CHEMISTRY LETTERS, pp. 2179-2182, 1991.

Sulfate-promoted Metal Oxide Catalysts for the Selective Reduction of Nitrogen Monoxide by Propane in Oxygen-rich Atmosphere

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The effect of pretreatment with sulfuric acid on several metal oxide catalysts for the title reaction was investigated. TiO_2, ZrO_2, and Fe_2O_3 pretreated with sulfuric acid showed high activity, whereas the activity of Al_2O_3 was decreased by the treatment.

The selective reduction of nitrogen oxides by hydrocarbons attracts much attention recently. Various zeolite-type catalysts have been reported such as Cu-,$^{1,2)}$ H-,$^{3)}$ Ce-exchanged zeolites,$^{4)}$ and Fe-silicates.$^{5)}$ Metal oxides$^{6)}$ such as alumina and zirconia have also been found effective. The activity of alumina and H-zeolite suggests that a solid acid material would be a possible candidate catalyst for the reaction. In this work, we investigated the reduction of nitrogen monoxide by propane in the presence of oxygen on sulfate-promoted solid superacid metal oxides reported by Hino et al.$^{7-10)}$ We found that TiO_2, ZrO_2, and Fe_2O_3 pretreated with sulfuric acid showed good catalytic performance.

$Ti(OH)_4$ and $Fe(OH)_3$ were synthesized by hydrolyzing $Ti[OCH(CH_3)_2]_4$ and $Fe(NO_3)_3$ solutions, washing, and drying at 100 °C. $Zr(OH)_4$ was a commercial reagent (Soekawa Chemicals). TiO_2, ZrO_2 and Fe_2O_3 were prepared by calcining these hydroxides for 3 h in air stream. Al_2O_3 was a commercial catalyst (Catalyst and Chemicals, pellet-type). Sulfuric acid-pretreated metal oxides (abbreviated as SO_4/M_xO_y) were prepared according to the method reported by Hino et al.$^{7-10)}$ 10 g of metal hydroxide or oxide was exposed to 150 cm^3 of diluted sulfuric acid. After filtering and drying, the samples were calcined in flowing air for 3 h. Table 1 indicates the preparation conditions and properties of the catalyst samples.

The reaction was performed with a fixed-bed flow reactor by passing a mixture of about 1000 ppm of NO, 10% of O_2 and 329 ppm of propane in helium at a rate of 62 cm^3 min^{-1} over a 1 g of catalyst. The effluent gas

Table 1. List of catalyst

Catalyst	Starting material	Conc. of H_2SO_4 /mol·dm^{-3}	Calcn. temp/°C	Surface area/m^{3}g^{-1}	Content of S/wt%
TiO_2	$Ti(OH)_4$	--	500	45	0
ZrO_2	$Zr(OH)_4$	--	600	27	0
Fe_2O_3	$Fe(OH)_3$	--	500	12	0
Al_2O_3	commercial	--	600	209	0
SO_4/TiO_2	$Ti(OH)_4$	0.5	500	111	2.2
SO_4/ZrO_2	ZrO_2[a)]	0.5	500	79	1.4
SO_4/ZrO_2	ZrO_2[a)]	0.5	600	75	1.1
SO_4/Fe_2O_3	$Fe(OH)_3$	0.25	500	49	1.3
SO_4/Al_2O_3	Al_2O_3	2.5	600	174	5.3

a) Calcined at 400 °C.

was analyzed by gas chromatography. The catalytic activities were evaluated by the conversion of NO to N_2 and that of propane to CO_2 and CO.

Figure 1 shows the activities of TiO_2 and SO_4/TiO_2 as functions of reaction temperature. It is apparent that SO_4/TiO_2 is much more active for NO reduction than TiO_2 in the temperature range of the experiments. The difference in activity was remarkable especially at low temperatures. The efficiency of propane consumed, defined as NO/propane conversion ratio, was also higher for SO_4/TiO_2. This can be seen by comparing the extent of increase of the two conversion values by the treatment with sulfuric acid. Although an increase of surface area seems to be responsible for the activity enhancement (Table 1), the results described above cannot be explained by surface area only.

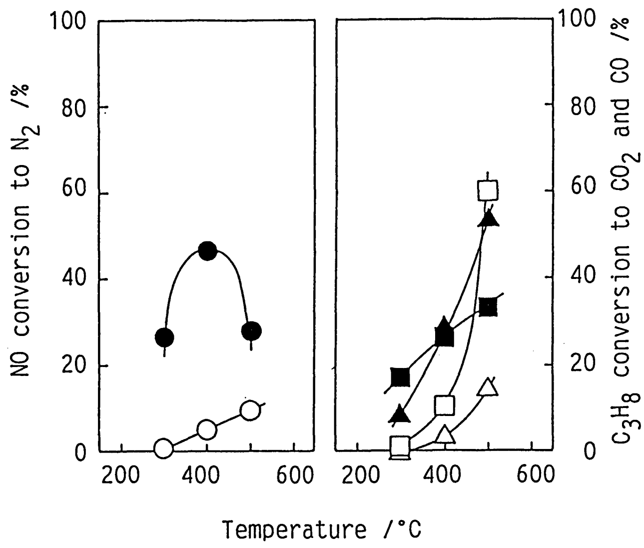

Fig. 1. Catalytic activity of TiO_2 and SO_4/TiO_2.
Conv. for TiO_2: ○,NO to N_2; □,C_3H_8 to CO_2; △,C_3H_8 to CO.
Conv. for SO_4/TiO_2: ●,NO to N_2; ■,C_3H_8 to CO_2; ▲,C_3H_8 to CO.

The effect of pretreatment with sulfuric acid on ZrO_2 is presented in Fig.2 for the samples calcined at 600 °C. An increase in activity for NO reduction was also observed, although the effect was not so remarkable as in the case of TiO_2. This may be partly because of the higher calcination temperature than for TiO_2, since calcination at 500 °C gave a more active catalyst (NO conversion: 31% at 400 °C, 42% at 500 °C). High efficiency of propane consumed is also a characteristic of SO_4/ZrO_2.

The pretreatment resulted in a drastic change of catalytic performance of Fe_2O_3 as shown in Fig.3. For Fe_2O_3, NO was not reduced at all while the oxidation of propane proceeded. On the other hand, SO_4/Fe_2O_3 showed activity for NO reduction with maximum conversion at 300 °C. The extent of propane oxidation was decreased by the treatment.

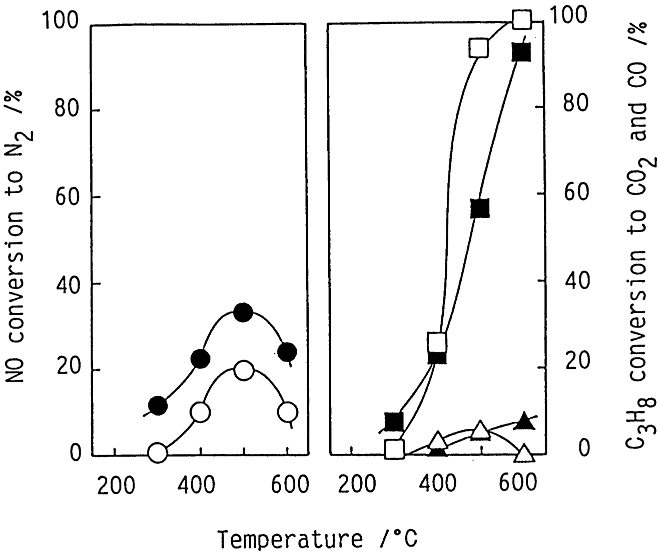

Fig. 2. Catalytic activity of ZrO_2 and SO_4/ZrO_2.
Conv. for ZrO_2: ○,NO to N_2; □,C_3H_8 to CO_2; △,C_3H_8 to CO.
Conv. for SO_4/ZrO_2: ●,NO to N_2; ■,C_3H_8 to CO_2; ▲,C_3H_8 to CO.

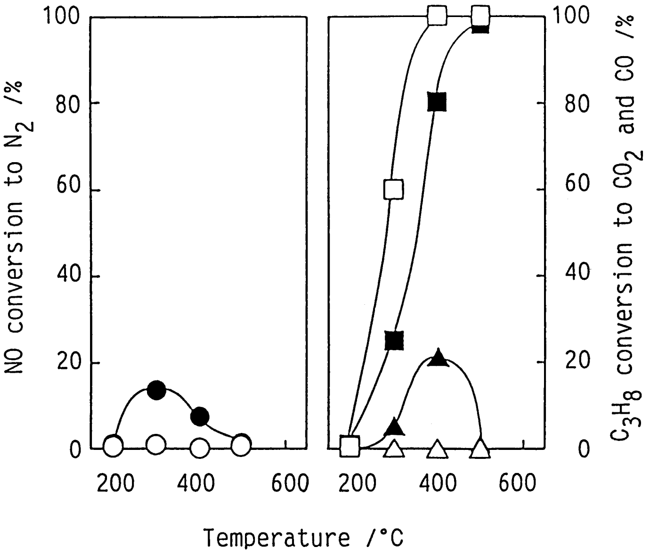

Fig. 3. Catalytic activity of Fe_2O_3 and SO_4/Fe_2O_3.
Conv. for Fe_2O_3: ○,NO to N_2; □,C_3H_8 to CO_2; △,C_3H_8 to CO.
Conv. for SO_4/Fe_2O_3: ●,NO to N_2; ■,C_3H_8 to CO_2; ▲,C_3H_8 to CO.

In contrast to the above three oxides, the treatment of Al_2O_3 with sulfuric acid did not give good effect. As shown in Fig.4, the activity for NO reduction was decreased along with the conversion of propane in the range over 400 °C. The sulfur content of SO_4/Al_2O_3 is considerably higher than the other sulfuric acid-pretreated oxides, suggesting the formation of aluminum sulfate on the surface, which is less active than Al_2O_3.[11] It is noted, however, that the activity for NO reduction was promoted at 300 °C.

In conclusion, sulfuric acid-pretreated TiO_2, ZrO_2, and Fe_2O_3 show good catalytic performance for the present reaction. It is noteworthy that these catalysts show high activity by containing sulfate species, since catalysts for exhaust gas treatment are often sensitive to coexisting sulfur oxide. Iwamoto et al.[12] also reported that Cu-ZSM-5 is not deactivated by sulfur dioxide. The effect of treatment with sulfuric acid is probably related to the change of oxidation ability of the catalysts because medium oxidation activity of hydrocarbon is preferable for the selective reduction of NO to occur. However, the role of their acid properties in this reaction has not been clarified yet.

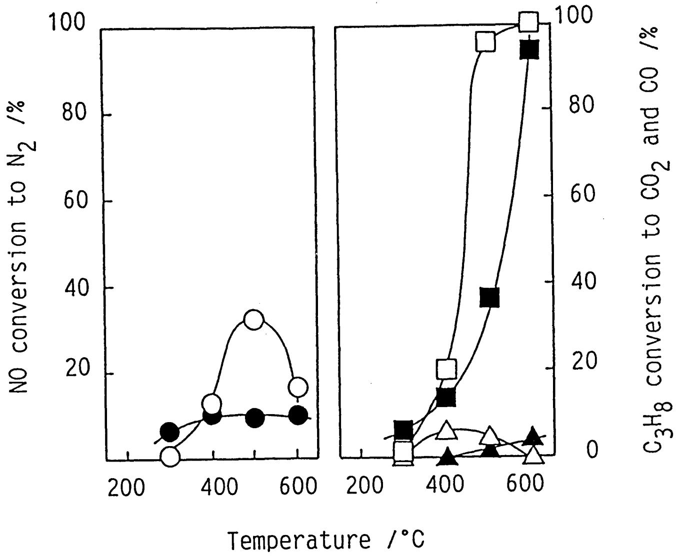

Fig. 4. Catalytic activity of Al_2O_3 and SO_4/Al_2O_3.
Conv. for Al_2O_3: ○, NO to N_2; □, C_3H_8 to CO_2; △, C_3H_8 to CO.
Conv. for SO_4/Al_2O_3: ●, NO to N_2; ■, C_3H_8 to CO_2; ▲, C_3H_8 to CO.

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(Received August 31, 1991)