[Review Paper]

A New Dry Process for Simultaneous Removal of SO₂ and NO from Flue Gas by Powder-particle Fluidized Bed

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A new process, which is a combination of dry processes for flue gas desulfurization and selective catalytic reduction of NO_x with NH₃ for simultaneous removal of SO_x and NO_x from the flue gas, was developed using a powder-particle fluidized bed. In the process, SO_x was removed by fine sorbent, and NO_x was reduced to N₂ with NH₃ catalyzed by coarse DeNO_x catalyst in a powder-particle fluidized bed reactor. The powder-particle fluidized bed was made of a stainless steel tube of 0.053 m internal diameter and 1.0 m in height above the distributor. Three kinds of fine sorbents, iron oxide dust (a by-product of steel production), sodium-based sorbents (sodium bicarbonate and sodium carbonate), and copper-based sorbents (CuO, CuO·V₂O₅/Al₂O₃, and CuO·V₂O₅·K₂SO₄/Al₂O₃), were evaluated in this study. Coarse particles of inactive silica sand and DeNO_x catalysts of WO₃/TiO₂ and V₂O₅·WO₃/TiO₂ were used as fluidized medium particles. The effects of various operating conditions and properties of DeSO_x sorbent and DeNO_x catalyst on removal of SO₂ and NO were investigated. The iron oxide dust appeared to be a potential low-cost sorbent for removal of SO_x and also a catalyst for reduction of NO_x. Both sodium-based and copper-based sorbents had sufficient reactivity for removal of SO₂. The powder-particle fluidized bed reactor was effective for simultaneous removal of SO_x and NO_x from the flue gas. In the proposed process, the simultaneous removal of over 90% of SO₂ and NO was achieved by proper combination of fine sorbent and coarse catalyst.

1. Introduction

Power plants are the major source of sulfur oxides (SO_x) and nitrogen oxides (NO_x). The rapid increase in demand for electric power aggravates the pollution problems caused by the oxides. Currently, the most widely used technologies for cleaning up the deleterious oxides in the flue gas of power plants are wet Flue Gas Desulfurization (FGD) and dry Selective Catalytic Reduction (SCR) of NO_x with ammonia^{1),2)}. These technologies are widely used in the developed countries, *e.g.*, Japan, United States, and Germany for achieving 90% removal of SO_x and NO_x from the flue gas.

The traditional SCR technology used NH₃ over a metal oxide catalyst to reduce NO_x to N₂ in the range, 623–723 K, which coincides with the temperature range of flue gas between the economizer and preheater at power plants. The main reactions are:

Besides these reactions, catalytic oxidation of SO₂ to SO₃ may occur as a side reaction. The SCR process was identified suitable for controlling the emission of NO_x, based on its efficiency, selectivity, and economy^{3),4)}.

On the other hand, the wet FGD process suffers from the problems of low heat efficiency and high cost. To eliminate such problems of wet FGD process, the dry FGD process was found to reduce the cost effective by promoting the heat efficiency. In the dry FGD process, some sorbents such as alkalized alumina^{5),6)} (Na₂O·Al₂O₃, an active form of NaAlO₂), active manganese oxide⁷⁾ (MnO_x·*n*H₂O, *x*=1.5–1.8, *n*=0.3–1.0), copper oxide supported on alumina⁸⁾ (CuO/Al₂O₃), sodium bicarbonate and sodium carbonate^{9)–11)} (NaHCO₃ and Na₂CO₃) can be used for removing the SO₂ in the same SCR reaction temperature range. The copper oxide supported on alumina was used also as DeSO_x sorbent and DeNO_x catalyst for simultaneous removal of SO_x and NO_x^{12),13)}. The waste material of red mud, a by-product of

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Fig. 1 Conceptual Illustration of Powder-particle Fluidized Bed for Simultaneous Removal of SO_x and NO_x

aluminum smelting plants, containing significant amounts of iron oxide and other oxides exhibited sufficient rate for SO_2 absorption, and it could be considered as a low-cost sorbent for SO_2 removal^{(14), (15)}. The iron oxide contained in the low-cost material of ocher also exhibited catalytic activity for reduction of NO_x by ammonia^{(16), (17)}.

For removal of SO_2 above 80%, the dry FGD process, however, suffers frequently from the problems associated with handling large amounts of solid sorbent due to their low SO_2 removal rates. Reducing the size of sorbent to increase its surface area proved to be effective for accelerating the reaction rate and for increasing the overall utilization of the sorbent^{(18), (19)}. Because of the tendency of fine sorbents to agglomerate readily, there could be a serious problem on their use in the flue gas.

By adopting a Powder-Particle Fluidized Bed (PPFB), which was developed by Kato *et al.*^{(20), (21)}, a new dry process, which is a combination of dry FGD and SCR processes for simultaneous removal of SO_x and NO_x from the flue gas was proposed^{(22)~(25)} by the authors. A conceptual illustration of PPFB for simultaneous removal of SO_x and NO_x is shown in Fig. 1. The PPFB is a fluidized bed of binary-solids, consisting of coarse particles and fine powders. In the PPFB system, fine powders are fed continuously to the bed in which the coarse particles are fluidized. The fine powders, which are fluidized with the coarse particles in the bed, move through the bed, adhere to the coarse particles, and finally elutriate from

Fig. 2 Schematic Diagram of Experimental Apparatus

the bed. Advantages of PPFB are as follows: (1) Fluidization of coarse particles prevents fine powders from agglomeration and makes it possible for the fine powders to disperse and fluidize uniformly. Thus, PPFB can be used to smoothly fluidize such easily agglomerative fine powders as those of group C of the Geldart classification. (2) The average residence time of fine powders is quite long, that is, from ten to hundred times longer than that of gases by adhering on the surfaces of the coarse particles⁽²¹⁾. (3) With the use of fluidized medium particles having catalytic properties, catalytic reactions can be carried out in PPFB. Because of its several obvious advantages as gas-solid contactor for fine powders in the range of size from several to some tens of microns in diameter, it has been successfully applied to decarbonization of SiC powders⁽²⁰⁾, drying of fine particles^{(26), (27)}, reduction of fine iron oxide particles⁽²⁸⁾, catalytic pyrolysis of coal^{(29)~(31)} and desulfurization using lime and limestone powders and slurries^{(19), (32)}.

The object of this work is to search for optimum combination of DeSO_x sorbents and DeNO_x catalysts and to optimize operating conditions in PPFB for simultaneous removal of SO_2 and NO .

2. Experimental

2.1. Apparatus and Procedure

A schematic diagram of the experimental apparatus^{(22)~(25)} is shown in Fig. 2. The system consisted essentially of a micro-feeder, a powder-particle fluidized bed reactor, a bag filter, and analyzers for monitoring the concentrations of SO_2 and NO .

The PPFB reactor was made of a stainless steel

Table 1 Properties of Fine SO₂ Sorbents

Particles	d_p [μm]	ρ_p [kg/m^3]	$U_{mf} \times 10^3$ [m/s]	U_t [m/s]
Iron oxide dust	49	5003	7.18	0.36
NaHCO ₃	45	2210	2.67	0.13
Na ₂ CO ₃	45	2530	3.06	0.15
CuO	10	6400	0.38	0.019
CuO·V ₂ O ₅ /Al ₂ O ₃	25	1180	0.44	0.022
CuO·V ₂ O ₅ ·K ₂ SO ₄ /Al ₂ O ₃	8	980	0.038	0.0019
CuO·V ₂ O ₅ ·K ₂ SO ₄ /Al ₂ O ₃	36	980	0.76	0.038

tube of 0.053 m I.D. and 1 m in height above the distributor. A porous sintered plate was used as a distributor. The sorbent from the micro-feeder was continuously fed to the bottom of the fluidized bed, placed 0.03 m above the distributor. Below the distributor, a stainless steel tube packed with porcelain pipes was used as preheater and premixer. The reactor and preheater were heated by two separate external electric furnaces, both controlled with PID controllers. The reaction temperature was measured with a thermocouple immersed in the fluidized bed.

The experimental procedure was as follows: The fluidized bed was first loaded with a certain amount of coarse particles such as silica sand or DeNO_x catalyst to a desired static height of bed. Air from a compressor was passed through an oil filter and the flow rate was measured using orifice meters. The air, preheated and premixed, was fed to the bottom of the fluidized bed. The coarse particles in the bed were fluidized by air at a desired flow rate, and the temperature was raised to a desired level. After a steady temperature profile was established throughout the bed, SO₂ and NO from the cylinders were introduced at such rates to yield predetermined concentrations of SO₂ and NO at inlet. The flow rates of SO₂ and NO were controlled by rotameters and their concentrations at inlet were measured by SO₂ and NO analyzers through a by-pass line. When the system was in a steady state under the desired operating conditions, the fine powders of sorbent from the micro-feeder were continuously fed to the bottom of the fluidized bed in which the coarse particles were fluidized and SO₂ absorption was in progress. The used sorbent elutriated from the fluidized bed was collected in a bag filter. The sorbent could be regenerated or disposed of. Ammonia was introduced directly to the bottom of the reactor for catalytic reduction of NO to yield N₂.

Concentrations of SO₂ and NO at outlet were measured continuously with an infrared gas analyzer (Shimadzu IRA-107 continuous gas analyzer) and a chemiluminescence analyzer (Yanaco ECL-77A automatic NO_x analyzer), respectively. Leakage of NH₃ was measured with NH₃ detecting

Table 2 Chemical Analysis of Iron Oxide Dust

Materials	FeO	Fe ₂ O ₃	SiO ₂	CaO	Others
wt%	74.42	12.80	1.44	1.76	9.58

Table 3 Compositions of Supported Copper Oxide Sorbents [wt%]

Sorbents	CuO	V ₂ O ₅	K ₂ SO ₄	Al ₂ O ₃
CuO·V ₂ O ₅ /Al ₂ O ₃	9.6	3.3	0	87.1
CuO·V ₂ O ₅ ·K ₂ SO ₄ /Al ₂ O ₃	7.3	3.3	6.0	83.4

Table 4 Properties of Coarse Fluidized Medium Particles

Particles	d_p [μm]	ρ_p [kg/m^3]	U_{mf} [m/s]	U_t [m/s]
Silica sand	393	2600	0.24	3.18
WO ₃ /TiO ₂	530	1690	0.28	3.22
V ₂ O ₅ ·WO ₃ /TiO ₂	470	1780	0.23	2.95

tubes. Used sorbents were examined for measuring the sulfur distribution in the used sorbent with a Scanning Electron Microscope (SEM), equipped with an Energy-Dispersive Spectrometer (EDS) analytical system.

2. 2. Materials

The properties of fine SO₂ sorbents used in this study are shown in **Table 1**. The iron oxide dust, a by-product of steel production, contains considerable amounts of iron oxides along with silicon and calcium and several other metal oxides. The result of chemical analysis of the iron oxide dust is given in **Table 2**. Sodium bicarbonate, sodium carbonate, and copper oxide (CuO) were commercially available. Sorbents of copper oxide supported on alumina particles with addition of vanadium oxide and potassium sulfate (CuO·V₂O₅/Al₂O₃ and CuO·V₂O₅·K₂SO₄/Al₂O₃) were supplied by JGC Corporation. Compositions of the supported copper oxide sorbents are shown in **Table 3**.

Three kinds of coarse particles, inactive silica sand, DeNO_x catalysts of WO₃/TiO₂, and V₂O₅·WO₃/TiO₂, were used as coarse Fluidized Medium Particles (FMP). Their properties are shown in **Table 4**. Silica sand was used as inert reference

for comparison of the effects of DeNO_x catalyst on SO₂ removal. The commercially available DeNO_x catalysts of WO₃/TiO₂ and V₂O₅·WO₃/TiO₂ were from the Catalysts & Chemicals Ind. Co., Ltd. Active temperature ranges for catalytic reduction of NO were from 673 to 803 K for WO₃/TiO₂ catalyst and from 573 to 643 K for V₂O₅·WO₃/TiO₂ catalyst, respectively.

2.3. Equations of Chemical Reactions for Removal of SO₂

When sulfur dioxide reacts with the above sorbents in the presence of oxygen below the decomposition temperature of sulfate, the principal product is the sulfate. The following overall reactions are adequate for predicting the system behavior.

For iron oxide dust:

For sodium bicarbonate and sodium carbonate:

For copper oxide:

One mole of copper, two moles of sodium, 2/3 mole of iron, are required theoretically to remove one mole of SO₂.

The efficiency of removal of SO₂ and NO is defined as the ratio of the difference between inlet and outlet concentrations of SO₂ and NO to the inlet concentrations of SO₂ and NO. The following experiments were conducted under usual constant conditions, *i.e.*, superficial gas velocity (U_g) of 0.5 m/s, static bed height (L_s) of 0.3 m, inlet concentrations of SO₂ and NO of 500 ppm.

3. Results and Discussion

3.1. Experiments Using Sorbent of Iron Oxide Dust

The effect of reaction temperature on the removal of SO₂ for iron oxide dust is shown in Fig. 3. The removal of SO₂ using WO₃/TiO₂ catalyst as fluidized medium particle is clearly greater than that using silica sand, since the catalyst for removal of NO_x is also active for

Fig. 3 Effect of Reaction Temperature on the Removal of SO₂ for Iron Oxide Dust

catalytic oxidation of SO₂ to SO₃⁴⁾. Studies indicated that absorption of SO₃ on metal oxides was more favorable compared to that of SO₂^{15), 33)}. The reaction scheme in presence of DeNO_x catalyst may be catalytic oxidation of SO₂ to SO₃ followed by absorption on the metal oxide. Thus, the reaction rate of sulfation is increased in the presence of DeNO_x catalyst. At low and high temperatures, 573 K and 873 K, the removal of SO₂ using WO₃/TiO₂ catalyst as fluidized medium particle was almost equal to that using silica sand. The reason may be that the active temperature range of WO₃/TiO₂ catalyst for catalytic oxidation of SO₂ to SO₃ was the same as the active temperature range (673-803 K) for catalytic reduction of NO. The activity for catalytic oxidation of SO₂ to SO₃ can be neglected at low and high temperatures, that is, the greater the distance from the active temperature, the lower was the activity for catalytic oxidation of SO₂ to SO₃. Thus, the efficiency of removal of SO₂ using WO₃/TiO₂ catalyst and that using silica sand as fluidized medium particles showed no significant difference at 573 K and 873 K.

The effect of static height of bed on the removal of SO₂ for iron oxide dust is shown in Fig. 4. The removal of SO₂ increased with increasing static height of bed. This is because the average residence time of sorbent increases with the increase in height of bed²¹⁾. The removal of SO₂ increased from 20 to 75% when the static height of bed was increased from 0 to 0.3 m. The removal of SO₂ was significantly low when no fluidized medium particles existed in the bed. This meant that the contact time between sorbent and gas was extremely short in this case. This observation confirmed that large fluidized medium particles used in this work were very useful to disperse the

Fig. 4 Effect of Static Height of Bed on the Removal of SO_2 for Iron Oxide Dust

fine sorbent uniformly and to increase its average residence time in the reactor, a significant advantage of PPFB.

Experimental results²²⁾ showed that the removal of SO_2 increased with increase in the mole ratio of Fe/S and decrease in the superficial gas velocity. The removal of SO_2 turned out to be almost independent of NH_3 concentration.

The dependence of the removal of NO on mole ratio of NH_3/NO at inlet, reaction temperature, and mole ratio of Fe/S, for iron oxide dust using silica sand as fluidized medium particle, is shown in Fig. 5. It is interesting to note that the removal of NO is significantly low without iron oxide dust feeding ($\text{Fe}/\text{S}=0$), but it increases sharply with increasing iron oxide dust feeding to $\text{Fe}/\text{S}=3$. It is obvious that iron oxide dust not only serves as SO_2 sorbent but also contributes to catalytic reduction of NO to N_2 in the presence of NH_3 . This result is consistent with that of the study by Wallman and Carlsson¹⁷⁾ who reported that reduction of NO_x occurred at much lower temperatures by using fire clay and bed ash containing iron oxide than by using quartz. The removal of NO increased by increasing the temperature from 573 to 773 K. Moreover, by increasing the temperature above 823 K, the concentration of NO at outlet was greater than that at inlet due to the oxidation of NH_3 to NO. The removal of NO also increased with increasing the mole ratio of NH_3/NO . However, when the mole ratio was above 1.5, the removal of NO appeared to be almost independent of the concentration of NH_3 . Although only 50% removal of NO was obtained at temperature of 773 K and NH_3/NO mole ratio of 1, the result showed that the present process was much more efficient for the removal of NO as compared to the commercially used process of Selective Non-

Fig. 5 Dependence of the Removal of NO on Mole Ratio of NH_3/NO at Inlet, Reaction Temperature and Mole Ratio of Fe/S for Iron Oxide Dust Using Silica Sand as Fluidized Medium Particle

Fig. 6 Effect of Mole Ratio of NH_3/NO on the Removal of NO for Iron Oxide Dust Using WO_3/TiO_2 Catalyst as Fluidized Medium Particle

catalytic Reduction (SNR) with ammonia, which yielded 30-50% removal of NO at much higher temperatures, 1173-1273 K, and at higher NH_3/NO mole ratios, 1.5-2³⁴⁾. Leakage of NH_3 is a serious problem in this process; the problem usually exists also in the SNR process. The use of DeNO_x catalyst as fluidized medium particle was superior in suppressing NH_3 leakage as indicated by the leakage level as low as 3 ppm in SCR processes achieved⁴⁾.

The effect of mole ratio of NH_3/NO on the removal of NO for iron oxide dust using WO_3/TiO_2 catalyst as fluidized medium particle is shown in Fig. 6. The removal of NO increased with increasing mole ratio of NH_3/NO when it

(A)

(B)

○: $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ catalyst, $\text{NH}_3/\text{NO}=1$; ◇: WO_3/TiO_2 catalyst, $\text{NH}_3/\text{NO}=1$; △: silica sand, $\text{NH}_3/\text{NO}=0$.

Fig. 7 Effects of Reaction Temperature on the Removal of SO_2 for NaHCO_3 and Na_2CO_3 Sorbents Using Three Kinds of Fluidized Medium Particles

was less than 1, and approached 100% when it was greater than 1; however, the optimal condition for the reaction is to perform at nearly one mole ratio of NH_3/NO . There was no significant effect of reaction temperature on removal of NO in the temperatures range 573-773 K. The concentration of leaked NH_3 was almost zero when the NH_3/NO ratio was less than 1.

3. 2. Experiments Using Sodium-based Sorbents

The effects of reaction temperature on the removal of SO_2 for Na_2CO_3 and NaHCO_3 sorbents using three kinds of fluidized medium particles are shown in Figs. 7(A), (B). The removal of SO_2 increased with increasing temperature for Na_2CO_3 sorbent. The removal of SO_2 for NaHCO_3 sorbent increased with increasing temperature from 373 K up to 473 K, the optimum temperature, and

Fig. 8 Effect of Reaction Temperature on the Removal of NO for NaHCO_3 Sorbent Using WO_3/TiO_2 and $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ Catalysts as Fluidized Medium Particles

above it, the removal declined. Minimum values for removal of SO_2 were found in the temperature range of 673-723 K, and above this range, the removal of SO_2 increased with increasing temperature.

Desulfurization behavior of NaHCO_3 may stem from the thermal decomposition of NaHCO_3 to porous Na_2CO_3 , CO_2 , and H_2O vapor while undergoing a simultaneous reaction with SO_2 ¹¹⁾. Although the formation of porous Na_2CO_3 was beneficial for SO_2 reaction, the evolution of CO_2 and H_2O vapor was not beneficial by prevented the SO_2 from diffusing into the interior of the particles: indicating that optimal conditions existed for the SO_2 reaction. Complete decomposition of NaHCO_3 into Na_2CO_3 at very fast rate may occur around the temperature range of 673-723 K, and a reaction similar to that of initial Na_2CO_3 then results. The removal of SO_2 for NaHCO_3 was greater than that for Na_2CO_3 below the temperature range of 673-723 K. However, above this range removal of SO_2 for NaHCO_3 sorbent is almost the same with that for Na_2CO_3 sorbent.

Removal of SO_2 is significantly greater using $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ catalyst as fluidized medium particle than that using WO_3/TiO_2 catalyst and silica sand. From 573 to 673 K, SO_2 removals of about 68-71% and 27-69% were obtained using $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ catalyst as fluidized medium particle for sorbents of NaHCO_3 and Na_2CO_3 , respectively. The vanadium oxide in the $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ catalyst promoted oxidation of SO_2 to SO_3 . Thus, the presence of $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ catalyst enhanced SO_2 removal.

Under the optimal condition of NH_3/NO mole ratio of 1, the effect of reaction temperature on the removal of NO for NaHCO_3 sorbent using WO_3/TiO_2

Fig. 9 Effects of Reaction Temperature on the Removal of SO_2 and NO for CuO Sorbent Using WO_3/TiO_2 Catalyst as Fluidized Medium Particle

TiO_2 and $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ catalysts as fluidized medium particles is shown in Fig. 8. The above catalysts were effective in the temperature ranges of 573-773 K and 473-673 K, respectively. The same result was obtained for Na_2CO_3 sorbent.

3. 3. Experiments Using Copper-based Sorbent

The effects of reaction temperature on the removal of SO_2 and NO for CuO sorbent using WO_3/TiO_2 catalyst as fluidized medium particle are shown in Fig. 9. The removal of SO_2 increased with increasing reaction temperature, and achieved 10-86% removal in the temperature range of 573-873 K. The removal of NO approached 100% in the range of 573-773 K, but decreased above 773 K.

The effects of reaction temperature on the removal of SO_2 and NO for $\text{CuO} \cdot \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ sorbent using silica sand and $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ catalyst as fluidized medium particles are shown in Figs. 10(A), (B). The level of SO_2 removal was held constant at 60% for silica sand as fluidized medium particle in the range from 573 to 723 K and for $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ catalyst in the range from 573 to 623 K. However, the SO_2 removal achieved was 80% for silica sand at 773 K and 70% for $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ at 673 K. From the data obtained when silica sand was used as fluidized medium particle, it was shown that $\text{CuO} \cdot \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ sorbent was not only capable of removing SO_2 but was also capable of reducing NO with NH_3 , and NO removal of 60-70% was achieved in the temperature range from 623 to 723 K. The optimal removal temperature was 673 K using $\text{CuO} \cdot \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ as both DeSO_x sorbent and DeNO_x catalyst. With the use of $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ catalyst as fluidized medium particle instead of silica sand, the NO removal was nearly 100% in the range from 573 to 673 K.

(A)

(B)

Fig. 10 Effects of Reaction Temperature on the Removal of SO_2 and NO for $\text{CuO} \cdot \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ Sorbent Using Silica Sand and $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ Catalyst as Fluidized Medium Particles

The effects of reaction temperature and sorbent size on the removal of SO_2 and NO for $\text{CuO} \cdot \text{V}_2\text{O}_5 \cdot \text{K}_2\text{SO}_4/\text{Al}_2\text{O}_3$ sorbent using silica sand, $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$, and WO_3/TiO_2 catalysts as fluidized medium particles are shown in Figs. 11(A), (B). Regardless of the size of sorbent particles (8 and 36 μm) and kind of fluidized medium particles, complete removal of SO_2 was achieved in the temperature range 573-873 K. The effect of particle size on the removal of SO_2 can be neglected for $\text{CuO} \cdot \text{V}_2\text{O}_5 \cdot \text{K}_2\text{SO}_4/\text{Al}_2\text{O}_3$ sorbent of sizes below 36 μm . This may be due to the action of the inert constituents contained in the sorbent such as V_2O_5 , K_2SO_4 , and Al_2O_3 that can prevent the sorbents from pore plugging.

Unlike the CuO sorbent shown in Fig. 9, which was strongly dependent on the reaction temperature for removal of SO_2 , the effect of reaction temperature on removal of SO_2 for $\text{CuO} \cdot \text{V}_2\text{O}_5 \cdot \text{K}_2\text{SO}_4/\text{Al}_2\text{O}_3$ sorbent could be neglected. This

Fig. 11 Effects of Reaction Temperature and Sorbent Size on the Removal of SO₂ and NO for CuO·V₂O₅·K₂SO₄/Al₂O₃ Sorbent Using Silica Sand, V₂O₅·WO₃/TiO₂ and WO₃/TiO₂ Catalysts as Fluidized Medium Particles

result showed that the rate of reaction of CuO·V₂O₅·K₂SO₄/Al₂O₃ and SO₂ was large enough for complete removal of SO₂ under the residence time of the sorbent in the reactor. The amount of SO₂ removed approached the stoichiometric amount for complete conversion of the copper oxide to sulfate. Only 60-80% removal of SO₂ was obtained under the same reaction conditions for CuO·V₂O₅/Al₂O₃ sorbent shown in Fig. 10(A). Thus, the CuO·V₂O₅·K₂SO₄/Al₂O₃ sorbent was more reactive than CuO·V₂O₅/Al₂O₃ sorbent for removal of SO₂.

The efficiency of NO removal decreased with increasing reaction temperature. It is shown in Fig. 11(B) that NO removal was below 37% when silica sand was used as fluidized medium particle. This result showed that activity of CuO·V₂O₅·K₂SO₄/Al₂O₃ sorbent was low in the catalytic reduction of NO. The DeNO_x catalyst, therefore,

is necessary for enhancing the efficiency of NO removal. The NO removals obtained were 76-88% and 82-94%, in the temperature range from 573 to 673 K, using V₂O₅·WO₃/TiO₂ and WO₃/TiO₂ DeNO_x catalysts as fluidized medium particles, respectively. While the addition of K₂SO₄ increased the reactivity of the sorbent for removal of SO₂, it decreased the activity of the DeNO_x catalyst for reduction of NO as compared to the sorbent of CuO·V₂O₅/Al₂O₃ that yielded 100% removal of NO under the same operating conditions. The effect of K₂SO₄ on the removal of NO was confirmed in previous studies^{35)~37)}. It was found that the activity of DeNO_x catalyst was suppressed by potassium salts, such as K₂SO₄.

From the removal of SO₂ shown in Fig. 11(A), and the removal of NO in Fig. 11(B), it was observed that simultaneous removal of over 90% of SO₂ and NO was achieved using CuO·V₂O₅·K₂SO₄/Al₂O₃ as sorbent and using WO₃/TiO₂ catalyst as fluidized medium particle under the following conditions: Cu/S mole ratio of 1, NH₃/NO mole ratio of 1, gas velocity of 0.5 m/s, static height of bed of 0.3 m, and reaction temperature range of 573-613 K.

3. 4. Analysis of Used Sorbents

The SEM photomicrographs and sulfur intensity profiles measured by scanning along the bright line for used sorbents of iron oxide dust, NaHCO₃, CuO, and CuO·V₂O₅/Al₂O₃ are shown in Figs. 12(A), (B), (C), (D), respectively. The results of Na₂CO₃ and CuO·V₂O₅·K₂SO₄/Al₂O₃²⁵⁾ sorbents were similar to those of NaHCO₃ and CuO·V₂O₅/Al₂O₃ sorbents, respectively. The samples were covered with epoxy resin, cut by microtome, and carbon evaporation was then carried out. Thus, the edge of the particle represented the outer shell of the particle, and the other section of the particle represented inside of the particle. The cross section of the sorbent can be surveyed, and the sulfur distribution from outer shell to the inside of particle can be measured. The sulfur intensity of particles was measured using an energy dispersive spectrometer along the bright horizontal line. The sulfur intensity at the section in which no particle existed along the bright horizontal line was the level of background of sulfur intensity, indicating that the sulfur content was zero.

From sulfur intensity profiles, the sulfur intensities of used sorbents of NaHCO₃, Na₂CO₃, and CuO were high at outer shell of the particles and low at inside of the particles. These sorbents reacted with SO₂ and formed a product layer of sulfate that prevented SO₂ from diffusing into the interior of the particles. Sulfur intensities of used

The length of bright line shown in left side represented 1 μm .

(A) Iron Oxide Dust

The length of bright line shown in left side represented 1 μm .

(C) CuO

The length of bright line shown in left side represented 10 μm .

(B) NaHCO_3

The length of bright line shown in left side represented 1 μm .

(D) $\text{CuO} \cdot \text{V}_2\text{O}_5 / \text{Al}_2\text{O}_3$

Fig. 12 SEM Photomicrographs and Sulfurs Intensity Profiles for Used Sorbents of Iron Oxide Dust, NaHCO_3 , CuO and $\text{CuO} \cdot \text{V}_2\text{O}_5 / \text{Al}_2\text{O}_3$

sorbents of iron oxide dust, $\text{CuO} \cdot \text{V}_2\text{O}_5 / \text{Al}_2\text{O}_3$ and $\text{CuO} \cdot \text{V}_2\text{O}_5 \cdot \text{K}_2\text{SO}_4 / \text{Al}_2\text{O}_3$ appeared, however, almost constant throughout, from outer shell to inside of the particles. The inert constituents presented in the iron oxide dust may prevent pore plugging. The copper oxide supported on alumina was sulfated uniformly and was more active than CuO. Dispersing copper oxide on alumina considerably increased the reactivity of CuO and enhanced its utilization.

4. Conclusions

A new dry process for simultaneous removal of SO_2 and NO from flue gas using a powder-particle fluidized bed was developed. The following results were obtained.

1) Iron oxide dust appeared to be a potential low-cost sorbent for removal of SO_2 and a catalyst for reduction of NO with NH_3 .

2) Sodium-based sorbents such as sodium bicarbonate and sodium carbonate were appropriate as DeSO_x sorbent with selected DeNO_x catalyst as fluidized medium particles.

3) The $\text{CuO} \cdot \text{V}_2\text{O}_5 / \text{Al}_2\text{O}_3$ sorbent showed high activity for both removal of SO_2 and reduction of NO. The $\text{CuO} \cdot \text{V}_2\text{O}_5 \cdot \text{K}_2\text{SO}_4 / \text{Al}_2\text{O}_3$ sorbent showed highest activity for removal of SO_2 , but showed relatively low activity for reduction of NO as compared with that of CuO and $\text{CuO} \cdot \text{V}_2\text{O}_5 / \text{Al}_2\text{O}_3$ sorbents. The K_2SO_4 contained in the sorbent promoted the sulfating reaction, but interfered slightly with the activity of DeNO_x catalyst for reduction of NO.

4) The iron oxide dust and supported copper oxide sorbents were sulfated uniformly. Copper oxide, sodium bicarbonate, and sodium carbonate reacted with SO_2 only in the outer shell of the particles.

5) The reaction rate of sulfation was promoted in

the presence of DeNO_x catalyst. By using DeNO_x catalyst as fluidized medium particle, a complete conversion of NO occurred at the mole ratio of NH₃ to NO of about 1 for all sorbents tested except CuO·V₂O₅·K₂SO₄/Al₂O₃ sorbent.

6) Simultaneous removal of over 90% of SO₂ and NO was achieved by combining CuO·V₂O₅·K₂SO₄/Al₂O₃ sorbent and WO₃/TiO₂ DeNO_x catalyst.

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Nomenclatures

d_p	: average particle diameter	[μm]
L_s	: static height of bed	[m]
T	: reaction temperature	[K]
U_g	: superficial gas velocity	[ms^{-1}]
U_{mf}	: minimum fluidization velocity	[ms^{-1}]
U_t	: terminal velocity of a single particle	[ms^{-1}]
Y_{NO}	: efficiency of NO removal	[—]
Y_{SO_2}	: efficiency of SO ₂ removal	[—]
ρ_p	: particle density	[kgm^{-3}]

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要 旨

粉粒流動層を用いた新規な乾式同時排煙脱硫脱硝プロセス

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粉粒流動層を用いて乾式排煙脱硫と NH_3 触媒還元脱硝法を組み合わせ、新しい乾式同時排煙脱硫脱硝プロセスの開発を行った。このプロセスでは、粉粒流動層反応器を用いて、微粒子脱硫剤により SO_x を除去し、粗粒子脱硝触媒を用い、 NH_3 還元法により NO_x を N_2 に還元した。粉粒流動層は内径 0.053 m, 分散板からの高さ 1.0 m のステンレス管である。本研究では、脱硫剤として酸化鉄ダスト（製鉄の副生成品）、ナトリウムベースの脱硫剤（炭酸水素ナトリウムと炭酸ナトリウム）、銅ベースの脱硫剤（ CuO と $\text{CuO} \cdot \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ と $\text{CuO} \cdot \text{V}_2\text{O}_5 \cdot \text{K}_2\text{SO}_4/\text{Al}_2\text{O}_3$ ）を用いて、三種類の微粒子脱硫剤

を評価した。粗粒子媒体粒子として不活性のシリカサンドと脱硝触媒（ WO_3/TiO_2 と $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$ ）を使用した。脱硫率と脱硝率に及ぼす操作条件および脱硫剤と脱硝触媒の影響を調べた。酸化鉄ダストは安価な脱硫剤と脱硝触媒として利用できる可能性を示した。ナトリウムベースの脱硫剤と銅ベースの脱硫剤はかなり高い脱硫活性を持っていた。粉粒流動層反応器を用いて、高効率に乾式同時排煙脱硫脱硝が行えることが分かった。本プロセスでは、適当な微粒子脱硫剤と粗粒子脱硝触媒を組み合わせ、90% 以上の脱硫率と脱硝率が得られた。

Keywords

Desulfurization, Denitrification, Fluidization, Powder, DeSO_x sorbent, DeNO_x catalyst