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Decomposition of Nitrous Oxide on Chromic Oxide

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The catalytic decomposition of nitrous oxide was studied with two differently prepared chromic oxides, Catalyst A and Catalyst B. It was found that the reaction proceeded on a limited part of the catalyst surface and the reaction rate could be expressed by the following equation for the two catalysts, $r = kP_{N_2O}/(1 + KP_{O_2}^{1/2})$. The adsorption of oxygen during the progress of the reaction increased approximately linearly with $KP_{O_2}^{1/2}/(1 + KP_{O_2}^{1/2})$ in the pressure range between 0.1 and 2.5 cm Hg; however, at oxygen pressures lower than this range, such a linear relation was not expected. This fact proves that the Langmuir-Hinshelwood assumption is established on the surface on which the active sites are partly occupied by oxygen adatoms.

The catalytic decomposition of nitrous oxide has been adopted as a test reaction to investigate the catalytic action of oxides, especially to deduce a relation between the catalytic activity and the semiconductivity of oxides. Dell, Stone, and Tiley (*1*) presented a reactivity series of pure oxides for this reaction as *p*-type oxides > insulator > *n*-type oxides.

Nevertheless, fundamental aspects of the reaction are unsettled, and, as Winter (*2*) pointed out, it is desirable to know more details about the kinetics and the state of the catalyst surface.

In order to throw some light on the state of the surface and on the role of the adsorbed species in catalysis, direct adsorption measurements during catalysis are desirable, as has already been emphasized by Tamaru (*3*). In a previous paper (*4*), the authors reported on the decomposition of nitrous oxide on manganese sesquioxide. The same procedure was applied, in this work, to the measurement of adsorption during the progress of reaction on chromic oxide catalyst.

EXPERIMENTAL

The apparatus employed for this experiment was a closed circulating system, the volume of which corresponded to 322 ml at 29°C with the reaction vessel at 436°C.

Two differently prepared chromic oxides were used: Catalyst A, reagent grade commercial chromic oxide, comprising 25g, had a specific surface area of 2.4 m^2/g (the BET method using nitrogen as an adsorbate); and Catalyst B, prepared by the thermal decomposition of ammonium dichromate in a porcelain crucible followed by heating at 700°C for 7 hr, comprising 4.7 g, had a specific surface area of 15.7 m^2/g.

The oxides were outgassed for 5 hr at 500°C and then were treated with nitrous oxide at the reaction temperature and outgassed for a few minutes at that temperature. These treatments gave stable and reproducible surfaces.

Nitrous oxide from a commercial cylinder was purified by freezing it with liquid nitrogen and subliming it at −78°C. The analysis of the circulating gas mixture, nitrogen and oxygen, was carried out by gas chromatography with a molecular sieve column. The nitrous oxide content was computed from the total pressure and the partial pressures of oxygen and nitrogen.

The amount of nitrous oxide and oxygen adsorbed on the catalyst during the progress of the reaction can be computed from the material balance, that is, from the amount of nitrous oxide introduced, and the pressure and composition of circulating gas during the reaction (nitrogen can not be adsorbed on the oxide surface).

Results

A typical result for Catalyst B is shown in Fig. 1. As the decomposition proceeds, the partial pressure of nitrous oxide decreases with time, and that of oxygen and nitrogen increase; simultaneously, the adsorption of oxygen increases with time (the amount of adsorption in Fig. 1 is expressed by the amount of oxygen atoms); on the other hand, the adsorption of nitrous oxide is very small. When the partial pressure of nitrous oxide was abruptly increased, the adsorption of oxygen changed little, but the rate of the reaction showed a marked acceleration.

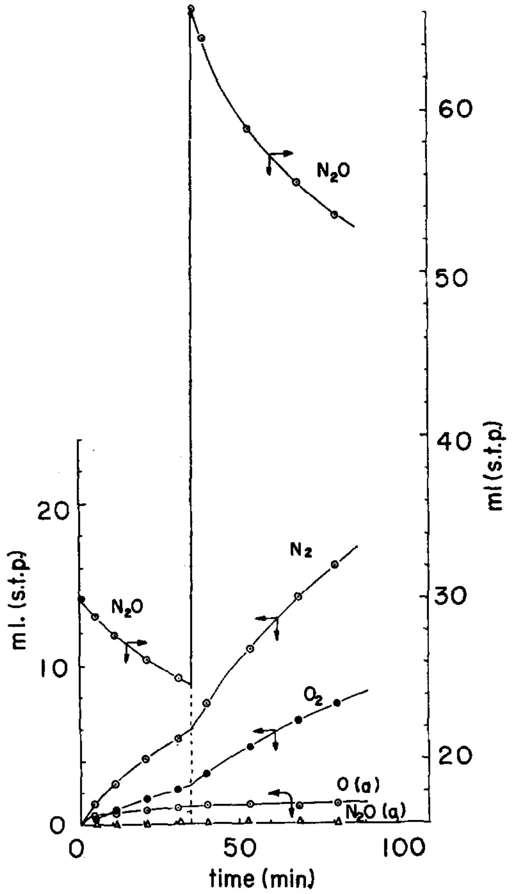

FIG. 1. Decomposition of nitrous oxide on Catalyst B at 430°C; (a) denotes adsorbed state.

The reaction rate was obtained by drawing tangents to the time-course curves of nitrogen evolved, and the resulting kinetic relations for Catalyst A and Catalyst B are shown in Figs. 2 and 3. These figures show that the values of P_{N_2O}/rate are fairly well proportional to the square root of oxygen pressures for a series of runs at different temperatures.

When oxygen was added to the circulating gas, the reaction rate was affected according to the same function, as shown in Fig. 2 (the filled circles in the figure). The retardation by nitrous oxide itself was not observed in the pressure range between 4 and 13 cm Hg. Accordingly, the following equation was established for the two catalysts:

$$r = \frac{kP_{N_2O}}{1 + KP_{O_2}^{1/2}} \tag{1}$$

where P_{N_2O} and P_{O_2} are the partial pressure of nitrous oxide and oxygen, respectively, and k and K are the constants.

Figure 4 shows the relation between the reciprocal of the square root of the oxygen pressure and the reciprocal of the adsorption of oxygen during catalysis. This figure shows that the adsorption of oxygen approaches the same limit as the oxygen pressure increases in the temperature range studied; owing to the scatter of results, an accurate value for the adsorption at infinite oxygen pressure is difficult to obtain, however, it can be concluded that the saturated adsorption of oxygen is about 1.0 ml (STP). (Note that the adsorption of oxygen in Fig. 4 is expressed by the amount of oxygen molecules, and the adsorption in Fig. 1 is expressed by the amount of oxygen atoms.)

The logarithms of the rate constant k and the adsorption equilibrium constant K in Eq. (1) are plotted against the reciprocal of the temperatures in Fig. 5. The apparent activation energies for Catalyst A and Catalyst B were 34 kcal/mole and 31 kcal/mole, respectively, and the heats of adsorption of oxygen on Catalyst A and Catalyst B were 20 kcal/mole and 23 kcal/mole, respectively.

Discussion

It is generally accepted that the p-type oxides are most active and the n-type oxides are least active for the decomposition of

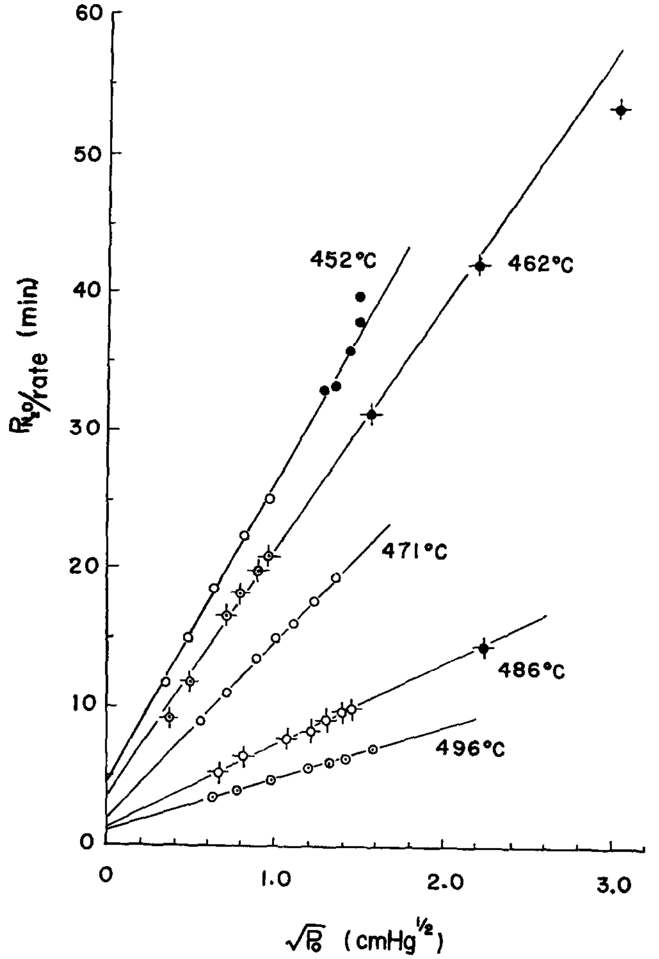

FIG. 2. Dependence of the value of P_{N_2O}/rate upon $(P_{O_2})^{1/2}$, Catalyst A.

nitrous oxide. Engell and Hauffe (*5*), assuming the rate-controlling step to be the desorption of oxygen, illustrated the above reactivity sequence on the basis of the boundary layer concept; the high activity of the *p*-type oxides was attributed to their low Fermi level.

If we postulate that the oxygen desorption is the rate-controlling step, the adsorption of oxygen should increase when the partial pressure of nitrous oxide is abruptly increased, which is contrary to the experimental result shown in Fig. 1; abrupt change of the partial pressure of nitrous oxide markedly influences the reaction rate, but the adsorption of oxygen changes little. This fact indicates the adsorption equilibrium of oxygen during the progress of reaction. The kinetic behavior of the oxygen added to the circulation system also supports the adsorption equilibrium (the filled circles in Fig. 2). If we assume that the rate of adsorption of nitrous oxide on the active sites is rapid and weak, that is, the surface decomposition of adsorbed nitrous oxide is the rate-controlling step, the reaction mechanism is described as follows:

$$\begin{aligned} &N_2O \rightleftharpoons N_2O(a) && K_1 \\ &N_2O(a) \rightarrow N_2 + O(a) && k_2 \\ &2O(a) \rightleftharpoons O_2 && K_3 \end{aligned}$$

and the rate equation is easily derived as follows, postulating the establishment of the Langmuir-Hinshelwood assumption,

$$r = k_2K_1P_{N_2O}/[1 + (K_3P_{O_2})^{1/2}] \qquad (2)$$

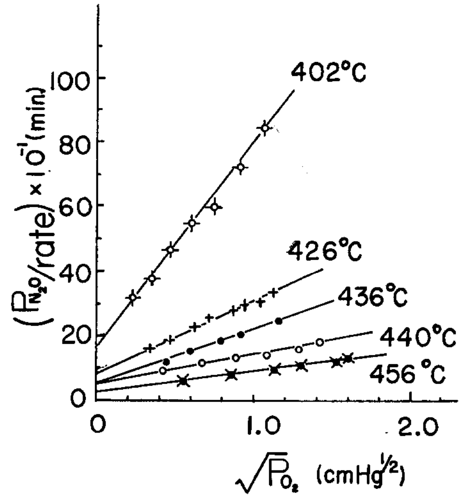

FIG. 3. Dependence of the value of P_{N_2O}/rate upon $(P_{O_2})^{1/2}$, Catalyst B.

where K_1 and K_3 are the adsorption equilibrium constants of nitrous oxide and oxygen, respectively, and k_2 is the rate constant at the rate-controlling step. It is obvious that the apparent rate constant k and the adsorption equilibrium constant K in Eq. (1) are defined as $k = k_2K_1$ and $K = K_3^{1/2}$, respectively.

Equation (2) indicates that the effective sites for the reaction should be occupied by the oxygen atoms and the occupation increases with the value of $(K_3P_{O_2})^{1/2}/[1 + (K_3P_{O_2})^{1/2}]$. It should be of interest to compare the actual adsorption of oxygen during catalysis with the values of $(K_3P_{O_2})^{1/2}/[1 + (K_3P_{O_2})^{1/2}]$ (coverages expected from the

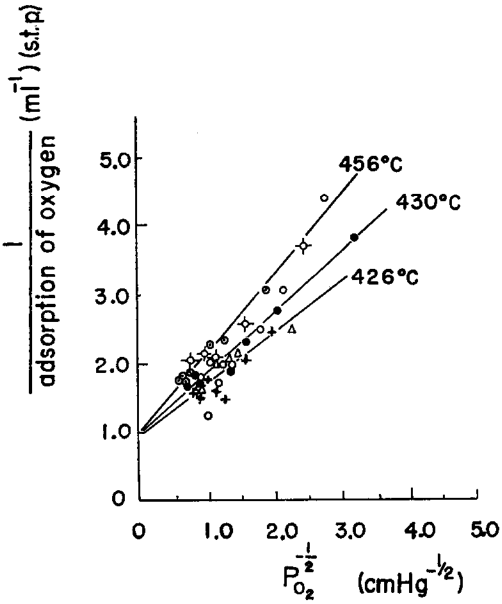

FIG. 4. Dependence of oxygen adsorption during nitrous oxide decomposition upon the pressure of oxygen over Catalyst B: ○, 402°C; △, 426°C; +, 430°C; -○-, 436°C; ⊙, 440°C; ●, 456°C.

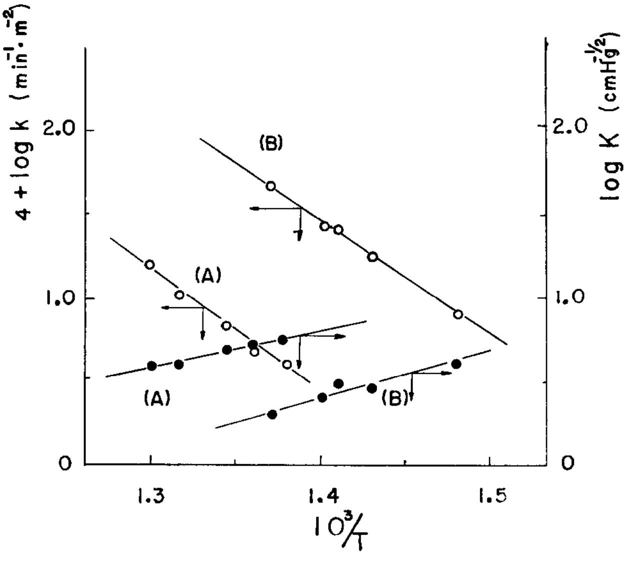

FIG. 5. Temperature dependence of the rate constant (k) and the adsorption equilibrium constant (K) of Catalyst A and Catalyst B.

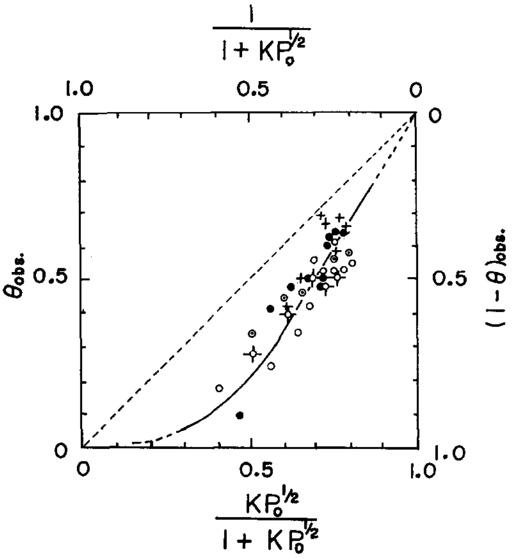

FIG. 6. Relationship between the coverages evaluated from the actual adsorption during catalysis (θ_{obs}) and the coverages expected from the kinetics, $(K_3P_{O_2})^{1/2}/[1 + (K_3P_{O_2})^{1/2}]$, on Catalyst B: ○, 402°C; ●, 426°C; +, 436°C; ⌖, 440°C; ⊙, 456°C.

rate equation). Figure 6 shows the correlation between the occupied fraction of the active sites given in terms of $(K_3P_{O_2})^{1/2}/[1 + (K_3P_{O_2})^{1/2}]$ and the coverages calculated from the actual adsorption [the value used for the saturated adsorption of oxygen was 1.0 ml (STP), and this saturation value was about 7% of a monolayer*].

If the adsorption takes place on the active sites which are homogeneous, the coverages evaluated from the actual adsorption should agree with the values of $(K_3P_{O_2})^{1/2}/[1 + (K_3P_{O_2})^{1/2}]$. However, the actual adsorption is lower than that expected from $(K_3P_{O_2})^{1/2}/[1 + (K_3P_{O_2})^{1/2}]$ in the temperature range studied. This discrepancy is notable at the initial stage of the reaction, that is, at the lower coverages of the oxygen. However, the actual occupation of the active sites changes approximately linearly with $(K_3P_{O_2})^{1/2}/[1 + (K_3P_{O_2})^{1/2}]$ on the surface on which the rate equation (1) is established. In this respect, the surface seems not to be homogeneous at the initial stage of the reaction, but it changes to a homogeneous one. Namely, in the pressure range studied (oxygen pressure was between about 0.1 and 2.5 cm Hg), the surface is homogenized and the Langmuir-Hinshelwood assumption is established on it. On the other hand, at oxygen pressure lower than that of the experimental range, the reaction mechanism is by no means certain and the Langmuir-Hinshelwood assumption would not be established.

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* The monolayer is defined as the coverage of 0.20 ml/m^2 (STP) of oxygen. Winter (*6*) reported that the saturation coverage of oxygen on Cr_2O_3 outgassed at 520°C was about 10% of a monolayer at around 450°C. The adsorption observed in this experiment was a reversible one in the temperature range studied (at around 430°C).