Promotive effect of Sn on the catalytic activity of Al_2O_3 for the selective reduction of NO by methanol

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The effect of various metal additives on the catalytic performance of Al_2O_3 was investigated for the selective reduction of NO by methanol in oxidizing atmosphere. The addition of Sn promoted the catalytic activity of alumina for the NO reduction at low temperatures. Moreover, it was found that Sn/Al_2O_3 catalyst maintained its high activity even in the presence of SO_2.

Keywords: Nitrogen oxides; selective reduction; methanol; alumina; silica; Sn

1. Introduction

Selective reduction of NO by hydrocarbons in oxidizing atmosphere is attracting much attention recently as a practical method for NOx removal from exhausts of diesel and lean-burn gasoline engines. Until now various catalysts have been reported for this reaction such as ion-exchanged zeolites [1–6], metal oxides [7–9] and noble metals [10,11]. Among metal oxides, alumina is a promising catalyst candidate for practical applications because of its high stability and activity. However, it turned out that the reaction is inhibited by the presence of water vapor [12,13].

In an attempt to examine various reducing agents for NO reduction over pure alumina catalyst, we found that oxygenated hydrocarbons serve as good agents for the NO reduction in the presence of water vapor [12,13]. In particular, methanol reduces NO at temperatures as low as around 400°C [12–14]. However, it is still

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desirable to improve catalytic activity at lower temperatures because the temperature of diesel exhaust is often lower than 300°C.

In this study, we have investigated the additive effect of various metal elements on the catalytic activity of alumina for the selective reduction of NO by methanol. We wish to report an excellent effect of Sn to enhance the activity of alumina at low temperatures.

2. Experimental

Alumina with a surface area of 190 $m^2\ g^{-1}$ was obtained from Mizusawa Chemical Industries. Metal-added alumina catalysts (Sn, W, Mo, Ga, Bi and Sb/Al_2O_3) were prepared by impregnating the alumina with aqueous solutions of $SnCl_4$, H_2WO_4–NH_4OH, $(NH_4)_6Mo_7O_{24}$, $Ga(NO_3)_3$, $Bi(NO_3)_3$–HNO_3, $SbCl_3$–HCl, respectively, followed by drying and calcination in air stream at 600°C. The surface area of alumina was little affected by impregnation with the metals. For example, the surface area of Sn/Al_2O_3 was 192 $m^2\ g^{-1}$.

The catalytic reduction of NO was carried out with a fixed-bed flow reactor by passing a reactant gas mixture (gas mixture 1 or 2) over a catalyst. Reactant gas mixture 1 contained NO (1000 ppm), O_2 (10%), methanol (1000 ppm) and H_2O (8%) diluted in He, and reactant gas mixture 2 contained NO (1000 ppm), O_2 (10%), methanol (2000 ppm), H_2O (5%) and SO_2 (100 ppm) diluted in N_2. For the reactions using gas mixture 1, the catalyst weight was 0.4 g and the gas flow rate was 120 $cm^3\ min^{-1}$. The effluent gas was analyzed by gas chromatographs equipped with a molecular sieve 5A column for the analysis of N_2 and CO, and a Porapak Q column for the analysis of N_2O and CO_2. The catalytic activity was evaluated by NO conversion to N_2 and N_2O, and methanol conversion to COx. For the reactions using gas mixture 2, the catalyst weight was 6.7 g and the flow rate was 2000 $cm^3\ min^{-1}$. The effluent gas was analyzed with a chemiluminescence NOx analyzer and the catalytic activity was evaluated by NO conversion.

3. Results and discussion

Table 1 shows the activity of Mo, W, Ga, Sn, Bi and Sb/Al_2O_3 (metal loading: 1%) along with that of alumina itself for the reduction of NO by methanol. In these experiments, gas mixture 1 was used as the reactant gas. Although alumina showed activity for NO reduction, the NO conversion at lower temperatures than 300°C was not so high.

The addition of Mo, W and Ga to alumina decreased both NO conversion and methanol conversion. In the case of Bi and Sb, NO conversion was also decreased. It is noted, however, that methanol conversion to COx was increased. This sug-

Table 1
Catalytic activities for the selective reduction of NO by methanol [a]

Catalyst	NO conv. to N_2 (%) (N_2O)					CH_3OH conv. to $CO + CO_2$ (%) (CO, CO_2)				
	250°C	300°C	350° C	400°C	500°C	250°C	300°C	350°C	400°C	500°C
Al_2O_3	0.0	27	43	36	11	22	50	87	100	100
	(33)	(15)	(2.5)			(15, 7)	(27, 23)	(50, 37)	(65, 35)	(64, 36)
1 wt% Mo/Al_2O_3		14	20	29	10		23	44	92	100
		(3.2)					(11, 12)	(29, 15)	(69, 23)	(77, 23)
1 wt% W/Al_2O_3		14	15	27	21		21	45	84	100
							(0, 21)	(0, 45)	(0, 84)	(0, 100)
1 wt% Ga/Al_2O_3		21	32	39	7.3		32	58	100	100
		(6.2)	(1.7)				(15, 17)	(26, 32)	(33, 67)	(37, 63)
1 wt% Bi/Al_2O_3	0.0	19	21	13	0.0	40	88	100	100	100
	(35)	(17)	(4.2)			(22, 18)	(44, 44)	(57, 43)	(65, 35)	(62, 38)
1 wt% Sb/Al_2O_3	0.0	17	36	23	0.0	38	78	100	100	100
	(41)	(26)	(4.9)			(28, 10)	(52, 26)	(60, 40)	(68, 32)	(73, 27)
1 wt% Sn/Al_2O_3	6.7	40	46	33	9.6	47	87	100	100	100
	(45)	(23)	(4.0)			(31, 16)	(52, 35)	(60, 40)	(66, 34)	(68, 32)
SiO_2		0.0		0.0	0.0		0.0		1.1	13
							(0.0)		(0, 1.1)	(6, 7)
1 wt% Sn/SiO_2	0.0	0.0	0.0	0.0	0.0	0.0	1.5	13	51	100
						(0, 0)	(0, 1.5)	(0, 13)	(0, 51)	(0, 100)

[a] Conditions: NO = 1000 ppm, O_2 = 10%, CH_3OH = 1000 ppm, H_2O = 8%, flow rate = 120 cm^3 min^{-1}, catalyst weight = 0.4 g, W/F = 0.2 g s cm^{-3}.

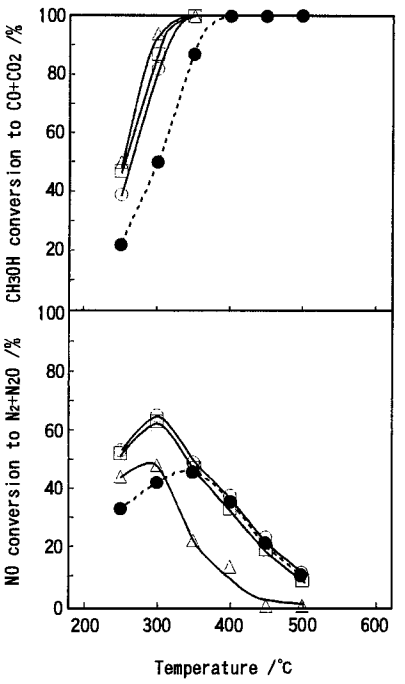

Fig. 1. Effect of Sn loading on the catalytic activities of Sn/Al_2O_3. (●) 0.0 wt%, (○) 0.5 wt%, (□) 1.0 wt%, (△) 2.0 wt%. NO = 1000 ppm, O_2 = 10%, CH_3OH = 1000 ppm, H_2O = 8%, flow rate = 120 $cm^3\ min^{-1}$, catalyst weight = 0.4 g, W/F = 0.2 g s cm^{-3}.

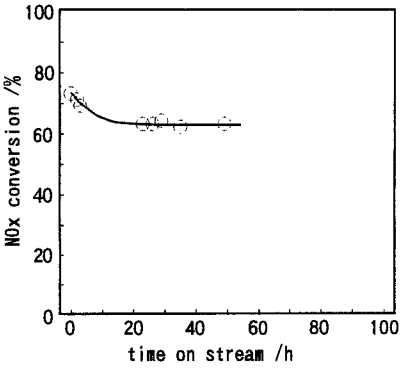

Fig. 2. Time course of the catalytic activity of 0.5 wt% Sn/Al_2O_3 for NO reduction in the presence of SO_2. NO = 1000 ppm, O_2 = 10%, CH_3OH = 1000 ppm, H_2O = 5%, flow rate = 2000 $cm^3\ min^{-1}$, catalyst weight = 6.7 g, W/F = 0.2 g s cm^{-3}.

gests that methanol oxidation by oxygen prevails over NO reduction by methanol on Bi and Sb/Al_2O_3.

In contrast to the metal-supported alumina mentioned above, the addition of Sn showed excellent effect to enhance the activity of alumina for NO reduction into N_2 and N_2O especially in the low temperature region below 350°C. Since methanol conversion also increased by Sn addition, it is suggested that the effect of Sn additive is related directly to the promotion of a reaction step which leads to the formation of N_2 and COx.

In order to elucidate the effect of Sn, the catalytic performance of Sn supported on silica, which has no catalytic activity, was examined. It can be seen from table 1 that Sn/SiO_2 did not catalyze NO reduction at all but promoted only the oxidation of methanol. Consequently it can be speculated that the promotive effect of Sn is due to the interaction of Sn and alumina.

The effect of Sn loading on the activity of Sn/Al_2O_3 is shown in fig. 1. 0.5% Sn/Al_2O_3 and 1% Sn/Al_2O_3 showed almost the same good catalytic performance for NO reduction in the temperature region below 300°C compared to alumina. However, loading of 2% Sn decreased the deNOx activity of Sn/Al_2O_3. The NO conversion in the high temperature region over 2% Sn/Al_2O_3 was lower than that over alumina.

For practical applications to diesel exhaust, catalyst durability in the presence of SO_2 is an important factor. Fig. 2 shows the variation of catalytic activity of 0.5% Sn/Al_2O_3 with time on stream at 400°C for the reaction using gas mixture 2 containing 100 ppm SO_2. Although a slight decrease in the activity was observed in the initial stage of the reaction, NO conversion did not change afterwards. Thus it was proved that Sn/Al_2O_3 maintains its high activity even in the presence of SO_2 and water.

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