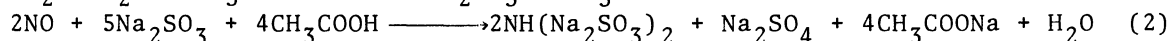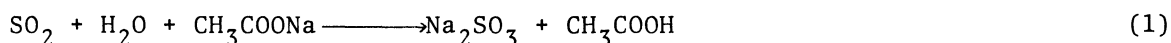# THE DEVELOPMENT OF CATALYSTS FOR SIMULTANEOUS CONTROL OF NO_x AND SO_x IN FLUE GASES

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A technique to remove simultaneously NO_x and SO_x from flue gases of stationary sources was investigated based on the principle that NO_x could be reduced by NH_3 over a catalyst while SO_x removed by forming the sulfate. Of all the oxides employed as catalysts, Mn_2O_3 was proved to be effective for the removal of SO_x. The catalytic activity of Mn_2O_3 for the NO_x reduction was improved by addition of Co_3O_4. The way of preparing the mixed catalyst in the optimum ratio was developed for the simultaneous removal of NO_x and SO_x.

The stack gas cleaning techniques for removal of both NO_x and SO_x have been in progress with wet methods, which have an advantage over dry methods that the dust components in the stack gas may be removed in the same process.

The principle of the removal of NO_x and SO_x by a wet technique would be expressed, for example, in the following equations:

$$SO_2 + H_2O + CH_3COONa \longrightarrow Na_2SO_3 + CH_3COOH \qquad (1)$$

$$2NO + 5Na_2SO_3 + 4CH_3COOH \longrightarrow 2NH(Na_2SO_3)_2 + Na_2SO_4 + 4CH_3COONa + H_2O \qquad (2)$$

In these equations, it is found that NO_x could be reduced by SO_x which is not an unusual component in a flue gas and is absorbed into the solution. Therefore, SO_x is an inevitable constituent in the wet technique for the simultaneous abatement of SO_x and NO_x. According to the mechanism described above, the concentration of SO_x in a flue gas should be 2.5 times larger than the NO_x, though practically it is more than four times the NO_x concentration. If the wet method is applied to a flue gas with 200ppm of NO_x and 500ppm of SO_x, one has to add 300ppm more SO_x to the flue gas to reduce the NO_x completely.

Thus, the development of a dry process for the simultaneous removal of NO_x and SO_x has been desired. There have been a few papers on a dry technique for the removal. A process using active carbon, which is effective for the oxidation of SO_2 to SO_3 at lower temperatures, has been investigated to remove SO_x as ammonium salts such as $(NH_4)_2SO_4$ or NH_4HSO_4 around 200°C, where the salts may not decompose to NH_3 and SO_x. By supporting a metal oxide or sulfate on the active carbon, more than 90% of SO_x and NO_x can be removed from a flue gas.[1] The space velocity employed in the process is, however, as low as $1,000 \sim 1,500 hr^{-1}$. Shell has developed a dry process for the removal of SO_x with two reactors in swing operation for acceptance of SO_x and regeneration of the acceptor.[2] In this process, CuO supported on Al_2O_3 is used as an acceptor of SO_x at $350 \sim 450$°C under the space velocity of $6,000 \sim$

$10,000hr^{-1}$. The SO_x can be removed as its sulfate by the acceptor and the sulfate can be converted to the metal by means of a reducing gas such as H_2, CO or a light hydrocarbon. On the basis of the principle similar to this process, ESSO has also developed a dry technique using CuO on Al_2O_3 catalyst. In this process, NO_x is reduced to N_2 by NH_3 and SO_x is absorbed into CuO to form $CuSO_4$ at $316\sim482°C$.[3] $CuSO_4$ can be regenerated to CuO by heating it in H_2 and then in air, but the amount of SO_x accepted by CuO is not so large that the cycle between acceptance and regeneration must be a short period.

The purpose of the present work is to develop a catalyst for the simultaneous removal of NO_x and SO_x in a flue gas, and screening of catalysts was concentrated upon the transition metal oxides which are expected to reduce NO_x to N_2 by NH_3 and to absorb SO_x in the form of their sulfates.

The catalysts employed in the present work were prepared by the precipitation method using various metal nitrate solutions and Na_2CO_3 as a precipitant. The precipitates obtained were calcined at 550°C in air for 3 hrs. The metal oxide catalysts thus prepared were crushed to particles with ~1 mm diameters. The experiments were carried out using a conventional flow reactor with 5 ml of catalysts under the space velocity of $10,000hr^{-1}$. The activities of the catalysts were measured at $350\sim400°C$, where the ammonium salts were known to decompose to NH_3 and SO_x. The composition of the gas passed through the catalyst bed was as follows: ~500ppm of SO_2, ~250ppm of NO, ~250ppm of NH_3, $\sim3\%$ of O_2, $\sim10\%$ of water vapor and nitrogen as a balance gas. The concentration of SO_2 was measured by an SO_2 analyser of NDIR type and those of NO_x and NH_3 by an analyser of chemiluminescence type. The composition of the mixed oxide catalysts was analysed by means of X-ray fluorescence spectroscopy. The surface areas of the catalysts were measured by BET method using nitrogen at its liquid temperature.

Of all the metal oxides employed in the present work, Mn_2O_3 was the most effective for the sorption of SO_2 in the form of the sulfate(Fig.1). The activities
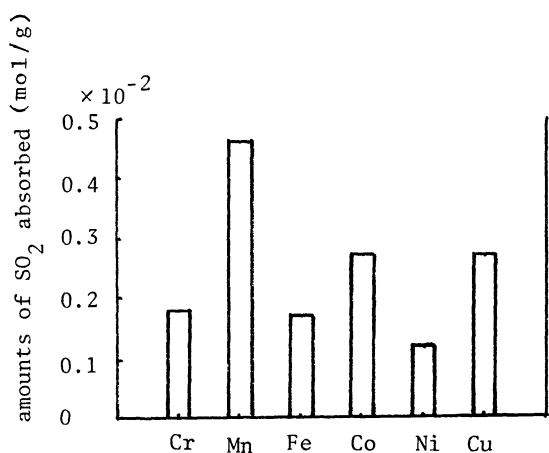

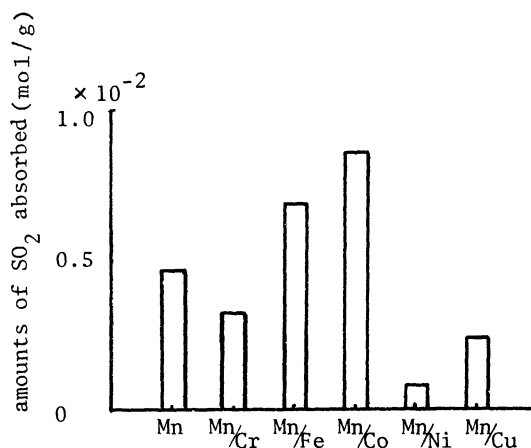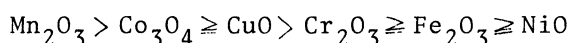Fig.1 Activities of metal oxides for SO_2 absorption

Fig.2 Activities of 1:1 mixed oxides for SO_2 absorption

of the metal oxides used for the removal of SO_2 were in the following sequence:

$Mn_2O_3 > Co_3O_4 \gtrsim CuO > Cr_2O_3 \gtrsim Fe_2O_3 \gtrsim NiO$

This sequence is close to the orders of the activities for the oxidation of NO[4] and CH_4.[5] This seems to mean that the catalysts which are active in oxidation reactions are also effective in the removal of SO_2. The sulfate formation must be considered to follow the oxidation of SO_2, as is shown below:

$SO_2 + 1/2\ O_2 \text{------}\rightarrow SO_3$ (3)

$SO_3 + \text{metal oxide} \text{------}\rightarrow \text{metal sulfate}$ (4)
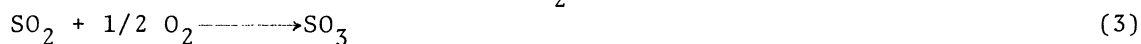
The results obtained on the activities for the removal of SO_2 by various mixed metal oxides are shown in Fig.2, and it was found that the Co_3O_4 doped Mn_2O_3 catalyst absorbed more SO_2 than a single catalyst such as Mn_2O_3 and Co_3O_4.

The doping of Co_3O_4 to Mn_2O_3 was also effective to improve the catalytic activity of Mn_2O_3 for the reduction of NO by NH_3 (Fig.3). This would be explained by the reaction mechanism proposed by Tamaru et al.[6] that the reaction of NO with NH_3 proceeds through the formation of NO_2 adsorbed on a catalyst surface, since doping Mn_2O_3 with Co_3O_4 catalyst was enhanced in the activity for the oxidation of NO to NO_2.[4]

The activity of SO_2 removal was proved to be sensitive to the changes in the ratio of Mn_2O_3 and Co_3O_4 (Fig.4). The best ratio of the mixed oxide catalyst for the removal of SO_2 was found to be 9:1 as is shown in Fig.4.

One of the most important problems for practical use of the catalyst would be the development of a technique to regenerate the catalyst. In the present work, the regeneration has been investigated as to Mn_2O_3 catalyst. Mn_2O_3 absorbs SO_2 in
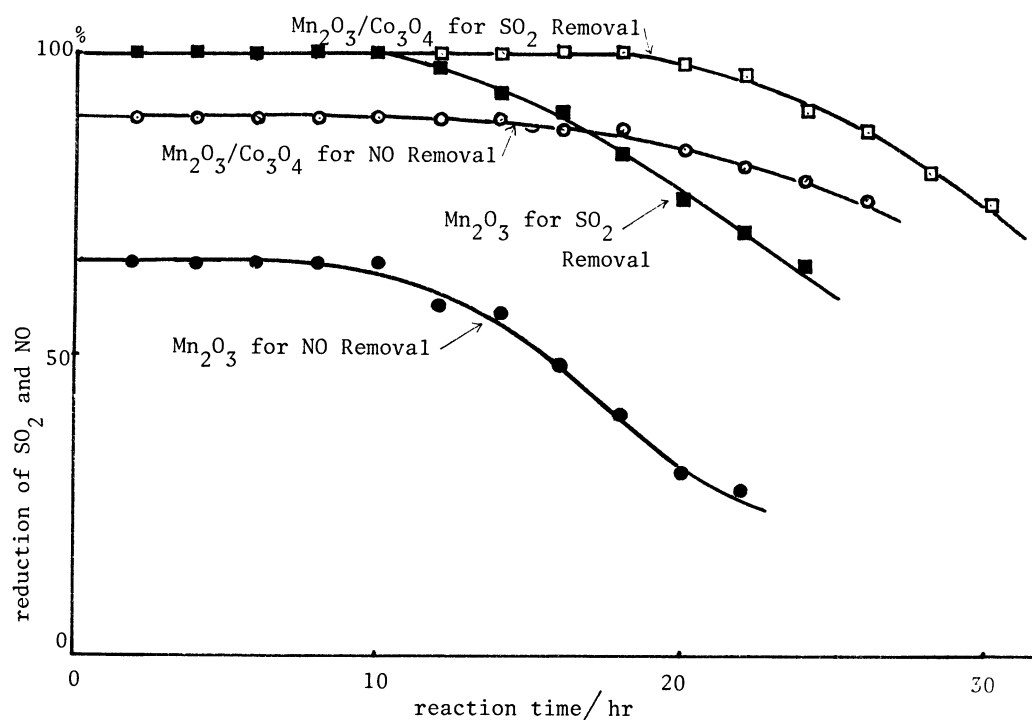

Fig.3 Simultaneous Removal of SO_2 and NO by Mn_2O_3/Co_3O_4 catalyst at 350°C

the form of $MnSO_4$, and, accordingly, the charges of the metal ions change to Mn^{2+} from Mn^{3+} after the absorption of SO_2. On the basis of this fact, an oxidative reagent such as H_2O_2 has been tested for the oxidation of Mn^{2+} to Mn^{3+} to get Mn_2O_3 from $MnSO_4$. The addition of H_2O_2 diluted by N_2 to $MnSO_4$ at 600°C resulted in the formation of Mn_2O_3, while in air it was necessary to heat $MnSO_4$ at 800°C to get Mn_2O_3. Further investigation to regenerate the present catalyst is continued.
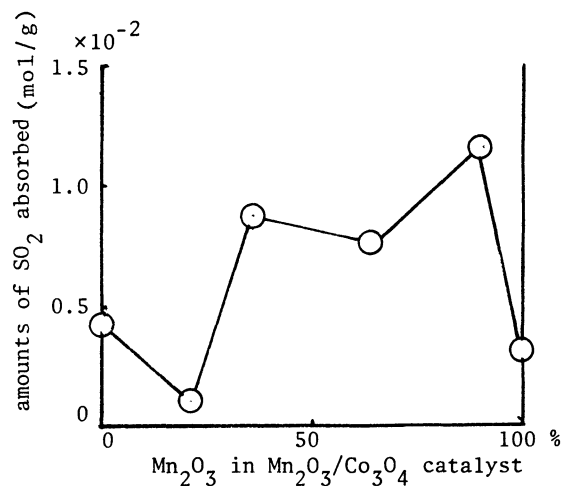

Fig.4 Effects of the composition ratio Mn_2O_3/Co_3O_4 on the catalytic activity

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