Study on the Regeneration of Mn_2O_3 Catalyst for Simultaneous Abatement of NO_x and SO_x

Toshio Sato, Akifumi Ueno,*,† Naoyuki Todo, Minoru Kurita, Hiroyuki Hagiwara,
Akiko Nishijima, and Yoshimichi Kiyozumi
National Chemical Laboratory for Industry, Yatabe-cho, Tsukubagun, Ibaraki 305

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A technique to regenerate catalysts used for the simultaneous abatement of NO_x and SO_x in flue gases was investigated. Formation of sulfate ions on the metal which is an active component of the catalyst was proved to be a poison for the catalysis. The most effective means to remove the sulfate ions on the catalyst is to heat the used catalyst at 300 °C in NH_3–water vapor.

It has been proposed to make use of coal for saving liquid fuels, although emission of NO_x and SO_x may be enhanced by the coal combustion. Hence, the development of catalysts to remove NO_x and SO_x simultaneously has been desired. The present authors have investigated catalysts for the removal of NO_x in flue gases using NH_3 as reducing reagent,[1] and have started to develop catalysts for the simultaneous removal of NO_x and SO_x on the basis of the results obtained so far. The principle of our techniques for the simultaneous abatement was reported in the previous paper.[2] It was also reported that Mn_2O_3 and Mn_2O_3/Co_3O_4 had the highest activities for the removal of NO_x and SO_x of all the transition metal oxides and their mixtures.[2] The activities, however, decreased with the reaction time, and became about 50% of the initial values. The purpose of the present work is to study the mechanism of the catalyst deactivation and to develop the techniques to regenerate the used catalysts.

Experimental

The catalyst employed in the present work is Mn_2O_3 which was prepared by the precipitation method using $Mn(NO_3)_2 \cdot 6H_2O$ and Na_2CO_3. The precipitates obtained were calcined in air at 550 °C for 3 h. The catalyst thus prepared was crushed to particles with ≈1 mm in diameter. The experiments were carried out using a conventional flow reactor with 5 ml of the catalyst at a space velocity of 10000 h^{-1}. The composition of the gas passed through the catalyst bed was as follows; ≈500 ppm of SO_2, ≈250 ppm of NO, ≈500 ppm of NH_3, ≈3% of oxygen, ≈10% of water vapor, and nitrogen as a balance gas. The activities were measured by the analyses of NO and SO_2 concentrations at the inlet and outlet of the reactor, which were made using an NO analyser of chemiluminescence type and an SO_2 analyser of NDIR type, respectively. The surface area of the catalyst was measured by the BET method using nitrogen at −196 °C. An infrared spectroscopy was used to identify the species formed on the catalyst during the reaction. Experiments for the catalyst regeneration were made in the same reactor employed for the activity measurements. The catalysts used were regenerated in the following gases: 1) ≈20% of water vapor in N_2, 2) ≈20% of water vapor in CO_2, and 3) ≈20% of water vapor and ≈5% of NH_3 in N_2 stream. The temperature employed in the regeneration experiment was in the range of 250—350 °C. To estimate the performance of the catalyst for practical use, a life test was performed for 200 h with the regeneration of the catalyst after every 20 h of the reaction. In this experiment a swing reactor[3] was employed, which consisted of two reactors with the same amount of catalyst peacked in each reactor. While one reactor was used for the reaction, the other was used for the regeneration.

Results

The activity of Mn_2O_3 catalyst for SO_2 acceptance was measured at the temperatures between 150—400 °C (Fig. 1). The amount of SO_2 absorbed in the catalyst was estimated in a similar way shown in the previous paper.[2] Infrared spectra were measured for the catalysts used at various temperatures so as to identify the species formed by SO_2 absorption (Fig. 2). The regeneration of the catalyst which was used for the reaction at 200 °C for 40 h was done by heating it in various gases. The results obtained were summarized in Table 1. In Fig. 3 the surface area of the catalysts regenerated is shown. The result seems to indicate that the activities of the catalysts recovered were proportional to the surface areas of the catalysts regenerated. Accordingly, the life test of the catalyst was carried out with subsequent regeneration using ≈20% of water vapor and ≈5% of NH_3 in N_2 stream at 300 °C, under whose conditions the surface areas of the used catalysts were recovered almost completely. Infrared spectra of the catalysts regenerated were shown in Fig. 4. Figure 4-c shows an infrared spectrum of the catalyst regenerated by water vapor and NH_3 in N_2 stream at 300 °C for 2 h. Figure 4-d shows an infrared spectrum of the catalyst after 4 cycles of the reaction (20 h) and

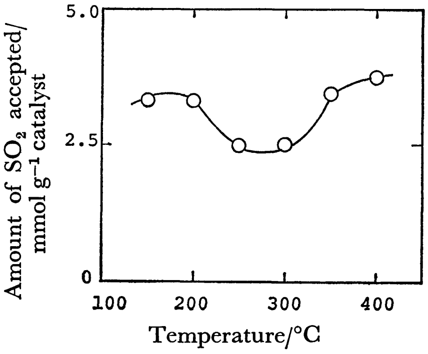

Fig. 1. Amount of SO_2 accepted in Mn_2O_3 at various temperatures.

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† Present address: School of Materials Science, Toyohashi Univ. of Technology, 1-1 Hibariga-oka, Tempaku-cho, Toyohashi 440.

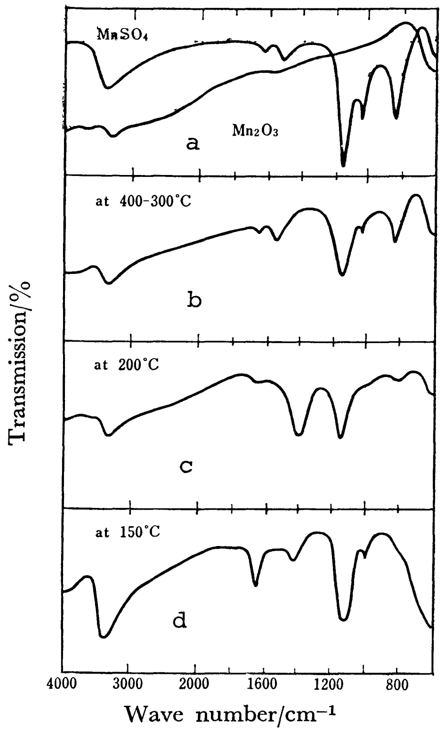

Fig. 2. Infrared spectra of the species formed on Mn_2O_3 by SO_2 adsorption at various temperatures. a): Infrared spectrum of Mn_2O_3, b): SO_2 adsorbed at 300—400 °C, c): SO_2 adsorbed at 200 °C, d): SO_2 adsorbed at 150 °C.

Table 1. Surface area and SO_2 acceptance of the catalyst regenerated by various regeneration methods

(The space velocity of the gases used for the regeneration was 5000 h^{-1} in each regeneration method.)

Regeneration methods	Surface area $m^2\,g^{-1}$	SO_2 acceptance $mmol\,g^{-1}$
(Fresh catalyst)	55.0	3.4
(Used at 200 °C for 30 h)	18.6	—
Water vapor/N_2 at 350 °C	35.1	2.1
CO_2-water vapor/N_2 at 350 °C	35.5	2.4
NH_3-water vapor/N_2 at 300 °C	42.5	3.1
N_2 at 850 °C	0.1	0

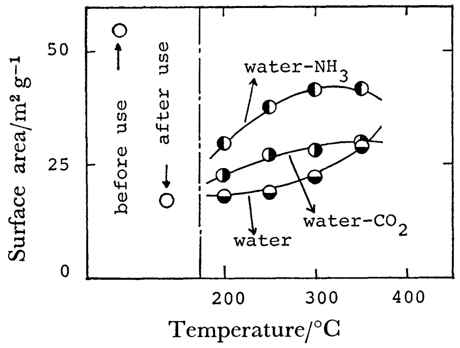

Fig. 3. Surface area of the catalyst regenerated. ◐: Regenerated by water-NH_3, ◑: regenerated by water-CO_2, ◒: regenerated by water.

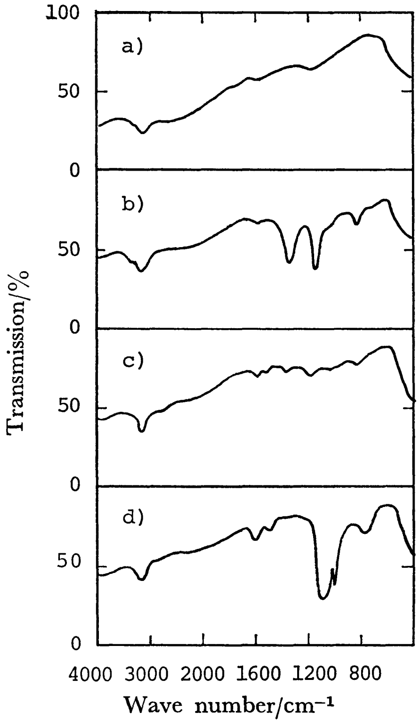

Fig. 4. Infrared spectra of the catalysts used and regenerated.
a): Fresh Mn_2O_3, b): used at 200 °C for 20 h, c): regenerated at 300 °C by water-NH_3, d): after 4th regeneration.

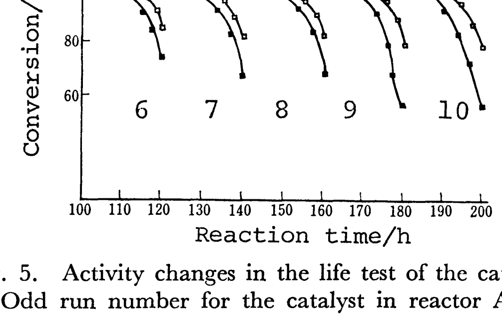

Fig. 5. Activity changes in the life test of the catalyst. (Odd run number for the catalyst in reactor A and even run number in reactor B. Reaction conditions: SV 5000 h^{-1}. Reaction temperature 200 °C. For gas composition see Experimental.)

the regeneration (2 h). These results mean that the sulfate ions accumulated in the catalyst during the cycle of the reaction and regeneration.

The change in the activity and the surface area during the life test were shown in Figs. 5 and 6, respectively. In this work a swing reactor was employed and the change in the activity in the reactor

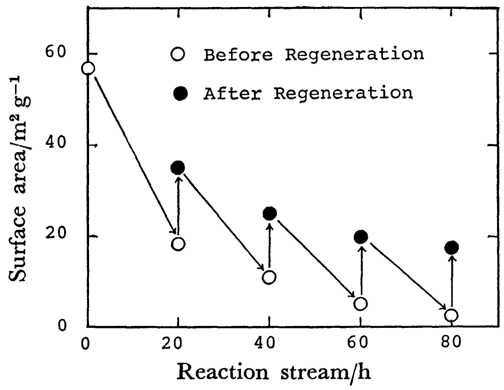

Fig. 6. Change in the surface area of the catalyst during the life test (Catalyst packed in reactor A). ○: Before regeneration, ●: after regeneration.

A was indicated by odd run numbers and those in the reactor B by even run numbers.

Discussion

The adsorption of SO_2 on metal oxides was studied by Galderbank *et al.*,[4] who reported that the adsorption isotherms at low temperatures were expressed in a different form from those at high temperatures. In the present work it was observed that the amount of SO_2 accepted in the catalyst decreased up to 250 °C, and then increased with the elevation of the temperature (Fig. 1). To understand this result, it is important to know the species formed on the catalyst when SO_2 was accepted at various temperatures. The catalyst used for the reaction was submitted to an infrared analysis. As is seen in Fig. 2, the species formed in the catalyst were different depending on the temperatures of the reaction. Manogue[5] and Lunsford[6] studied the adsorption of SO_2 on CuO and MgO, respectively, by means of infrared spectroscopy. They observed formation of sulfate and sulfite ions on both oxides. Furthermore, they revealed that sulfate ions in the bulk oxides showed infrared bands at the lower wave numbers (704 cm^{-1} for CuO and probably 860 cm^{-1} for MgO), while those on the surface of the oxides were not detected because of their structual symmetry. In the present study, an infrared band appeared at 820 cm^{-1} for the catalyst used at the temperatures higher than 300 °C (Fig. 2-b), while a trace or no absorption band was observed in the temperatures lower than 300 °C (Fig. 2-c). This means that the migration of the sulfate ions into the bulk of the catalyst will be enhanced at the temperatures higher than 300 °C, as was reported by Keppler[7] who observed the formation of bulk sulfate ions around 350 °C in metal oxides. When the catalyst was used at 200 °C, infrared bands were observed at 1410 cm^{-1} and 1175 cm^{-1}, and weakly around 3300 cm^{-1}. These bands mean that ammonium sulfates or sulfites were formed on the catalyst at this reaction temperature, since the band at 1410 cm^{-1} is characteristic of ammonium ions and that at 1175 cm^{-1} of both sulfates and sulfites. The weak band around 3300 cm^{-1} showed an existence of the species containing NH_x group. These bands were not observed at the higher temperatures due to the decomposition of the ammonium salts, their decomposition temperatures being about 250 °C. A band appeared at 1610 cm^{-1} when the reaction was carried out at 150 °C (Fig. 2-b). This band may be assigned to the water vapor condensed on the surface of the catalyst. As SO_2 and SO_3 on the catalyst may react with this water vapor to form H_2SO_3 and H_2SO_4, the band at 1175 cm^{-1} characteristic of sulfates and sulfites became strong (Fig. 2-d). The band at 1410 cm^{-1} shows that a small amount of ammonium salts were produced. From these observations it was concluded that the species formed on the catalyst were classified as follows depending on temperatures;

1) Temperatures around 150 °C: SO_2 was accepted in the forms of H_2SO_4 and H_2SO_3 as well as in the forms of ammonium salts.
2) Temperatures around 200 °C: Main species produced were ammonium salts.
3) Temperatures around 250 °C: The ammonium salts were decomposed to ammonia and SO_x adsorbed on the catalyst. A part of SO_x was released to gas phase and the others migrated into the bulk of the catalyst.
4) Temperatures higher than 300 °C: The migration of the sulfate ions was enhanced, and a large amount of the bulk sulfates was produced.

Thus, SO_2 was trapped and accumulated in the catalyst in the present experimental conditions. Hence, a regeneration technique was necessary to be developed for practical use of this catalyst. There have been several papers which proposed catalyst regenerations by heating at high temperatures. Kasaoka *et al.*[8] studied the sulfation of metal oxides and the thermal regeneration of the metal sulfates to the oxides at 700—750 °C in N_2 and air streams. After 30 min of sulfation, the catalysts were well regenerated. They did not mention, however, how well the catalysts were regenerated when the catalysts had been used for a prolonged time. In our experiments, it was observed that about 30% of Mn_2O_3 became $MnSO_4$ or $MnSO_3$ after 30 h reaction at 400 °C. It was also observed that the regeneration to Mn_2O_3 needed the temperature as high as 850 °C in N_2 and air streams. The surface area of the catalyst thus regenerated was less than 0.1 m^2/g, and no activity for the SO_2 acceptance was recovered (Table 1 and Fig. 3). Accordingly, we studied the regeneration at lower temperatures using a few kinds of gas mixtures to prevent reduction of the surface area of the catalyst.

Another point to be mentioned in our regeneration experiments was that the abatement reaction of both NO_x and SO_x was carried out at the temperatures as low as 200 °C, since the bulk sulfates formed at high temperatures were hard to be removed from the catalyst by our regeneration methods. The space velocity employed for the regeneration was 5000 h^{-1}. As the gas for regeneration CO_2 was employed, since $MnSO_4$ was expected to be regenerated to Mn_2O_3 through the formation of $MnCO_3$.[9] Ammonia was employed to let it react with SO_x adsorbed on the catalyst surface and form ammonium salts which are then decomposed to NH_3 and SO_2 in the gas phase. This method seems to prevent the surface sulfate ions from migrating into the bulk of the catalyst. As is seen in Fig. 3 and Table 1, the most effective means to regenerate the surface area and the activity of the catalyst was to heat in the gas stream containing $\approx 20\%$ water vapor and $\approx 5\%$ of ammonia at 300 °C for 2 h. The infrared spectrum of the catalyst thus regenerated showed that a small amount of the sulfates remained unremoved (Fig. 4-c). Unfortunately, this bulk sulfates unremoved proved to accumulate in the catalyst in the every regeneration procedure, reducing the life of the catalyst. The most important point for the regeneration techniques seems to sweep out the sulfates completely from the catalyst. During the life test of the catalyst with the subsequent regeneration after 20 h of the reaction, a small part of the catalyst was submitted to the measurement of the surface area. The surface area of the catalyst regenerated decreased after every regeneration probably due to the accumulation of the sulfates. The rate of deactivation of the catalyst regenerated also became higher after every regeneration (Figs. 5 and 6). The infrared spectrum shown in Fig. 4-d corresponds to the catalyst observed after 4th regeneration procedure. This represents the accumulation of the sulfate ions in the catalyst.

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