[Note]

Selection of SO₂ Sorbents for Simultaneous Removal of SO₂ and NO in the Powder-particle Fluidized Bed

Shiqiu GAO, Hironori SUZUKI, Nobuyoshi NAKAGAWA,
Dingrong BAI, and Kunio KATO*

Dept. of Biological & Chemical Engineering, Gunma University, Kiryu, Gunma 376

(Received June 2, 1995)

Several kinds of SO₂ sorbents or catalysts have been evaluated in a process for simultaneous removal of SO₂ and NO from flue gas using a powder-particle fluidized bed. In the process, SO₂ was captured by fine sorbents and NO was reduced with NH₃ catalyzed by a coarse DeNO_x catalyst or by both coarse and fine catalysts. Experiments were carried out in a laboratory scale powder-particle fluidized bed reactor of 1.0 m in length above the distributor, 0.053 m inside diameter, in a temperature range from 373 to 873 K. Several kinds of fine sorbents including sodium aluminate, manganese oxide, copper oxide, sodium bicarbonate, and copper oxide supported on alumina with addition of vanadium oxide (CuO·V₂O₅/Al₂O₃) were tested in this study. The coarse particles of inactive silica sand and active DeNO_x catalysts of WO₃/TiO₂ and V₂O₅·WO₃/TiO₂ were used as fluidized medium particles. The SO₂ and NO removal efficiencies by using fine sorbents and coarse catalysts were investigated under the following conditions: static bed height of 0.3 m, superficial gas velocity of 0.5 m/s, and inlet concentrations of SO₂ and NO of 500 ppm. Experimental results suggested that CuO·V₂O₅/Al₂O₃, sodium aluminate, and sodium bicarbonate were suitable as SO₂ sorbents. In a typical temperature range (573–673 K) of flue gas, the SO₂ removal achieved was 60–70% for CuO·V₂O₅/Al₂O₃ at Cu/S mole ratio of 1, about 55% and 40–65% at Na/S mole ratio of 3 for sodium aluminate and sodium bicarbonate. The NO removal approached nearly to 100% at NH₃/NO mole ratio of 1 in the active temperature range of the DeNO_x catalyst.

1. Introduction

Sulfur oxides (SO_x) and nitrogen oxides (NO_x) emitted by combustion of fossil fuels cause serious atmospheric pollution. Thus, it is very important to remove such harmful components in the flue gas from combustion processes.

In authors' previous study¹⁾, a new process of applying a powder-particle fluidized bed (PPFB) to the simultaneous removal of SO₂ and NO was proposed. The process is a combination of the selective catalytic reduction (SCR) of NO_x and dry flue gas desulfurization (FGD) processes and is featured by using both fine SO₂ sorbent and coarse DeNO_x catalyst. Iron oxide dust, a byproduct of steel plants, was tested as SO₂ sorbent in the process in order to reduce the cost of sorbent. Its low SO₂ removal efficiency was a problem which could, however, be solved to meet the serious environment standards.

The traditional SCR technology uses NH₃ over metal oxide catalysts at 623–723 K to reduce NO_x to

N₂. The main component of NO_x is NO, which can react selectively with NH₃ in the presence of oxygen:

Besides the main reaction, catalytic oxidation of SO₂ to SO₃ might occur as a side reaction²⁾.

Because the SCR process is well developed, the key to success in developing the dry PPFB process is to find an appropriate sorbent for SO₂ removal. In the dry FGD process, some sorbents such as alkalinized alumina^{3),4)} (Na₂O·Al₂O₃, an active form of NaAlO₂), active manganese oxide⁵⁾ (MnO_x·*n*H₂O, *x*=1.5–1.8, *n*=0.3–1.0), copper oxide supported on alumina⁶⁾ (CuO/Al₂O₃) and sodium bicarbonate^{7),8)} (NaHCO₃) can be used for capturing the SO₂ in the temperature range of SCR. The copper oxide supported on alumina is known as both SO_x sorbent and NO_x reduction catalyst for simultaneous removal of SO_x and NO_x^{9),10)}. When sulfur dioxide reacts with the above sorbents in the presence of oxygen at temperatures below the decomposition temperature of the sulfate, the principal products are sulfates. The overall

* To whom correspondence should be addressed.

reaction for the sorbents can be described as follows.

The effort for simultaneous removal of SO_x and NO_x that combined dry FGD and SCR processes using these sorbents in a single unit may offer the possibilities for reducing the cost of environmental control. The objective of this work is to evaluate the possibilities using the above sorbents in a PPFB and to select a proper sorbent in the active temperature range of DeNO_x catalyst. The sorbent should have the ability to capture the SO_2 at sufficient rate and with sufficient adsorption capacity in the typical temperature range for SCR process.

2. Experimental

A schematic diagram of the experimental apparatus is shown in **Fig. 1**. Details regarding the experimental apparatus and procedures may be found elsewhere¹⁾; however, a brief description is presented here. The system consisted essentially of the following: a micro-feeder of fine sorbent, a PPFB reactor, a bag filter to collect the spent sorbent, and monitoring equipment for measuring concentrations of SO_2 and NO . The PPFB reactor was made of a stainless steel tube of 1.0 m in length above the distributor, 0.053 m inside diameter. The reactor was first loaded with coarse particles to a static bed height of 0.3 m. The air mixed with SO_2 and NO was fed to the bottom of the bed to fluidize the coarse particles. When the system was in a steady state at desired

Fig. 1 Schematic Diagram of Experimental Apparatus

operating conditions, a continuous feed of fine sorbent was introduced from the micro-feeder into the bottom of the fluidized bed of the coarse particles to initiate the SO_2 removal reaction. When ammonia was fed directly into the bottom of the reactor, catalytic reduction of NO to N_2 occurred.

Commercially available sodium aluminate (NaAlO_2), manganese oxide (MnO_2), copper oxide (CuO), and sodium bicarbonate (NaHCO_3) were used as SO_2 sorbents. The copper oxide supported on alumina with addition of vanadium oxide ($\text{CuO} \cdot \text{V}_2\text{O}_5 / \text{Al}_2\text{O}_3$), supplied by JGC Corporation, was also tested as SO_2 sorbent and DeNO_x catalyst to improve the SO_2 removal efficiency at low temperatures. The properties of the fine SO_2 sorbents are shown in **Table 1**.

Three kinds of coarse particles, inactive silica sand and active DeNO_x catalysts of $\text{WO}_3 / \text{TiO}_2$ and $\text{V}_2\text{O}_5 \cdot \text{WO}_3 / \text{TiO}_2$, were used as coarse fluidized medium particles. Their properties are shown in **Table 2**. Silica sand was used as inactive fluidized medium particle for separating the ef-

Table 1 Properties of Fine SO_2 Sorbents

Particles	Average particle diameter d_p [μm]	Particle density ρ_p [kg/m^3]	Bulk density ρ_b [kg/m^3]	Minimum fluidization velocity U_{mf} [10^{-3} m/s]	Terminal velocity U_t [m/s]
NaAlO_2	41	3080	565	3.10	0.16
MnO_2	43	5030	1780	5.56	0.28
CuO	10	6400	1550	0.38	0.019
NaHCO_3	45	2210	1160	2.67	0.13
$\text{CuO} \cdot \text{V}_2\text{O}_5 / \text{Al}_2\text{O}_3$	25	1180	650	0.44	0.022

Table 2 Properties of Coarse Fluidized Medium Particles

Particles	d_p [μm]	ρ_p [kg/m^3]	ρ_b [kg/m^3]	U_{mf} [m/s]	U_t [m/s]
Silica sand	393	2600	1340	0.24	3.18
WO_3/TiO_2	530	1690	930	0.28	3.22
$\text{V}_2\text{O}_5\cdot\text{WO}_3/\text{TiO}_2$	470	1780	980	0.23	2.95

fect of DeNO_x catalyst on SO_2 removal. The commercially available DeNO_x catalysts of WO_3/TiO_2 and $\text{V}_2\text{O}_5\cdot\text{WO}_3/\text{TiO}_2$ were from the Catalysts & Chemicals Ind. Co., Ltd. The active temperature ranges for catalytic reduction of NO were from 673 to 803 K for WO_3/TiO_2 catalyst and from 573 to 643 K for $\text{V}_2\text{O}_5\cdot\text{WO}_3/\text{TiO}_2$ catalyst, respectively.

All experiments were carried out at different temperatures under constant conditions, *i.e.*, static bed height of 0.3 m, superficial gas velocity of 0.5 m/s, inlet concentrations of SO_2 and NO of 500 ppm.

3. Results and Discussion

3.1. Desulfurization in PPFB

The effects of reaction temperature on SO_2 removal for NaHCO_3 , NaAlO_2 , CuO , and MnO_2 sorbents using silica sand and WO_3/TiO_2 catalyst as fluidized medium particles are shown in Fig. 2 (A), (B). The SO_2 removal increased with increasing reaction temperature for NaAlO_2 , CuO , and MnO_2 sorbents. The effect of reaction temperature on SO_2 removal for NaHCO_3 as SO_2 sorbent showed a different behavior compared to that of NaAlO_2 , CuO , and MnO_2 , as shown in Fig. 2 (A). The SO_2 removal increased with increasing reaction temperature from 373 K up to an optimum temperature of 473 K, then declined above it. The minimum SO_2 removal was found to be around 673–773 K and above this temperature range, the SO_2 removal increased with increasing reaction temperature.

The desulfurization behavior of NaHCO_3 may stem from the thermal decomposition of NaHCO_3 into porous Na_2CO_3 , CO_2 , and H_2O vapor while undergoing a simultaneous reaction with SO_2 ⁸⁾. The formation of porous Na_2CO_3 was beneficial for SO_2 reaction; on the contrary, the evolution of CO_2 and H_2O vapor prevented the SO_2 from diffusing into the interior of the particles; thus, optimum conditions existed for the SO_2 reaction.

It is apparent from the data in Fig. 2 that SO_2 removal is significantly greater using WO_3/TiO_2 as fluidized medium particle than silica sand without introducing NH_3 . This has been explained by the fact that DeNO_x catalyst acted as a catalyst both for reduction of NO_x by NH_3 and oxidation of SO_2 to SO_3 in the presence of oxy-

$\triangle, \diamond, \circ$: NaHCO_3 as sorbent
 $\blacktriangle, \blacklozenge, \bullet$: NaAlO_2 as sorbent

$\triangle, \diamond, \circ$: CuO as sorbent
 $\blacktriangle, \blacklozenge, \bullet$: MnO_2 as sorbent

$\triangle, \blacktriangle$: Silica sand, $\text{NH}_3/\text{NO}=0$. $\diamond, \blacklozenge$: WO_3/TiO_2 catalyst, $\text{NH}_3/\text{NO}=0$. $\circ, \bullet$: WO_3/TiO_2 catalyst, $\text{NH}_3/\text{NO}=1$.

Fig. 2 Effects of Reaction Temperature on SO_2 Removal for NaHCO_3 , NaAlO_2 , CuO , and MnO_2 Sorbents Using Silica Sand and WO_3/TiO_2 Catalyst as Fluidized Medium Particles

gen that enhanced the reaction of SO_3 with the sorbent^{1),2),11)}.

When ammonia was fed to the reactor, SO_2 adsorption on the sorbent and the selective catalytic reduction of NO were carried out simultaneously. Fig. 2 (A) reveals that concentration of NH_3 has almost no effect on the SO_2 removal for NaAlO_2 . This is consistent with the finding of a previous study using iron oxide as sorbent¹⁾. However, in some cases, the SO_2 removal decreased in the presence of NH_3 for NaHCO_3 , CuO , and MnO_2 . Reasons for such different effects of NH_3 on SO_2 removal for different sorbents have not yet been made clear. The SO_2 removal achieved was 56-73% for NaAlO_2 , 40-50% for NaHCO_3 , 26-65% for CuO , and 23-43% for MnO_2 between the temperatures of 673 and 803 K. In a typical temperature range of flue gas from 573 to 673 K, SO_2 removals of about 55% and 40-65% were obtained for NaAlO_2 and NaHCO_3 , respectively. Therefore, NaAlO_2 and NaHCO_3 sorbents can be considered appropriate for simultaneous removal of SO_2 and NO .

In order to improve the SO_2 removal efficiency in the temperature range from 573 to 673 K, highly porous and active $\text{CuO}\cdot\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ was used as fine SO_2 sorbent. The addition of vanadium oxide (V_2O_5) was for promoting oxidation of SO_2 to SO_3 and further for accelerating the rate of sulfation reaction. The $\text{V}_2\text{O}_5\cdot\text{WO}_3/\text{TiO}_2$ De NO_x catalyst, more active in a lower temperature range from 573 to 643 K, was used as fluidized medium particle for this purpose.

The effect of reaction temperature on SO_2 removal 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 is shown in Fig. 3. The level of SO_2 removal was held constant at 60% for silica sand as fluidized medium particle from 573 to 723 K and for $\text{V}_2\text{O}_5\cdot\text{WO}_3/\text{TiO}_2$ catalyst from 573 to 623 K. However, the SO_2 removals achieved were 80% and 70% for silica sand at 773 K and $\text{V}_2\text{O}_5\cdot\text{WO}_3/\text{TiO}_2$ at 673 K, respectively.

3. 2. Denitrification in PPFB

The relationships between NO removal, NH_3/NO mole ratio, and reaction temperature using NaAlO_2 as sorbent and WO_3/TiO_2 catalyst as fluidized medium particle are shown in Fig. 4. In the active temperature range of the catalyst, the NO removal was almost independent of temperature. The NO removal increased with increasing NH_3/NO mole ratio when it was less than 1 and approached toward 100% when it was greater than 1. The concentration of unreacted NH_3 was almost zero when the NH_3/NO mole ratio was less than 1. Similar results were also obtained using

Fig. 3 Effect of Reaction Temperature on SO_2 Removal 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

Fig. 4 Relationships between NO Removal, NH_3/NO Mole Ratio and Reaction Temperature Using NaAlO_2 as Sorbent and WO_3/TiO_2 Catalyst as Fluidized Medium Particle

NaHCO_3 , CuO , and MnO_2 as sorbents and WO_3/TiO_2 catalyst as fluidized medium particle.

At the optimum condition of NH_3/NO mole ratio of 1, the effect of reaction temperature on the NO removal 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 is shown in Fig. 5. It is shown from the data, using silica sand as fluidized medium particle, that the $\text{CuO}\cdot\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ sorbent not only has the activity for SO_2 removal as shown in Fig. 3 but also has the activity for reduction of NO with NH_3 . The NO removal of 60-70% was obtained in the temperature range from 623 to 723 K. The optimum temperature

Fig. 5 Effect of Reaction Temperature on NO Removal 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

was 673 K using $\text{CuO} \cdot \text{V}_2\text{O}_5 / \text{Al}_2\text{O}_3$ as both SO_2 sorbent and DeNO_x catalyst. With the use of the $\text{V}_2\text{O}_5 \cdot \text{WO}_3 / \text{TiO}_2$ DeNO_x catalyst as fluidized medium particle instead of silica sand, the NO removal approached nearly to 100% in the temperature range from 573 to 673 K.

4. Conclusions

1) Sodium aluminate and sodium bicarbonate were appropriate as DeSO_x sorbents; however, manganese oxide and copper oxide might not be so for simultaneous removal of SO_2 and NO in the powder-particle fluidized bed. In the typical flue

gas temperature range from 573 to 673 K, the SO_2 removals achieved were about 55% and 40-65% at Na/S mole ratio of 3 for sodium aluminate and sodium bicarbonate, respectively.

2) The copper oxide supported on alumina with addition of vanadium oxide resulted in high activity for both SO_2 removal and NO reduction. The SO_2 and NO removal of 60-70% was obtained at the Cu/S mole ratio of 1 in the temperature range from 573 to 673 K.

3) A complete conversion of NO was found to occur at the mole ratio of NH_3 to NO of about 1 using the DeNO_x catalyst as fluidized medium particle for all sorbents tested.

References

- 1) Gao, S., Suzuki, H., Nakagawa, N., Bai, D., Kato, K., *Sekiyu Gakkaishi*, **38**, (6), 399 (1995).
- 2) Bosch, H., Janssen, F. J., *Catal. Today*, **2**, 369 (1988).
- 3) Bienstock, D., Field, J. H., Myers, J. G., *J. Eng. Power*, **86**, (3), 353 (1964).
- 4) Town, J. W., Paige, J. I., Russell, J. H., *Chem. Eng. Prog. Symp. Ser.*, **66**, (105), 260 (1970).
- 5) Atsukawa, M., Nishimoto, S., Matsumoto, K., *Technical Report of Mitsubishi Heavy Industries*, **3**, (4), 363 (1966).
- 6) Dautzenberg, F. M., Nader, J. E., van Ginneken, A. J. J., *Chem. Eng. Prog.*, **67**, (8), 86 (1971).
- 7) Yeh, J. T., Demski, R. J., Joubert, J. I., *ACS Symp. Ser.*, **189**, 349 (1982).
- 8) Keener, T. C., Davis, W. T., *JAPCA*, **34**, (6), 651 (1984).
- 9) Yeh, J. T., Demski, R. J., Strakey, J. P., Joubert, J. I., *Environ. Prog.*, **4**, (4), 223 (1985).
- 10) Yeh, J. T., Drummond, C. J., Joubert, J. I., *Environ. Prog.*, **6**, (2), 44 (1987).
- 11) Kocacfe, D., Karman, D., Steward, F. R., *Can. J. Chem. Eng.*, **63**, 971 (1985).

要 旨

粉粒流動層を用いた同時脱硫脱硝における脱硫剤の選択

高 士秋, 鈴木 宏典, 中川 紳好, 白 丁栄, 加藤 邦夫

群馬大学工学部生物化学工学科, 376 群馬県桐生市天神町 1-5-1

粉粒流動層内で排煙ガスより SO_2 と NO を同時に除去するプロセスを用い, 何種類かの脱硫剤および触媒の特性を調べた。このプロセスでは微粒子脱硫剤で脱硫を行い, 粗粒子脱硝触媒のみ, あるいは微粒子と粗粒子の両方の触媒を用いて, アンモニア接触還元法により NO を N_2 に還元する。実験は分散板からの高さ 1.0 m, 内径 0.053 m の実験室規模の粉粒流動層反応器を用い 373~873 K の温度範囲で行った。この研究では微粒子脱硫剤として, アルミン酸ナトリウム, 酸化マンガン, 酸化銅, 炭酸水素ナトリウム, 酸化バナジウムを添加したアルミナに担持した酸化銅 ($\text{CuO} \cdot \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$) を使用した。そして粗粒子流動化媒体粒子として不活性のシリカサンドと二種類の活性の脱硝触媒 (WO_3/TiO_2 と $\text{V}_2\text{O}_5 \cdot \text{WO}_3/\text{TiO}_2$) を使用

した。微粒子脱硫剤, 粗粒子脱硝触媒を使い, 脱硫, 脱硝率を静止層高 0.3 m, 空塔基準ガス速度 0.5 m/s, 入口 SO_2 および NO 濃度ともに 500 ppm という条件で調べた。このプロセスでは, $\text{CuO} \cdot \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ とアルミン酸ナトリウムと炭酸水素ナトリウムが脱硫剤に適するということを示した。排煙ガスの典型的な温度範囲 (573~673 K) 内で $\text{CuO} \cdot \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ を脱硫剤に使った時, Cu/S のモル比 1 で 60~70%, アルミン酸ナトリウムと炭酸水素ナトリウムを使った時, Na/S のモル比 3 でそれぞれ約 55% と 40~65% の脱硫率が得られた。脱硝触媒の活性温度範囲で NH_3/NO のモル比 1 で約 100% の脱硝率が得られた。

Keywords

Environment, Desulfurization, Denitrification, SO_x sorbent, Powder, Fluidized bed