Decomposition of Nitrous Oxide on Manganese Sesqui-oxide

Ken-ichi TANAKA and Atsumu OZAKI

Reseaıch Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received July 11, 1966)

The catalytic decomposition of nitrous oxide has been adopted as a test reaction to investigate the catalytic action of an oxide surface. Dell, Stone and Tiley presented a reactivity series of pure oxides, showing a general tendency that *p*-type oxides were the best catalysts, *n*-type the worst and the insulator-type oxides occupying an intermediate position. Nevertheless, fundamental aspects of the reaction still remain unsolved, and, as Winter[1] pointed out, it is desirable to know more details about the kinetics and the state of the surface.

The importance of the direct measurement of the adsorption during the progress of reaction has already been emphasized by Tamaru.[2] The decomposition reaction of nitrous oxide might be a reaction in which the amounts of each adsorbed species (N_2O and O or O_2) during the progress of the reaction can be measured, in principle, since the nitrogen produced can not be adsorbed on the oxide surface. Tamaru's procedure was applied, in this report, to a measurment of the adsorption during the progress of the reaction.

Experimental

The apparatus employed for this experiment was a closed circulating system the volumes of which corresponded to 381 m*l* at 21°C with a reaction vessel at 269°C. The catalyst was prepared as follows: reagent-grade manganous carbonate suspended in an aqueous acetic acid solution was dried and heated slowly up to 430°C in a porcelain crucible, and then kept at that temperature for three hours. The oxide was then heated at 700°C for 13 hr. An X-ray pattern of the resulting oxide indicated α-manganese sesquioxide. The oxide so obtained was placed in the reactor and evacuated at 420°C for several hours. A surface-area determination, by means of the B. E. T. method using nitrogen as an adsorbate, gave a total surface area of 141 m^2 (10.8 m^2/g). Nitrous oxide, from a commercial cylinder, was purified by freezing it with liquid nitrogen and sublimating it at -78°C. Before initiating the experimental runs, the catalyst, evacuated at 420°C, was treated with nitrous oxide at the reaction temperatures and evacuated for a few minutes at that temperature. This procedure allowed us to obtain good reproducibility in one series of experiments. The analyses of the circulating gas, nitrogen, and oxygen were carried out by gas chromatography. The nitrous oxide composition was computed from the total pressure and the partial pressures of oxygen and nitrogen. The amounts of nitrous oxide and oxygen adsorbed on the catalyst surface were calculated from the material balance, *i. e.*, from the amount of nitrous oxide introduced, and the pressure and composition of the circulating gas during the reaction.

Results and Discussion.

A typical result of the decompostion at 269°C is shown in Fig. 1. As the decomposition proceeds, the partial pressure of nitrous oxide decreases with time, and those of nitrogen and oxygen increase; however, the adsorption of nitrous oxide and the reversible adsorption of oxygen are very small, and the dependency of these amounts on each partial pressure is obscure. The reaction rates are obtained from Fig. 1 by drawing tangents to the curve. In Fig. 2, the (P_{N_2O}/rate) values are plotted against the partial pressures of oxygen for a series of runs at different temperatures. A straight line can be drawn fairly well through the experimental points. No retardation was observed with nitrous oxide between 2.1 and 15

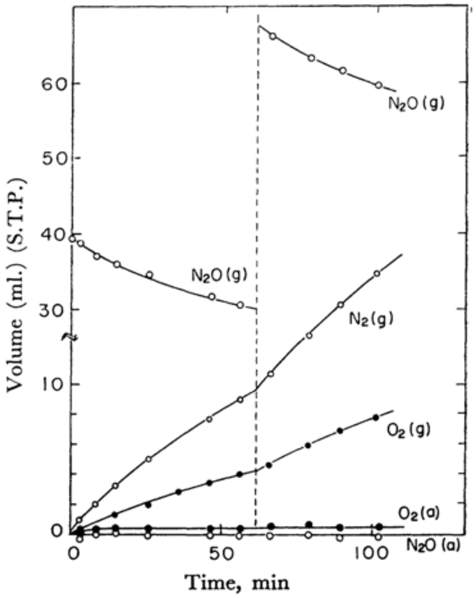

Fig. 1. Decomposition of nitrous oxide on α-manganese sesqui-oxide at 269°C.

---

[1] E. R. S. Winter, *Trans. Faraday Soc.*, **57**, 183 (1960).

[2] *Cf.* K. Tamaru, *Advances in Catalysis*, **15**, 65 (1964).

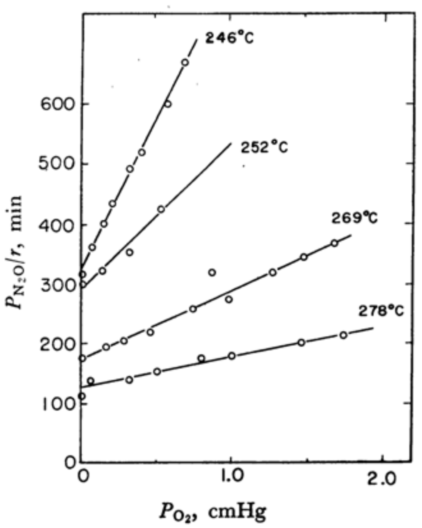

Fig. 2. Plots P_{N_2O}/rate *vs.* P_{O_2} for nitrous oxide decomposition on α-manganese sesqui-oxide at various temperaturs.

cmHg, and so the rate equation was written as follows:

$$r = \frac{kP_{N_2O}}{1+KP_{O_2}} \tag{1}$$

The kinetics obtained in this experiment differs from Rheaume and Parravano's result.[3)]

Equation (1) reveals that the available sites for the reaction should be occupied by oxygen molecules as the partial pressures of oxygen increase. However, the actual adsorption of oxygen during the progress of decomposition is very small, as is shown in Fig. 1. Assuming a monolyer coverage of oxygen molecules of 0.4 m*l*/m^2, it is obvious that even less than a 1% monolayer adsorption of oxygen effectively retards the reaction, since the value of $1/(1+KP_{O_2})$ at 269°C and $P_{O_2}=1$ cmHg is about 0.6. Thus, in this case, only a very small part of the catalyst surface is active in the decomposition of nitrous oxide.

The initial catalytic activity of the surface evacuated at about 400°C, *i. e.,* the surface untreated with nitrous oxide, was strikingly high, but it rapidly decreased as the catalyst took up the oxygen from nitrous oxide. The experiments were carried out on the surface which had a stabilized activity. Generally, the catalyst must be a reaction carrier; that is, it should repeatedly promote the reaction. A site such as that produced by a rigorous evacuation is inadequate as a catalyst, since such a site takes up oxygen strongly. On the other hand, the reaction can easily proceed on a site on which both oxygen and nitrous oxide are weakly adsorbed. In this experiment, after the treatment with nitrous oxide, a small part of the surface is available for the reaction; the measured adsorption reported here corresponds to the reversible adsorption on this site. The activation energy and heat of adsorption of the oxygen molecule on the active site are obtained by plotting the logarithms of the rate constant, *k*, and the adsorption equilibrium constant for the oxygen moleclue, *K*, obtained from Fig. 2, against the reciprocal of the temperature. These values are 17 kcal/mole and 23 kcal/mole respectively.

---

3) L. Rheaume and G. Parravano, *J. Phys. Chem.*, **63**, 264 (1959).