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CATALYTIC ACTIVITIES OF ALKALINE EARTH METAL OXIDES FOR DISPROPORTIONATION OF NITROGEN MONOXIDE

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The disproportionation of nitrogen monoxide over alkaline earth metal oxides was carried out at 0°C. The catalysts were found to exhibit high activity for the formation of dinitrogen oxide from nitrogen monoxide. The order of the catalytic activity per unit surface area was obtained as MgO > CaO > SrO > BaO.

The disproportionation of NO on zeolites was reported by Addison and Barrer.[1] From the measurement of the specific gravity of the products they concluded that the reaction $4NO = N_2O + N_2O_3$ occurred on chabazite, faujasite and A-type zeolites at 0°C or lower temperatures. It was concluded the intracrystalline environment of the zeolites was especially favorable in promoting reactivity. In the present work, we report the disproportionation is catalyzed not only by the zeolites but also by alkaline earth metal oxides.

NO was obtained from Takachiho Chemical Industry Ltd. and further purified by removing NO_2 and H_2O. MgO and CaO were prepared by calcining the guaranteed reagents of $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ and $Ca(OH)_2$, respectively. SrO and BaO were prepared similarly from the carbonates, respectively. Before the reaction, the catalysts were treated at a given temperature for 14 hours in a stream of dry air, and then for 2 hours at the same temperature in a stream of helium. After these treatments, the catalytic activity was measured at 0°C by a pulse method with the catalyst, the amount of which gave the same surface area. After the reaction, the measurement of TPD profile was made. Effluent gas was periodically sampled by gas chromatography. As a result of the reaction, the gaseous product was only N_2O in agreement with the results of Addison and Barrer. The catalytic activity decreased markedly with further pulse numbers so that it was expressed by the rate of N_2O formation in the first pulse.

Figure 1 shows the effect of pretreatment temperature in the case of CaO catalyst. The catalytic activity per unit surface area is increased linearly as the pretreatment temperature is increased from 400 to 600°C and becomes almost

constant with further increasing pretreatment temperature. The increase of the catalytic activity may be caused by the removal of H_2O or CO_2 from the catalyst surface.

The catalytic activities of various alkaline earth metal oxides were measured after the pretreatment at 600°C. Figure 2 shows the relationship between the radius of the metal ion of the alkaline earth metal oxide and the catalytic activity per unit surface area. The catalytic activity becomes lower in accordance with the increase of ionic radius. In the decomposition of diacetone alcohol[2] as well as the esterification of benzaldehyde,[3] the order of the catalytic activity of the alkaline earth metal oxide was BaO > SrO > CaO > MgO and agreed with the order of the basic strength.[4] In the disproportionation of NO, on the other hand, the order of the catalytic activity agreed with the order of ionization potentials of the metal elements. The metal cations of the alkaline earth metal oxides seem to act as the active sites of the disproportionation. It must be noted that this order was the same as that[5] of the catalytic activity per unit amount of Site II cation of the Y-type zeolite exchanged with alkaline earth metal ion.

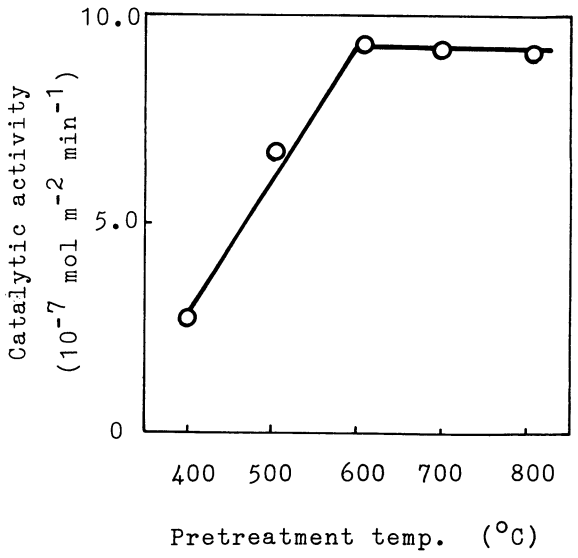

Fig. 1 Effect of pretreatment temperature on catalytic activity

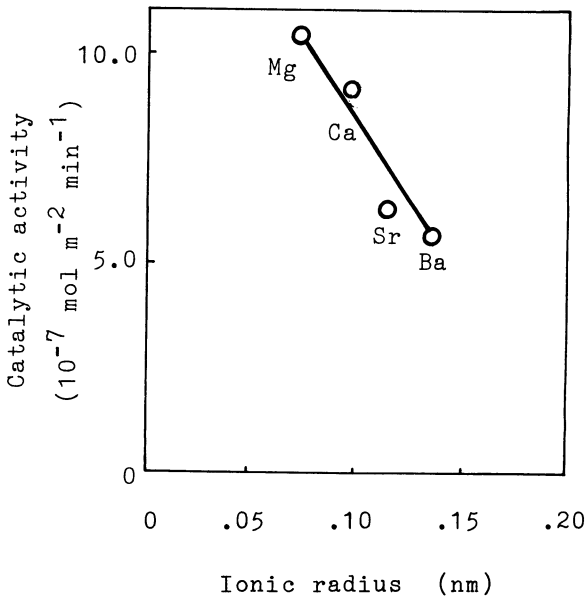

Fig. 2 Relationship between ionic radius and catalytic activity

The apparent activation energy was found to be -0.73 kcal/mol on CaO catalyst in the temperature range between -24 and 45°C. It was higher than that on CaY zeolite (-6.9 kcal/mol).[5]

In their study of sorption of NO on CaO, Low and Yang reported that N_2O had formed by way of disproportionation.[6] Fig. 3 shows TPD profile of NO adsorbed on CaO, which profile is gotten rid of NO_2 by use of dried NaOH. Three peaks around 45°C (peak A), 80°C (peak B) and 120°C (peak C) were found. From the analysis of desorbed gas, peak A and B mainly consisted of NO while N_2O contributed to peak C. Peak A is considered as the unreactive adsorbed NO and peak B seems to be NO arising from the decomposition of N_2O_3 formed by way of disproportionation : $N_2O_3 \rightarrow NO_2 + NO$. Peak C is regarded as the more strongly bonded N_2O. The amount of peak B was calculated to be 1.02×10^{-7}mol, on the other hand , N_2O which was formed by way of the reaction was 1.33×10^{-7}mol. Roughly speaking, the former is equal to the latter so that we can estimate the reaction ($4NO \rightarrow N_2O + N_2O_3$) was catalyzed by the alkaline earth metal oxides.

TPD profiles for the other alkaline earth metal oxides were composed of three peaks. The order of the amount of peak B agreed with that of the catalytic activity so that peak B could be regarded as the measure of the catalytic activity. TPD profiles for the alkaline earth cation-exchanged Y type zeolites were composed of three peaks.[5]

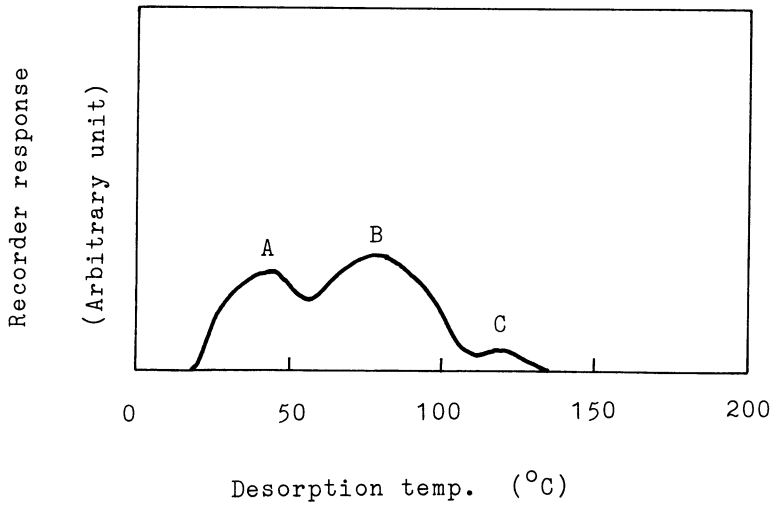

Fig. 3 TPD profile of NO adsorbed on CaO

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