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The Catalytic Decomposition of Nitrous Oxide on Titanium Dioxide; Anatase and Rutile

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Many investigations have been published on the catalytic reactions on various metallic oxides,[1] but few deal with the correlation between the catalytic activity and crystal form. From the studies on the catalytic oxidation of carbon monoxide on anatase and rutile, it was confirmed that the catalytic action of titanium dioxide differed with its crystal form.[2,3] In order to examine whether the same result is obtained in other reactions, the catalytic decomposition of nitrous oxide on titanium dioxide was carried out.

The catalytic decomposition of nitrous oxide on various metallic oxides[4] have been studied by many investigators, but there are few on titanium dioxide.

Experimental

The catalysts[2] used were anatase (A) of a guaranteed grade obtained from the East Merck Company, and rutile (R) and an anatase-rutile mixture (AR). The latter two were obtained by heating A at 1150°C for 3 hr and at 1050°C for 1 hr, respectively. Polymorphic forms of the three samples were confirmed by means of the X-ray diffraction method. The specific surface areas of the samples A, R, and AR estimated by the B.E.T. method using nitrogen as the adsorbate were 10.3 m^2/g, 1.0 m^{2}g, and 3.8 m^2/g, respectively. Nitrous oxide, oxygen, and nitrogen supplied from commercial cylinders were purified by vacuum distillation with liquid nitrogen, or by passing through a liquid nitrogen cooled trap.

The apparatus described in the preceding paper[2] was used. All precautions were taken to keep the samples from contamination. Traps were cooled with dry ice during the run to prevent grease and mercury vapors from the sample. Greaseless stop cocks were used between the traps and the sample tube. Prior to the measurements, the catalyst was pretreated in circulating oxygen of about 70 mmHg for 3 hr at 600°C for the cleaning of its surface.

It was ascertained by the analysis of the decomposition products that there are no side reactions to the main reaction, $N_2O \rightarrow N_2 + 1/2O_2$. The rate of the decomposition was determined by measuring the total pressure. It was confirmed that the gas phase decomposition of nitrous oxide was negligible under the experimental conditions.

Results and Discussion

The decomposition rates of nitrous oxide on three samples were measured under pressures 10^{-3}—80 mmHg at 600—800°C. The rates were proportional to P_{N_2O}. A typical result measured on anatase at 700°C is shown in Fig. 1. The decomposition rates did not change even when oxygen or nitrogen was intentionally introduced into the reaction system. The decomposition rate is thus represented by

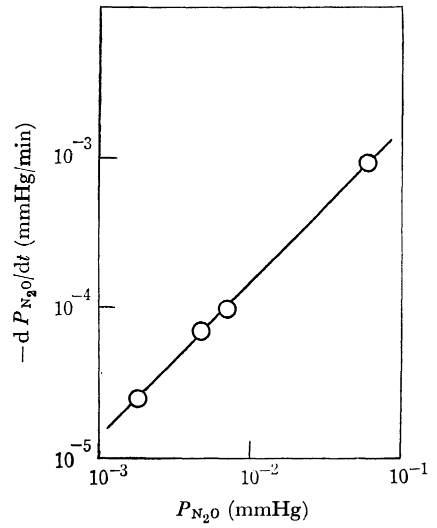

Fig. 1. Effect of N_2O pressure on the decomposition rate.

$$-\mathrm{d}(N_2O)/\mathrm{d}t = k_{N_2O} \cdot P_{N_2O} \qquad (1)$$

where k_{N_2O} is a constant. The Arrhenius plots of the k_{N_2O} values are given in Fig. 2. The k_{N_2O} value of rutile is much larger than that of anatase at the same temperature, as in the case of oxidation of carbon monoxide. The activation energies of anatase and rutile are 42.3 and 31.0 kcal/mol, respectively. The difference between these values, about 10 kcal/mol, is comparable to the difference in the activation energies of the oxidation of carbon monoxide and that of the thermal desorption of surface oxygen atoms from the catalysts in two crystal forms.[2]

On the catalytic oxidation of carbon monoxide on titanium dioxide,[2] the rate constants k were characteristic for both anatase and rutile, and the k values of the sample AR consisting of particles in both anatase and rutile forms were calculated by assuming that the

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[1] G. Parravano and M. Boudart, *Advan. Catal.*, **7**, 47 (1955); E. R. S. Winter, *ibid.*, **10**, 196 (1958); F. S. Stone, *ibid.*, **13**, 1 (1962).

[2] Y. Onishi and T. Hamamura, This Bulletin, **43**, 996 (1970).

[3] Y. Onishi, *ibid.*, **44**, 1460 (1971).

[4] G. M. Schwab and H. Schultes, *Z. Physik. Chem.*, **B9**, 265 (1930); C. Wagner, *J. Chem. Phys.*, **18**, 69 (1950); K. Hauffe, *Advan. Catal.*, **7**, 213 (1955); L. Rheaume and G. Parravano, *J. Phys. Chem.*, **63**, 264 (1959); I. Matsuura, Y. Kubokawa, and O. Toyama, *Nippon Kagaku Zasshi*, **81**, 377, 1205 (1960); H. B. Charman, R. M. Dell, and S. S. Teale, *Trans. Faraday Soc.*, **59**, 453 (1963); I. D. Gay and F. C. Tompkins, *Proc. Roy. Soc.*, **293**, 19 (1966); Z. Dzeventski, *Zh. Fiz. Khim.*, **40**, 2309 (1966); *Chem. Abstr.*, **66**, 14303a (1967); K. Tanaka and A. Ozaki, This Bulletin, **40**, 420 (1967); E. R. S. Winter, *J. Catal.*, **15**, 144 (1969).

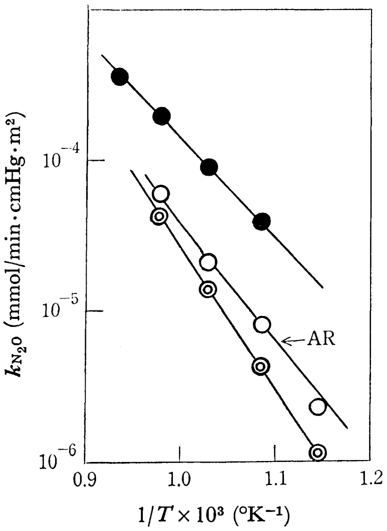

Fig. 2. Effect of temperature on the decomposition rate constant of nitrous oxide.
◎: A, ●: R, ○: AR

catalytic activity of an anatase-type surface and that of a rutile-type surface in AR were equal to those of pure anatase and rutile, respectively. The calculated values agreed well with the experimental values taken at different temperatures. The surface area ratio of the sample AR was estimated to be: anatase/rutile=86.8/13.2. Thus, if we assume that the rate constant k_{N_2O} is characteristic of the crystal form and the surface area ratio of two crystalline surfaces of the sample AR does not change, the rate constants k_{N_2O} of AR can be calculated by using the k_{N_2O} values of samples A and R. The calculated line of k_{N_2O} of the sample AR is shown by curve-AR in Fig. 2 with the experimental values shown by marks ○. The calculated line is in good agreement with the measured values.

It is found from the results that the catalytic action of titanium dioxide for the decomposition of nitrous oxide differs with its crystal form.

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