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Simultaneous Catalytic Removal of NO and SO_2 over Pt/ZSM-5 and V_2O_5-MoO_3/TiO_2 Catalysts

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The simultaneous catalytic removal of NO and SO_2 was examined over solid catalysts. SO_2 oxidation was found to be more difficult than NO reduction with NH_3. Pt/ZSM-5 and V_2O_5-MoO_3/TiO_2 showed high stationary activities for both reactions, suggesting a possibility of the simultaneous removal process of NO and SO_2 by using solid catalysts.

Nitrogen oxides (NOx) and sulfur oxides (SOx) are serious air pollutants, so that the effective removal of them from flue gases emitted from stationary combustion facilities has been very important in industry. At present, it is carried out by using two-stage consecutive process, that is, a dry process to reduce NOx with NH_3 over a solid catalyst and a wet process to fix SOx as sulfates. In order to meet sulfur rich fuels (coal and heavy oil), however, it is eagerly awaited to develop an alternative process in which NOx and SOx can be simultaneously removed. Several investigations have been made for this purpose. For example, catalytic removal methods were reported using a molten salt catalyst of NH_4HSO_4-$NaHSO_4$-V_2O_5 system,[1)] CuO-Al_2O_3-TiO_2[2)] and CuO-SiO_2-TiO_2[3)] oxides and V_2O_5-loaded activated carbon.[4)] We have examined possibilities of removing NO and SO_2 by using a solid catalyst on which NO is reduced to N_2 with NH_3 ($NO + NH_3 + 1/4\ O_2 \rightarrow N_2 + 3/2\ H_2O$) and SO_2 is oxidized to SO_3 ($SO_2 + 1/2\ O_2 \rightarrow SO_3$) with air to be removed as sulfates or sulfuric acid. As a result, supported V_2O_5-MoO_3 catalysts as well as supported Pt catalysts have been found to show high stationary activities for both reactions of NO reduction and SO_2 oxidation, as described below.

The catalysts used in this study are summarized in Table 1. TiO_2 (anatase type) and ZSM-5 type zeolite (Si/Al=11.65, Toyo Soda Manufacturing Co., Ltd.; TSZ-821) were used as supporting materials. TiO_2 was prepared by the hydrolysis of an aqueous solution of $TiCl_4$ with an ammonia solution, followed by filtration, drying at 120 °C for 10 h and calcination at 450 °C for 6 h. Active components were loaded on these supports by ion exchange or impregnation method as shown in Table 1. Cu(II)-ZSM-5 was calcined at 350 °C for 1 h in air. Supported Pt catalysts were calcined at 500 °C for 4 h in air, followed by the reduction at 400 °C for 2.5 h in a stream of H_2-N_2 mixture (3:7). Calcination of supported oxide catalysts in air was carried out in two consecutive steps at 300 °C for 2 h and at 450 °C for 5 h. The catalytic reactions were performed in a conventional flow reactor. A typical feed composition was SO_2 (500 ppm), NH_3 (1000 or 1250 ppm), O_2

Table 1. Catalysts used in this study

Catalyst	Loading		Starting material
	Amount /wt%	Method	
Cu(II)-ZSM-5	0.04	ion exchange	$(CH_3COO)_2Cu\cdot H_2O$
Pt/TiO_2	0.5	impregnation	$H_2PtCl_6\cdot 6\ H_2O$
Pt/ZSM-5	0.06	ion exchange	$[Pt(NH_3)_4]Cl_2$
MnO_2/TiO_2	10	impregnation	$(CH_3COO)_2Mn\cdot 4\ H_2O$
V_2O_5/TiO_2	10	impregnation	NH_4VO_3
$V_2O_5-MoO_3/TiO_2$ (V:Mo = 75:25)	10	impregnation	NH_4VO_3 $(NH_4)_6Mo_7O_{24}\cdot 4\ H_2O$

(5%), H_2O (11%), and N_2 (balance) with or without NO (250 ppm) at a space velocity 12000 h^{-1}. Concentrations of SO_2, NO, and NH_3 were analyzed by iodometry, chemiluminescence NO/NOx analyzer (Yanagimoto, ECL-77A) and absorption photometry of indophenol (JIS K 0099), respectively.

Figure 1 shows the time course of the SO_2 removal activity of each catalyst at 350 °C in the absence of NO, except the case of Cu(II)-ZSM-5 which was tested in the presence of NO. The amount of SO_2 removed was derived from a difference in SO_2 concentration between the feed and the effluent, and so it naturally counted the amounts of oxidized as well as adsorbed SO_2. The apparent changes in activity before stationary states in Fig. 1 were mainly associated with the part of adsorption. Among catalysts tested, Pt/ZSM-5 was the most active, exhibiting a stationary SO_2 conversion of 100% from the beginning, followed by Pt/TiO_2 and $V_2O_5-MoO_3/TiO_2$ which showed about 80% SO_2 conversion at the stationary state after 5 h on stream. It is remarkable that Pt/ZSM-5 showed higher activity than Pt/TiO_2 in spite of the less loaded amount of Pt (0.06 wt%) than that in Pt/TiO_2 (0.5 wt%).

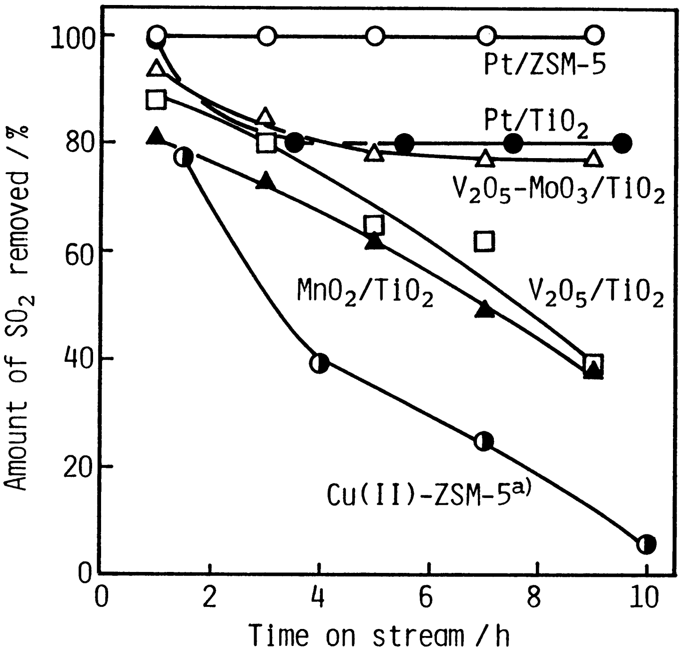

Fig. 1. Time courses of SO_2 removal activities at 350 °C. feed composition; SO_2(500 ppm)+NH_3(1000 ppm)+H_2O(11%)+O_2(5%)+N_2(balance), a) SO_2(500 ppm)+NO(250 ppm)+NH_3(1250 ppm)+H_2O(11%)+O_2(5%)+N_2(balance).

The effluent analyses indicated that, under the experimental conditions, 95, 90 and 14% of introduced NH_3 were consumed by oxidation to N_2 ($2\ NH_3 + 3/2\ O_2 \rightarrow N_2 + 3\ H_2O$) over Pt/ZSM-5, PT/$TiO_2$, and V_2O_5-MoO_3/TiO_2, respectively. This means that the oxidized SO_3 was removed mainly as sulfuric acid or ammonium sulfate over Pt or V_2O_5-MoO_3 catalysts, respectively. On the other catalysts, i.e., MnO_2/TiO_2, V_2O_5/TiO_2, and Cu(II)-ZSM-5, the amount of SO_2 removed decreased monotonously with an increase in time on stream due to several causes. For MnO_2/TiO_2, $MnSO_4$ formation was identified from IR measurements of the used catalyst. For Cu(II)-ZSM-5, the activity for SO_2 removal decreased to almost zero within about 10 h, and the total SO_2 amount removed was roughly equimolar to the amount of Cu(II) of the catalyst (0.61 mmol/g-catalyst). It is suggested that in this case the removed SO_2 was adsorbed strongly on each Cu(II) to form a 1:1 complex. The decrease in SO_2 removal activity of V_2O_5/TiO_2 was also likely to be brought about by the strong adsorption of SO_2 at V=O sites at the tested temperature.

The simultaneous removal of NO and SO_2 was tested over Pt/ZSM-5 and V_2O_5-MoO_3/TiO_2 catalysts as a function of temperature as shown in Fig. 2. The removal of NO was found to be far easier than the removal of SO_2. The NO conversion at 200 °C was 82% and 100% over V_2O_5-MoO_3/TiO_2 and Pt/ZSM-5 catalysts, respectively. With a rise in reaction temperature, the NO conversion increased to reach 100% at 250 °C over V_2O_5-MoO_3/TiO_2, while it decreased monotonously to 71% at 350 °C over Pt/ZSM-5. It is suspected that the decrease in NO conversion over Pt/ZSM-5 with increasing temperature was caused by increasing consumption of NH_3 for the oxidation with O_2. As for the SO_2 removal activity, Pt/ZSM-5 was more active than V_2O_5-MoO_3/ TiO_2 in the whole temperature range examined. Pt/ZSM-5 showed 55% SO_2 conversion even at 200 °C and achieved 100% at 350 °C. On the other hand, the SO_2 conversion over V_2O_5-MoO_3/TiO_2 was 16% at 200 °C and increased gradually to 40% at 350 °C with an increase in reaction temperature. It is noted that SO_2 oxidation activity of Pt/ZSM-5 was not affected by the presence of NO while that of V_2O_5-MoO_3/TiO_2 decreased to 40% from 78% in the NO-free gas (Fig. 1) at 350 °C.

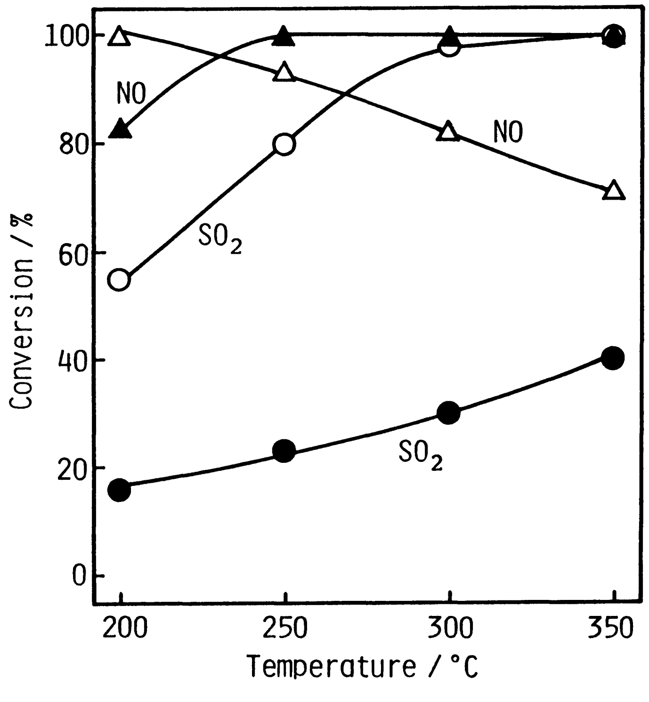

Fig. 2. Activities for the simultaneous removal of NO and SO_2. feed composition; SO_2(500 ppm)+NO(250 ppm)+NH_3(1250 ppm)+ H_2O(11%)+O_2(5%)+N_2(balance).
△ ○ ;Pt/ZSM-5 (Pt 0.06 wt%)
▲ ● ;V_2O_5-MoO_3/TiO_2 (10 wt%, V:Mo=25:75)

Table 2 summarizes the steady-state conversions of NO and SO_2 over the tested catalysts. It is clear again that the SO_2 oxidation is more difficult than the NO reduction. Some important conclusions are drawn from the table as follows. Although Cu(II)-ZSM-5 had no activity for the SO_2 oxidation, it had a high activity for the NO reduction as a SO_2-resistant catalyst. In spite of the largest activity for the SO_2 oxidation, Pt/ZSM-5 has a disadvantage in the NO reduction activity; because of the high activity for the undesirable NH_3 oxidation, a large excess of NH_3 is required for the complete removal of NO. Accordingly, it is inferred that Pt/ZSM-5 is better used as combined with a highly active NO removal catalyst such as Cu(II)-ZSM-5; the flue gas is subjected to the NO removal and the SO_2 removal successively on the serially located catalyst beds which are packed with the respective catalysts. It was actually confirmed that NO and SO_2 were completely removed from the model flue gas at 300 °C over serially packed Cu(II)-ZSM-5 and Pt/SZM-5 catalyst bed. Among oxide catalysts, high activity for the SO_2 oxidation was observed only with V_2O_5-MoO_3/TiO_2. With high activity for the NO removal and low activity for the NH_3 oxidation, this catalyst appears to have a latent potential to become a low cost catalyst for the simultaneous removal of NO and SO_2. The fact that the SO_2 oxidation activity of the catalyst resulted from the addition of MoO_3 to V_2O_5 suggests a possibility of enhancing the activity further by refining the catalyst preparation method and conditions.

Table 2. Simultaneous removal of NO and SO_2 over the catalysts tested

Catalyst	Temperature / °C	Conversion / %	
		NO	SO_2
Cu(II)ZSM-5	250	78	0
	300	100	0
	350	100	0
Pt/TiO_2 a)	300	---	32
	350	---	80
Pt/ZSM-5	200	100	55
	250	93	80
	300	82	98
	350	71	100
MnO_2/TiO_2 a)	350	---	0
V_2O_5/TiO_2	350	100	0
V_2O_5-MoO_3/TiO_2	200	82	16
	250	100	23
	300	100	30
	350	100	40

a) Tested only in the absence of NO.

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