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Selective Reduction of Nitrogen Monoxide with Hydrocarbons over SnO_2 Catalyst

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SnO_2 showed catalytic activity for the selective reduction of NO with hydrocarbons (C_2H_4, C_3H_8, and CH_4) in the presence of excess oxygen, and the activity was not so much decreased even after heat treatments in dry air at 900 °C as well as in humid air at 800 °C. These results show that SnO_2 is an active and stable catalyst for the reaction.

The selective reduction of nitrogen monoxide (NO) with hydrocarbons has recently attracted great attention because of its feasibility to reduce nitrogen oxides in an oxidizing atmosphere. In 1990, Iwamoto et al.$^{1)}$ and Held et al.$^{2)}$ independently reported that Cu ion-exchanged ZSM-5 (Cu-ZSM-5) showed high catalytic activity for the selective reduction of NO with hydrocarbons, and thereafter the following catalysts have been shown to catalyze the reaction; H-,$^{3)}$ Ce-,$^{4)}$ and Ga-$^{5)}$ form ZSM-5, Fe-silicate,$^{6)}$ Al_2O_3 with and without transition metal additives,$^{7-9)}$ Cu-loaded SiO_2-Al_2O_3,$^{10)}$ and sulfate-promoted TiO_2, ZrO_2, and Fe_2O_3.$^{11)}$ During investigations to develop new oxide catalysts which are active for the selective reduction of NO with hydrocarbons, we have revealed that SnO_2 is a good catalyst for the reaction, as reported in this paper.

SnO_2 catalysts were prepared by the calcination of hydrous SnO_2 at 600 °C and 900 °C for 4 h in air. Hydrous SnO_2 was obtained by treating metallic tin with heated nitric acid or by adding ammonia to an aqueous solution of $SnCl_4$, followed by filtration, washing with deionized water, and drying at 110 °C. SnO_2 prepared from metallic tin and $SnCl_4$ are referred to as SnO_2(m, T) and SnO_2(c, T), respectively, in which T represents the calcination temperature (°C). SnO_2(m) which was subjected to the heat treatment at 800 °C for 5 h in humid air (H_2O=10%) was denoted as SnO_2(m, 800HT). The selective reduction of NO with hydrocarbons was carried out with a fixed-bed flow reactor by feeding the reaction gas, NO(4400 ppm)–C_2H_4(4400 ppm)–O_2(4.4%)–He(balance), at a rate of 15 cm^3 min^{-1} over 0.25 g of catalyst. C_3H_8(2900 ppm) and CH_4(4400 ppm) were also used instead of C_2H_4. The effluent gas was analyzed by gas chromatography, and the NO reduction activity was evaluated by the conversion of NO into N_2. The selectivity to NO reduction is defined as [moles of NO reduced into N_2] / n × [moles of reacted C_nH_m] in this study.

Figure 1 shows the temperature dependence of the selective reduction of NO with C_2H_4 over SnO_2(c, 600). The reduction of NO into N_2 was observed above ca. 300 °C and the conversion of NO into N_2 showed a volcano-shape dependence on temperature with a maximum at 400 °C. C_2H_4 was converted practically into CO_2, though a slight amount of CO was detected below 400 °C. To confirm the promotion effect of coexisting oxygen, the effect of oxygen concentration on the NO reduction activity was investigated. In the absence of oxygen, NO reduction into N_2 started at around 500 °C, and the conversion of NO into N_2 increased monotonically with increasing temperature. In the presence of oxygen, on the other hand, the onset temperature of NO reduction into N_2 lowered as low as 300 °C and the maximum NO reduction activity was attained at 400 °C. This indicates that the coexisting oxygen promotes the reduction of NO with C_2H_4 over the present SnO_2 catalyst. The conversion of NO into N_2 and that of C_2H_4 at 400 °C over SnO_2(m, 600) are depicted in Fig. 2 as a function of the concentration of oxygen. At the oxygen concentration below ca. 4 vol%, conversions of both NO and C_2H_4 increased with an increase in oxygen concentration. Above ca. 4 vol%, on the other hand, an increase in oxygen concentration resulted in the slight decrease in the conversion of NO with the conversion of C_2H_4 remaining almost constant. The selectivity to NO reduction was 0.44(O_2=2%), 0.41(4.4%), 0.32(7%), and 0.28(10%). Accordingly, the steep increase in NO reduction activity at low oxygen concentration, where the selectivity is

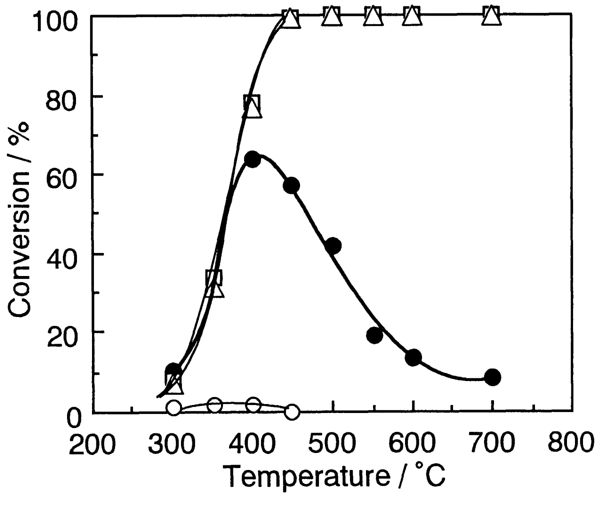

Fig. 1. Selective reduction of NO with C_2H_4 over SnO_2(m, 600). ●; Conversion of NO into N_2, □; Conversin of C_2H_4, △; Conversion of C_2H_4 into CO_2, ○; Conversion of C_2H_4 into CO.

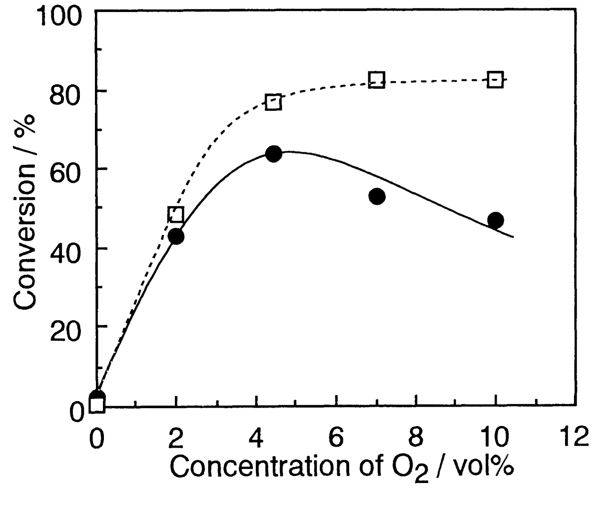

Fig. 2. Effect of the concentration of oxygen on the NO reduction activity of SnO_2(m,600) at 400 °C. NO(4400 ppm), C_2H_4(4400 ppm). ●; Conversion of NO into N_2, □; Conversion of C_2H_4.

almost constant, is due to the promotion effect of oxygen, while the slight decrease at high oxygen concentration is due to the decrease in selectivity. In view of the effect of oxygen concentration on the NO reduction activity, SnO_2 seems to be similar to transition metal-containing catalysts like Cu-ZSM-5[1)] rather than solid acid catalysts like Al_2O_3.[8)]

Effects of starting materials, calcination temperature and heat treatment in humid air on the NO reduction activity of SnO_2 were examined (Table 1). The NO reduction activities of SnO_2(m) and SnO_2(c) were comparable when calcined at the same temperature, indicating that the starting materials have little influence on the NO reduction activity of the resulting SnO_2 catalysts. The catalytic activity of SnO_2 was not so much decreased even after calcination at 900 °C. In addition, the treatment in humid air at 800 °C did not cause a serious decrease in activity, though the temperature for the maximum conversion rose from 400 °C to 450 °C; the NO reduction activity of Cu-ZSM-5 below 400 °C decreased tremendously by the treatment.[12)] These results strongly demonstrate that SnO_2 is an NO reduction catalyst resistant to the heat treatment in both dry and humid air. NO reduction activities of two representative catalysts, Cu-ZSM-5 and Al_2O_3, are also listed in Table 1; Al_2O_3(JRC-ALO-4) was the most active among various kinds of Al_2O_3 tested. Judging from the temperature at which the conversion of NO into N_2 reaches a maximum, the following order in catalytic activity is suggested; Cu-ZSM-5 > SnO_2 > Al_2O_3. Under the present experimental condition, the conversion of NO into N_2 over SnO_2 was comparable to that over Cu-ZSM-5 above 400 °C, though Cu-ZSM-5 was far more active at 300 °C. These results clearly demonstrate

Table 1. Catalytic activity of SnO_2, Cu-ZSM-5, and Al_2O_3 for the selective reduction of NO with C_2H_4

Catalyst	S.A.[a)]	Conversion of NO into N_2 / %					
	$m^2\ g^{-1}$	300 °C	400 °C	450 °C	500 °C	600 °C	700 °C
SnO_2(m, 600)	9.4	10.6	63.9	57.0	41.6	13.8	8.3
SnO_2(m, 900)	4.0	7.9	52.3	---	36.8	15.9	9.5
SnO_2(m, 800HT)[b)]	---	6.9	53.4	63.1	45.8	16.0	10.9
SnO_2(c, 600)	18.6	14.6	66.9	---	31.8	16.5	7.3
SnO_2(c, 900)	5.4	9.0	57.3	---	37.6	7.8	4.5
Cu(117)-ZSM-5[c)]	---	87.6	62.3	---	44.9	18.4	13.0
Al_2O_3(JRC-ALO-4)	---	11.3	19.5	---	29.2	56.8	18.5

a) Specific surface area. b) SnO_2(m) heat-treated at 800 °C for 5 h in humid air (H_2O=10%). c) Cu ion-exchanged ZSM-5 with ion exchange level of 117%, Reaction gas; NO(4400 ppm) – C_2H_4(4400 ppm) – O_2(4.4%) – He(balance).

that although the specific surface area of SnO_2 is rather smaller than those of Cu-ZSM-5 and Al_2O_3, SnO_2 is an efficient catalyst for the selective reduction of NO with hydrocarbons.

Temperature dependences of the NO reduction activity of SnO_2(m, 600) with CH_4, C_2H_4, and C_3H_8 are shown in Fig. 3. It is seen that the highest conversion of NO into N_2 and the lowest temperature for the maximum conversion are realized when using C_2H_4 as a reductant. The selectivity to NO reduction at the maximum conversion was the highest with C_2H_4 (0.41, 400 °C), followed by C_3H_8 (0.25, 450 °C) and CH_4 (0.17, 500 °C). These results show that C_2H_4 is the most efficient reductant among them over SnO_2. It should be noted that SnO_2 catalyzes the selective reduction of NO even with CH_4 though the conversion of NO into N_2 is about 10% at 500 °C under the present experimental condition.

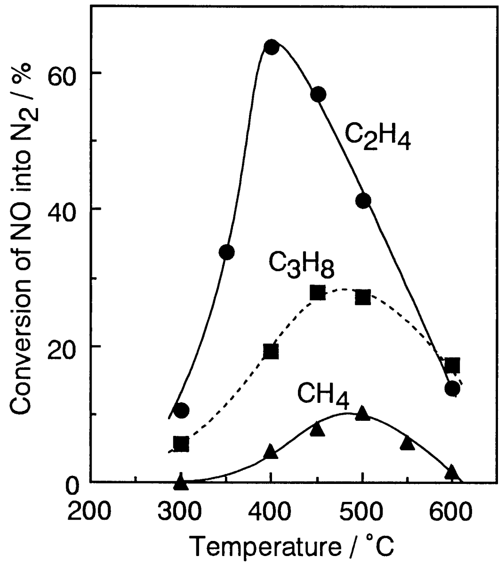

Fig. 3. Selective reduction of NO with CH_4 (4400 ppm), C_2H_4 (4400 ppm) and C_3H_8 (2900 pm) over SnO_2(m, 600). NO (4400 ppm), O_2 (4.4%).

In conclusion, this paper reveals that SnO_2 which exhibited relatively high activity and stability against the heat-treatment even in the humid condition is a good catalyst for the selective reduction of NO with hydrocarbons and thus a new candidate for NO reduction catalysts. Although C_2H_4 is a more efficient reductant than CH_4 and C_3H_8 over SnO_2, SnO_2 certainly shows the activity for the selective reduction of NO with CH_4.

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