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SIMULTANEOUS REMOVAL OF NO AND SO_2 WITH H_2S OVER SOLID CATALYSTS

Tokio IIZUKA,* Tsutomu ICHIKAWA, Shinji EGASHIRA, and Kozo TANABE
Department of Chemistry, Faculty of Science,
Hokkaido University, Sapporo 060

The reduction of NO and SO_2 with H_2S was examined over various metal oxide catalysts at 150-200 °C. Molybdenum oxide supported on MgO was most active for the reduction of NO and SO_2 among the catalysts used. Alumina also showed considerably high activity, but the activity depended markedly on the preparation of the catalyst.

The reduction of NO_x with NH_3 over solid catalysts has been widely developed. However, for SO_x containing stack gas, NO_x and SO_x have been removed separately. If the removal of NO_x and SO_x is achieved in the same catalytic system, the process might be very effective. The reaction of SO_2 and H_2S is well known as Claus reaction and Al_2O_3 is used as a catalyst industrially.1) Although the simultaneous removal of NO_x and SO_x with H_2S has been proposed as Princeton Research method,2) the detail of this reaction is not reported yet. The formulas are as follows.

$$2NO + 2H_2S \longrightarrow 2S + N_2 + 2H_2O \qquad (1)$$

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O \qquad (2)$$

In this work, the authors have examined the simultaneous reduction of NO and SO_2 with H_2S over various metal oxide catalysts and found that molybdenym oxide supported on MgO was best for the reaction.

The catalysts of Al_2O_3, ZrO_2, Fe_2O_3, and TiO_2 were prepared by the hydrolysis of corresponding metal salts and were calcined at 500 °C for 2 h. Niobium oxide was obtained by the calcination of niobium oxide hydrate (CBMM AD-108) at 500 °C for 2 h. Commercially available activated alumina (Nishio KAT-6) and silica-alumina (NIKKI N-631-L) were also used for comparison. Supported molybdenum oxide catalysts were prepared by a conventional impregnation method with an aqueous solution of ammonium heptamolybdate (MoO_3 12 wt%). The mixed oxide catalysts were prepared by a coprecipitation method as reported previously.[3-4] The catalysts were evacuated at 500 °C for 2 h before use. The mixture of NO (1067 Pa), SO_2 (1067 Pa), H_2S (4000 Pa) and argon (4000 Pa) was allowed to react in a recirculation reactor having a volume of 320 mℓ. The reacted gas was analyzed mass-spectrometrically. The products were N_2, H_2O and sulfur. The amounts of formed sulfur and H_2O were not analyzed. The conversion was calculated on the basis of the decrease of NO or SO_2.

The time course of reaction over MoO_3/MgO is depicted in Fig. 1. The MoO_3/MgO catalyst exhibited an excellent activity for the simultaneous reduction of

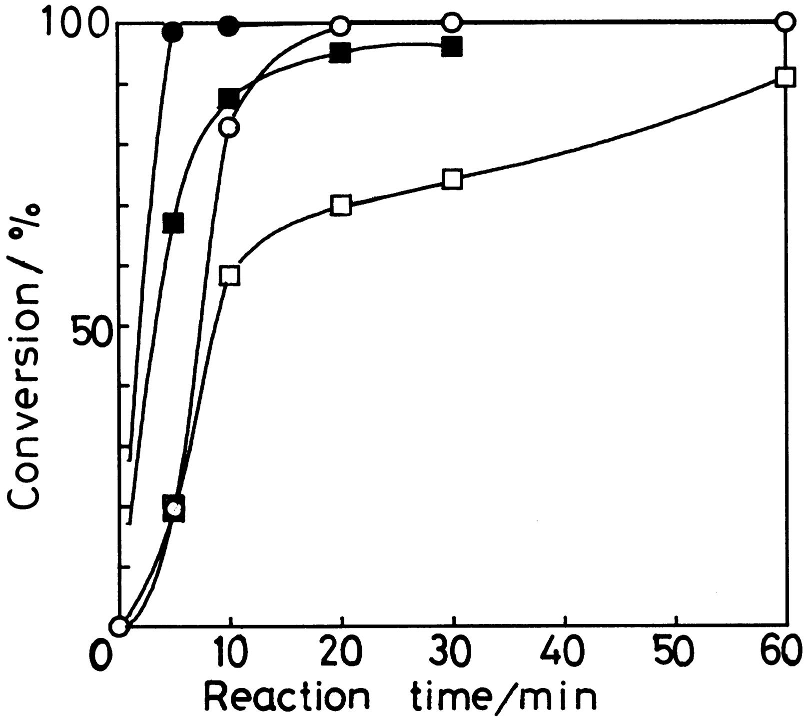

Fig. 1. Reduction of NO and SO_2 with H_2S over MoO_3/MgO.

□ NO, ○ SO_2 (150 °C reaction)

■ NO, ● SO_2 (200 °C reaction)

Table 1. NO + SO_2 + H_2S reaction over various catalysts

Catalyst	Surface area	Reaction temp	Reaction rate		Reaction rate	
	$m^2 \cdot g^{-1}$	°C	10^{-2} mol·min^{-1}·g^{-1}		10^{-5} mol·min^{-1}·m^{-2}	
			NO	SO_2	NO	SO_2
Al_2O_3 [from $Al(NO_3)_3$]	196	200	1.87	2.98	9.55	15.20
		150	0.40	0.14	2.04	0.76
Al_2O_3 a)	215	200	0.28	1.07	1.32	4.97
MgO	214	200	0.09	0.14	0.43	0.65
Fe_2O_3	13	200	0.15	0.23	11.30	17.30
Nb_2O_5	126	200	0.56	0.98	4.44	7.81
SiO_2-Al_2O_3 [Si/Al=17/3] b)	333	200	0.01	0.90	0.03	2.71
MoO_3/MgO	209	200	2.00	2.98	9.57	14.30
		150	0.86	1.22	4.09	5.81
MoO_3/Al_2O_3 a)	136	200	0.26	0.69	1.90	5.06
MoO_3/Nb_2O_5	36	200	0.23	0.78	6.33	21.70
MoO_3/ZrO_2	50	200	0.44	0.77	8.77	15.33
MoO_3/CaO	29	200	0.60	1.19	20.70	41.12
Nb_2O_5/Al_2O_3	167	200	0.10	0.20	0.60	1.17
Fe_2O_3-SiO_2 [Fe/Si=1/9]	286	200	0.29	0.49	1.00	1.72
Fe_2O_3-SiO_2 [Fe/Si=9/1]	149	200	1.01	0.53	6.81	3.53
Fe_2O_3-ZnO [Fe/Zn=2/1]	27	200	0.16	0.58	6.07	21.40
Fe_2O_3/MgO	111	200	0.28	0.47	2.54	4.24
Fe_2O_3-Al_2O_3 [Fe/Al=1/9]	228	200	1.48	2.36	6.49	10.35
Fe_2O_3-Al_2O_3 [Fe/Al=1/1]	166	200	1.24	2.72	7.49	16.39
Fe_2O_3-Al_2O_3 [Fe/Al=9/1]	50	200	1.27	2.55	25.43	51.06

a) Activated Al_2O_3 [Nishio KAT-6]. b) [Nikki N-631-L].

both NO and SO_2 with H_2S. The reduction of SO_2 was easier than that of NO and especially at a reaction temperature of 200 °C, SO_2 was almost completely decomposed within 5 min. The product of sulfur condensed on the reactor wall of unheated position and the deactivation of catalyst was not notable after the repeat of reaction several times at 200 °C. The initial activities of various catalysts are summarized in Table 1.

On the basis of unit surface area, Fe_2O_3-Al_2O_3 [Fe/Al=9/1], Fe_2O_3 and MoO_3/CaO showed high activities. However, MoO_3/MgO showed the highest conversion per unit weight and the activity was stable at 200 °C as mentioned above.

Activated alumina showed rather low activity for NO reduction, though the reduction of SO_2 was fast. In contrast to this, alumina prepared from nitrate was considerably active for the both reactions of NO and SO_2. This indicates the importance of preparation of Al_2O_3 catalyst to achieve high activity. Silica-alumina showed the lowest activity for the reaction, though NO + H_2S reaction was reported to be enhanced by silica gel or glass wool.5) As a whole, the catalysts which have a basic nature tend to have the high activity. Probably the basic sites are important for the dissociation of H_2S to HS^- and H^+ and HS^- is a key intermediate for the reduction of NO and SO_2.

In the reaction at 150 °C, MoO_3/MgO was more active than Al_2O_3 prepared from nitrate. Thus, MoO_3/MgO is promising for the simultaneous removal of NO and SO_2 with H_2S.

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