

Simultaneous Reduction of SO_x and NO_x in Manganese Oxides Particle Bed

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The present study is concerned with simultaneous reduction of SO_x and NO_x for dry gas cleaning of exhaust gas. Manganese oxides has a possibility of a reducing agent for De-SO_x and De-NO_x reactions. The simultaneous De-SO_x/NO_x experiments were conducted under common operation conditions.

From simultaneous De-SO_x/NO_x experiments, it was found that manganese oxides had the dual functions of De-SO_x and De-NO_x. The reducing efficiencies of simultaneous De-SO_x/NO_x were almost equal to those of individual De-SO_x and De-NO_x operations. Under high temperature region (573-673K), the extent of SO₂ removal efficiency for simultaneous De-SO_x/NO_x operations was higher than that obtained from the individual De-SO_x operation. This high De-SO_x effect might be attributed to the existence of water vapor which was produced by the reaction between O₂ and NH₃ which were injected for selective catalytic reduction of NO_x.

The emission level of NO_x was kept lower under the simultaneous De-SO_x/NO_x operations, even when the O₂ concentration was as high as that of the case where the De-NO_x experiment was individually conducted.

key words: simultaneous De-SO_x/NO_x, manganese oxides, activated manganese oxide, selective catalytic reduction

1. INTRODUCTION

The emission of sulfur oxides (SO_x) and nitrogen oxides (NO_x) through the combustion of fossil fuels in combustors and furnaces are related to the cause of environmental disasters such as acid rain and photochemical smog. In order to remove these acid gases, many gas cleaning technologies have been developed and carried out. Although these endeavors have resulted in the present low emission level, it is worthwhile to achieve zero emission process in order to protect the environment for future generation.

At present, De-SO_x and De-NO_x operations for exhaust gas have been carried out separately. SO_x is generally removed by injecting CaCO₃ into the combustor or ventilating the exhaust gas through an alkaline slurry. On the other hand, NO_x is usually removed by selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) with appropriate reducing agents. However, advanced studies for development of much effective and advantageous De-SO_x/NO_x process have been conducted. In recent years, adsorption and catalytic reduction by activated carbon, electron beam flue gas treatment [1] and combination of sorbent injection and selective non-catalytic reduction [2] have been developed and used experimentally as simultaneous De-SO_x/NO_x processes.

This present study is concerned with the applicability of simultaneous reduction of SO_x and NO_x by using manganese oxides. According to various reports, manganese oxides react with SO₂ in the exhaust gas to form manganese sulfate [3-5]. It was found that De-

SO_x capacity of manganese oxides enhanced under the presence of water vapor. On the other hand, it is well known that some metal oxides can work as catalysts of selective catalytic reduction (De-NO_x operations). Previous paper reported that selective catalytic reduction with reducing agent CH₃OH (by using alumina as a catalyst) has NO_x conversion under 673K and CH₃OH/NO_x mole ratio = 2[6]. For simultaneous De-SO_x/NO_x operations, several metal oxides supported on silica or alumina are used for gas cleaning. As a one of recent researches, copper oxide on silica was investigated the possibility of a reducing agents for simultaneous De-SO_x/NO_x operations[7],[8]. From these reports, copper oxide for SO_x removal can be recycled by the regeneration process, but De-NO_x reactivity of CuSO₄, produced by the desulfurization, became lower, compared to that of V₂O₅.

In this research, we evaluated the De-SO_x capacity and De-NO_x reactivity of two manganese samples (Manganese Type I & II) and focused on the effect of temperature and O₂ concentration for Manganese Type I on simultaneous De-SO_x/NO_x.

2. EXPERIMENTAL SECTIONS

2.1 Reaction

In the process of simultaneous De-SO_x/NO_x by using manganese oxides, the absorption of sulfur dioxide by MnO₂ can be described by following stoichiometric equation.

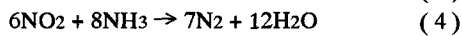
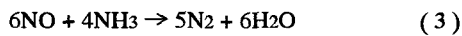


We used this equation to calculate De-SOx capacity, the conversion of MnO₂ to MnSO₄, X_{De-SOx} :

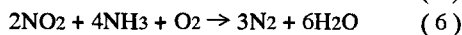
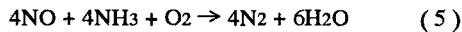
$$X_{De-SOx} [\%] = \frac{\frac{\Delta W}{W_0}}{w_{MnO_2} \times \left(\frac{M_{MnSO_4} - M_{MnO_2}}{M_{MnO_2}} \right)} \times 100 \quad (2)$$

On the other hand, the selective catalytic reduction can transform NOx to N₂ and H₂O by using reducing agents. As for this NOx reduction processes, in the presence of O₂, the reaction equations of NOx reducing will be different from those in the absence of O₂.

(I) In the absence of O₂



(II) In the presence of O₂



For evaluating De-NOx reactivity, we defined NOx removal efficiency.

$$De-NOx [\%] = \frac{[C]_{initial} - [C]_{final}}{[C]_{initial}} \times 100 \quad (7)$$

2.2 Experiments

Figure 1 shows a pyrex tubular flow reactor with an electric furnace for simultaneous De-SOx/NOx experiments. A distributor plate is located above the preheating zone at 900 mm height in the reactor for setting the sample in the reactor. After raising the temperature of the apparatus to a desired value, the simulated gas mixture with total flow rate 6.6 cm³/sec was introduced into the reactor tube from the bottom. Then the experiment was started by setting the sample in the reactor.

The composition of the mixing simulated gas was controlled by calibrated flow meters. The concentrations of SOx and NOx in the outlet gas were measured by ultra-red spectroscopy SOx meter and chemiluminescence NOx meter.

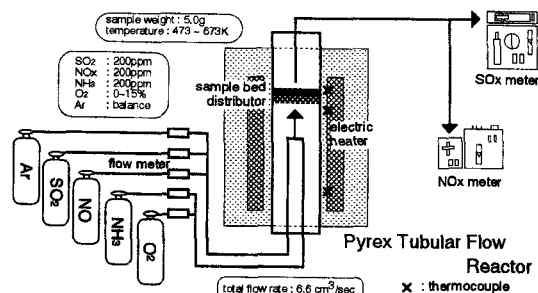


Fig.1 Schematic drawing of experimental apparatus

2.3 Samples

The chemical compositions and surface area of manganese samples that we used in these experiments are described in Table I. These manganese samples are ores that were produced at different mines. We crushed and screened these manganese ores, and prepared them to adjust the particles size with 1 mm diameter in the present experiments.

Table I Chemical compositions & surface area of manganese samples

	MnO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	SiO ₂	Bond Water	Surface Area
Manganese Type I	65.9	7.76	2.73	1.82	1.69	7.00	18.83
Manganese Type II	69.0	0.01	0.22	13.34	6.07	2.92	5.83

diameter of particles : 1 mm [wt %] [m²/g]

3. RESULTS AND DISCUSSION

3.1 De-SOx capacity and De-NOx reactivity of two manganese samples

Figure 2 shows the outlet SO₂/NOx concentration in simultaneous De-SOx/NOx experiments by using two manganese samples. The experiments were conducted at 573K with gas mixture containing 200 ppm SO₂, 200 ppm NOx, 200 ppm NH₃, 5% O₂ and Ar balance. We found that the outlet SO₂ concentration dropped

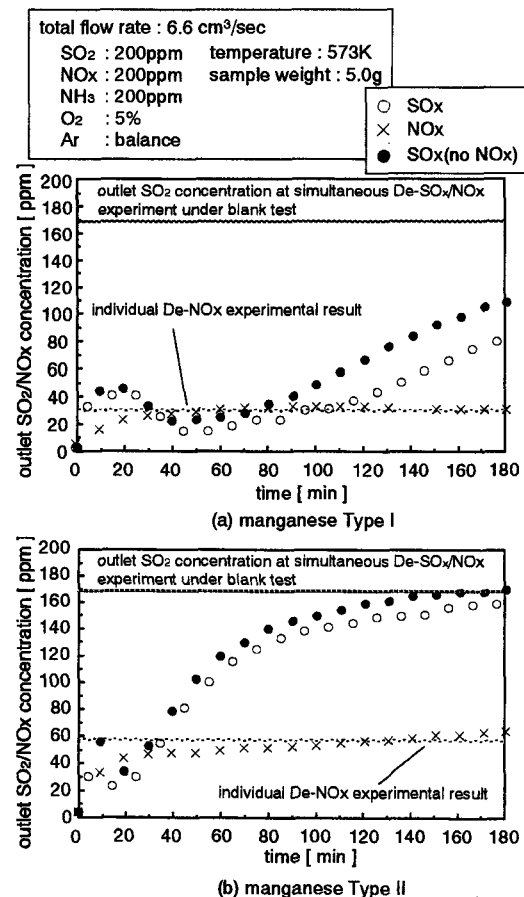


Fig.2 Time vs. outlet SO₂/NOx concentration (temp. : 573K ; O₂ concentration : 5% ; Manganese Type I (a) & Type II (b))

from 200 ppm to about 170 ppm even when the reactor was not charged with manganese sample. This may be attributed to the formation of sulfur based acids which might be produced by the reaction between SO₂ and H₂O derived from NH₃ oxidation. It was seen from Figure 2 that manganese oxides had the dual functions of SO₂ and NO_x removal from the simulated gas. Moreover, De-SO_x capacity and De-NO_x reactivity became almost equal to that of individual De-SO_x or De-NO_x experiments.

In desulfurization period, the outlet SO₂ concentrations increased as time passed for both two manganese samples. However, the outlet concentration of NO_x was not so much changed during experiments. One of the reasons why the above phenomenon took place is that iron oxides in the manganese samples might work as a catalyst for selective catalytic reduction with NH₃.

It was confirmed by SEM/EDS analysis that sulfur molecules were trapped onto manganese molecules for both two manganese samples employed. The sulfur was not observed on iron molecule. As for two manganese samples, it was indicated from Figure 2 that Manganese Type I had greater De-SO_x capacity and De-NO_x reactivity, compared with Manganese Type II. This result is explained by a larger surface area of Type I. The surface area of Manganese Type I is more than three times larger than that of Manganese Type II.

3.2 De-SO_x capacity

As for De-SO_x capacity in simultaneous De-SO_x/NO_x experiments, the effect of temperature, 473, 573, 673K is shown in Figure 3. In this figure, the results of individual De-SO_x experiments are described to compare with other experimental results. It was observed that the outlet SO₂ concentrations are almost same value at 473 and 673 K. On the contrary, we found the great difference of outlet SO₂ concentration

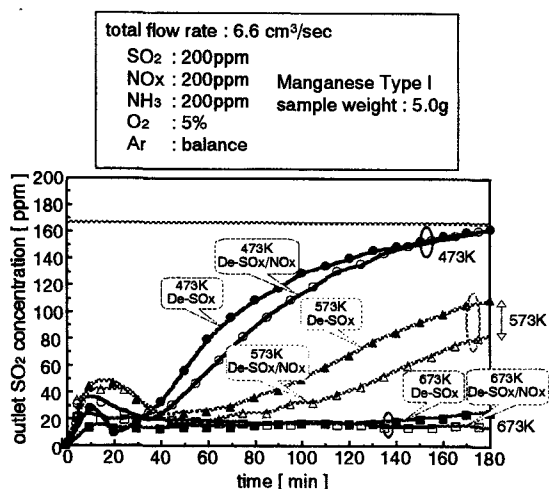
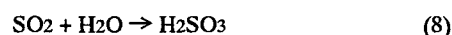


Fig.3 Time vs.outlet SO₂ concentration
(temp. : 473-673K ; O₂ concentration : 5% ;
Manganese Type I)

on 573 K. The obtained value of simultaneous De-SO_x/NO_x experiment was much better than that of individual De-SO_x experiment.

To explain the above results shown in Figure 3, we employed thermogravimetric analyzer to measure the weight change in both dry and wet De-SO_x experiments. Figure 4 shows the influence of temperature on the conversion attained at 35 min for both dry and wet De-SO_x experiments. In the presence of H₂O, the reaction between MnO₂ and SO₂ can be described as follows :



In the absence of H₂O, the absorption of SO₂ by MnO₂ occur as Equation (1). Then, the final product obtained through both reaction paths is MnSO₄ in these experiments. To evaluate SO_x absorption capacity, we used equation (2) to calculate the conversion MnO₂ to MnSO₄. It was seen that the conversion in the presence of water vapor is better than that in the absence of water vapor at all temperatures. This enhancement in reactivity of MnO₂ toward SO₂ under the presence of water vapor is considered to be affected by the formation of sulfur based acids. In simultaneous De-SO_x/NO_x experiments, water vapor was produced from the oxidation of NH₃ as a reducing agent of selective catalytic reduction. The presence of water vapor enhanced De-SO_x capacity of manganese oxides in simultaneous De-SO_x/NO_x experiments.

3.3 De-NO_x reactivity

Figure 5 shows the effect of temperature on De-NO_x reactivity of Manganese Type I under O₂ concentration 5 or 15%. It was seen that the difference of De-NO_x reactivities on both individual De-NO_x and simultaneous De-SO_x/NO_x experiments is not clearly at lower temperature. On the contrary, at higher temperature, De-NO_x reactivity on simultaneous De-

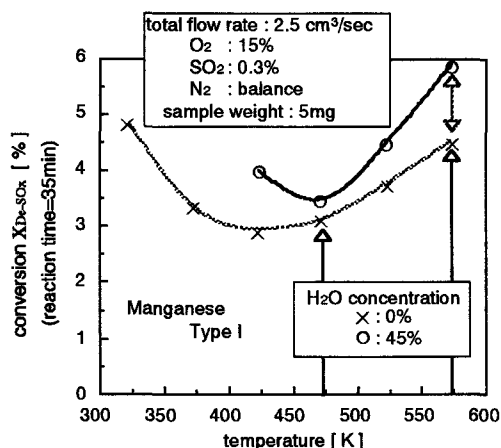


Fig.4 Effect of water vapor on MnO₂ conversion
into MnSO₄ after 35min reaction
(tested by Thermogravimetric Analyzer)

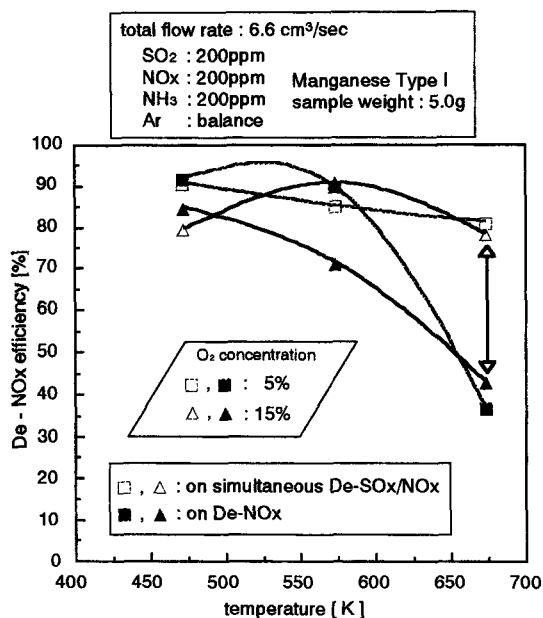


Fig.5 Effect of temperature on De-NOx reactivity of Manganese Type I

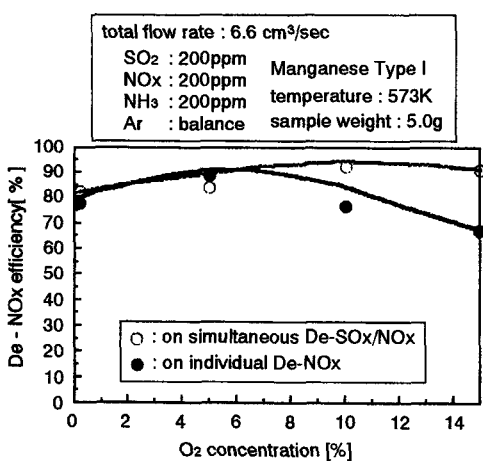


Fig.6 Effect of O₂ concentration on De-NOx reactivity of Manganese Type I

SOx/NOx experiments was over two times that on individual De-NOx experiments. This phenomenon that De-NOx reactivity on simultaneous De-SOx/NOx experiment is higher than that on individual De-NOx experiment was illustrated in previous paper [9]. The same trend was observed from the results with the O₂ concentration of 5 and 15%.

Figure 6 shows the effect of O₂ concentration De-NOx reactivity at simultaneous De-SOx/NOx experiments. From this figure, we found that De-NOx reactivity in simultaneous De-SOx/NOx experiments was enhanced, compared with the results of individual De-NOx experiments at higher O₂ concentration. The maximum NOx removal efficiency was observed at about 7% O₂ on individual De-NOx experiments. On the other hand, in simultaneous De-SOx/NOx experiments, the maximum efficiency became over 90% at about 10% O₂.

4. CONCLUSION

Based on De-SOx/NOx experimental results, it can be summarized as :

Simultaneous De-SOx/NOx experiments indicated that manganese oxides has the dual functions of removing SOx and NOx with values almost equal to that of the individual De-SOx and De-NOx processes.

As for De-SOx capacity, it was cleared that the MnO₂ conversion to MnSO₄ will be enhanced in the presence of water vapor, which was produced by the oxidation of NH₃. As a result, the outlet SO₂ concentrations in simultaneous De-SOx/NOx experiments were lower than that in individual De-SOx experiments.

On the other hand, MnO₂ has equal or greater activity, compared with the obtained results from individual De-NOx experiments. Especially, it was observed that at higher temperature and O₂ concentration De-NOx reactivity is greater enhanced.

5. NOMENCLATURE

- ΔW[g]: weight gain of the sample upon sulfurization
 W₀[g]: initial weight of sample
 W_{MnO₂} [-]: weight fraction of manganese oxide in sample
 M_{MnO₂} [-]: molecular weight of MnO₂
 M_{MnSO₄} [-]: molecular weight of MnSO₄
 [C]_{initial} [ppm]: initial concentration of NOx
 [C]_{final} [ppm]: final concentration of NOx

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