bed installed in an electric furnace and a filter for gas–solid separation. The fluidized-bed column was a stainless steel tube of 52.5 mm i.d. and 1235 mm high. Tests were performed in the 300–1000 ppm range of SO_2 concentration and 500 ppm of NO_x concentration. Coarse particles used were WO_3/TiO_2 of 24–42 mesh (calculated U_{mf} and U_t were 0.28 m/s and 3.22 m/s, respectively) and silica sand of 20–30 mesh (U_{mf} and U_t were 0.24 m/s and 3.18 m/s, respectively). Fine particles were CuO, ZnO, and dust (FeO: 74.4 wt%, Fe_2O_3: 12.0 wt%) from the steel plant. The mean diameters of fine particles were in the range of 2.5–25 μm. Fine sorbents were fluidized with coarse particles and the entrained particles were captured by a cylindrical thimble filter. SO_2 and NO concentrations of the outlet gas were measured continuously by SO_x and NO_x meters.

The entrained sorbent was examined under a scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS) analytical system. Back-scattered electron image (BEI) by EPMA was investigated to identify the sulfate product phase.

The conversions, X, of SO_2 and NO were calculated from SO_2 and NO concentrations at the inlet and outlet of the reactor using the following equation.

$$X_{SO_2,NO} = (C_{SO_2,NO_{in}} - C_{SO_2,NO_{out}})/C_{SO_2,NO_{in}}$$

3. Results and discussion

3.1. Kinetics

Results of SO_2 removal tests are given in Figs. 3 and 4, which show SO_2 removal efficiency as a function of the reaction temperature and as a function of the static bed height, respectively. When CuO and dust from a steel plant (FeO) were used as fine particle (sorbents), SO_2 conversion increased with increasing temperature and reached 80% at a bed temperature of 600°C. SO_2 removal efficiency is low in the 250–350°C temperature range, which is suitable for combined SO_2/NO_x removal from both economic and kinetic points of view [1]. This is because sorbent inside the unsupported particles is hardly utilized for desulfurization by diffusional limitations, which is discussed in Section 3.2 (sorbents analysis). We have been developing supported metal oxide with high dispersion as a high capacity and reactivity sorbent. SO_2

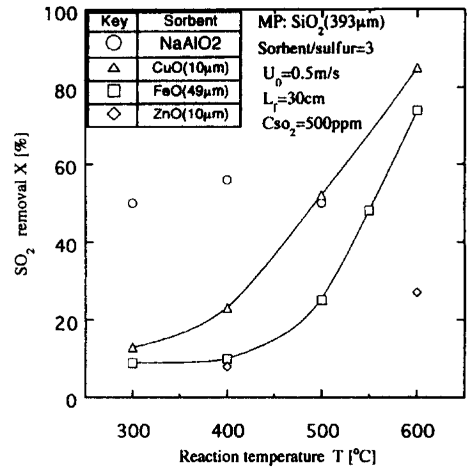

Fig. 3. SO_2 removal efficiency as a function of the reaction temperature.

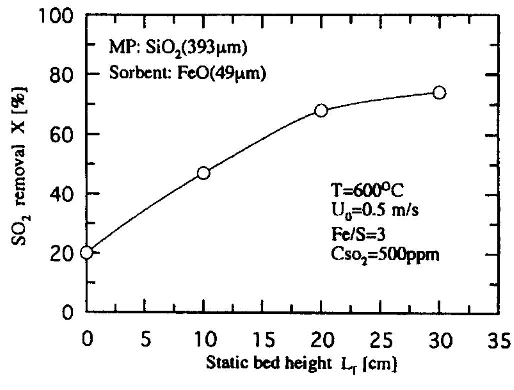

Fig. 4. SO_2 removal efficiency as a function of the static bed height.

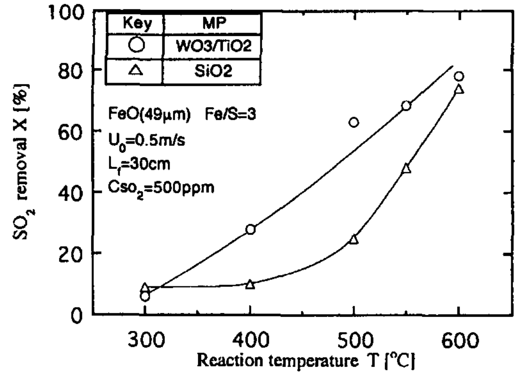

Fig. 5. Effect of de-NO_x catalyst on SO_2 removal efficiency.

conversion increased in proportion to bed height. This is because contact time between the sorbent and the gas increased linearly with static bed height.

The other process variables studied were superficial gas velocity, mean diameter of sorbents, sorbent/sulfur ratio, and concentration of SO_2. SO_2 conversion increased with decreasing gas velocity, increasing sorbent/sulfur ratio and decreasing mean diameter of sorbent particle. The latter observation is explained by the following two effects. The residence time of fine particles increases with decreasing size of fine particles [6]. The specific area of a particle increases with decreasing particle diameter.

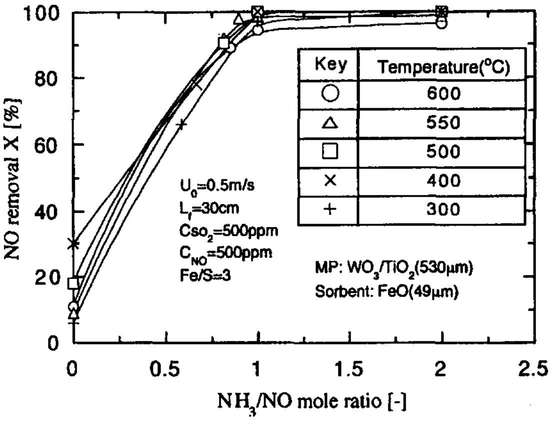

Fig. 6. NO_x removal efficiency as a function of NH_3/NO mole ratio.

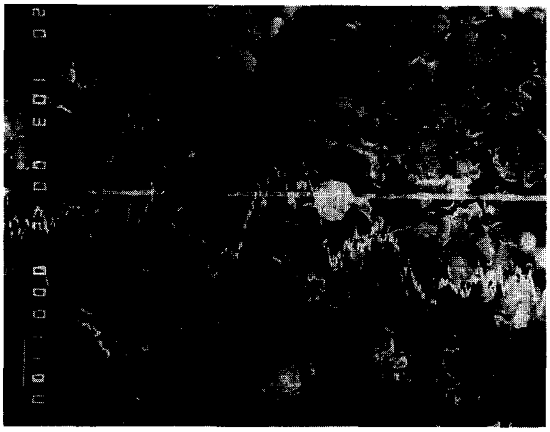

Fig. 7. SEI of spent dust and sulfur-profile measured by scanning line.

Fig. 5 shows the effect of de-NO_x catalyst on SO_2 removal. The de-NO_x catalyst enhanced the SO_x removal efficiency. This indicates that WO_3/TiO_2 catalyzes the oxidation of SO_2 to

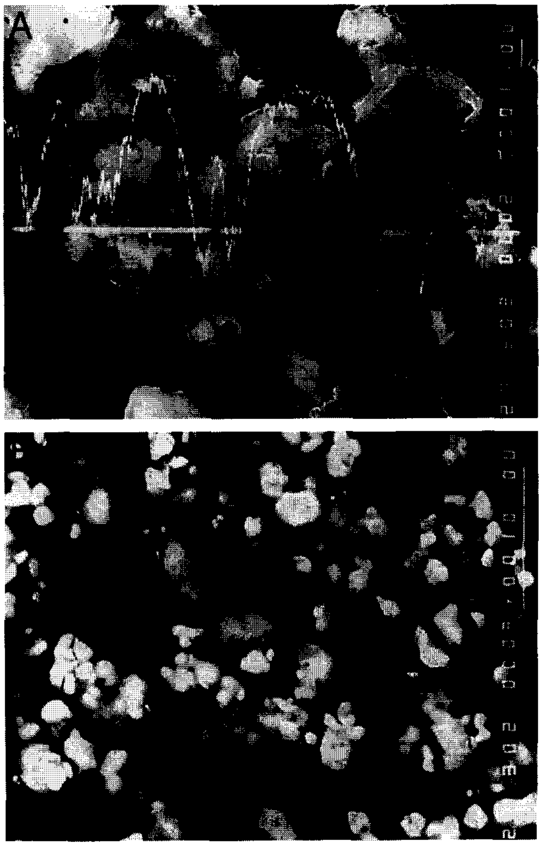

Fig. 8. (A) SEI of spent CuO, (B) BEI of spent CuO; the dark area is a region with high S content.

SO_3 in the presence of oxygen, which enhances the reaction of SO_3 with sorbent.

The NO_x removal efficiencies obtained under a NH_3/NO ratio of 1.0 using WO_3/TiO_2 are plotted in Fig. 6 as a function of reaction temperature. NO_x removal efficiencies in excess of 95% were achieved at NH_3/NO_x mole ratios of 1.0. In the optimum temperature range for SO_2 removal, which is 500–600°C, NO_x removal efficiencies are high enough.

3.2. Sorbents analysis

Figs. 7 and 8(a) show the secondary electron image (SEI) and sulfur-profile measured by scanning along the line for steel plant dust and CuO sorbents after desulfurization, respectively. Fig. 8(b) shows the back-scattered electron image (BEI) of spent CuO sorbent. In BEI, a region with low sulfur content appears as a bright area on the photograph. Both the sulfur-profile and BEI show that the bulk oxide of dust particles from the steel plant was sulfated uniformly, compared with spent CuO sorbent which formed sulfates in the outer shell of the particles. This may be due to the highly porous and reactive sorbent of steel plant dust.

4. Conclusions

The results of this study suggested the potential of applying the PPFB process to simultaneous dry SO_2/NO_x removal. In order to improve the PPFB process, we have been developing highly porous and reactive supported metal oxides, such as a copper oxide supported on alumina [1,8], in a lower temperature range of 250–350°C.

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