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Catalytic Reaction of Nitric Oxide and Chlorine over NH_4-Y Zeolite

It is well known that the reaction of nitric oxide and chlorine is a typical termolecular reaction and is reversible.

$$2NO + Cl_2 \rightleftharpoons 2NOCl. \qquad (1)$$

The reaction was, therefore, assumed to proceed by the homogeneous molecular reaction. Recently some experimental evidence has, however, been found that a part of the decomposition of nitrosyl chloride proceeds by other paths, atom mechanisms and heterogeneous mechanisms. Ashmore and Spencer (*1*) found evidence of a concurrent first order rate term in the decomposition in addition to the second order rate term which was attributed to the homogeneous molecular reaction. The additional rate term was attributed to heterogeneous reactions on the wall of the Pyrex reaction vessel. The activity of these surfaces after different treatments was correlated with the presence of surface hydroxyl groups of the vessel (*2*).

Zeolites have large surface area and have large amounts of surface hydroxyl groups. The amount of the hydroxyl groups of NH_4-Y zeolite varies by the change of the calcination temperatures (*3*). By using the zeolite as a catalyst, the reaction rate by the heterogeneous formation of nitrosyl chloride must be greater than the rate by the homogeneous molecular formation, and the correlation between the activity of the catalytic reaction and the presence of the surface hydroxyl groups must be revealed more clearly.

In this note the reaction of nitric oxide and chlorine over NH_4-Y zeolite calcined at various temperatures is described and the origin of the catalytic activity of the reaction is discussed.

The apparatus used consists of a 300 cc cylindrical Pyrex vessel equipped with an oil manometer which is connected with the vessel through a narrow tube filled with helium in order to prevent the oil (Dow Corning, 704 diffusion pump fluid) from direct contact with the reacting gases. The stopcocks used were Teflon greaseless ones to prevent the grease from absorbing the gases. NH_4-Y zeolite was prepared by ion exchange of the sodium ions of Y type zeolite with 10% aqueous solution of ammonium chloride and dried at 150°C for 2 hr. Sodium type of Y zeolite (SK-40) was supplied from Linde Division, Union Carbide. The percentage exchange of the ion was 70.5% measured with flame photometry. The surface area of the zeolite determined by nitrogen adsorption at liquid nitrogen temperature was 755 m^2/g. Nitric oxide and chlorine were supplied from Nihon Sanso Co. Ltd. and purified by repeated distillations. The zeolite was evacuated at temperatures 260, 350, 450 and 550°C) for 2 hr and chlorine was admitted at 250°C. Then nitric oxide was admitted into the vessel and 10 sec after admission, the stopcock was closed. After 1 min the first pressure reading was taken. Pressure readings were taken thereafter at convenient intervals. The readings were extrapolated graphically to zero time to get the initial pressure of nitric oxide. No products other than nitrosyl chloride were detected by gas chromatographic analyses of the reacting gases using 3-m ODPN column at room temperature. The initial rate was, therefore, obtained from the initial slope of the pressure–time curve. The room temperature was carefully kept at a constant temperature in the course of the

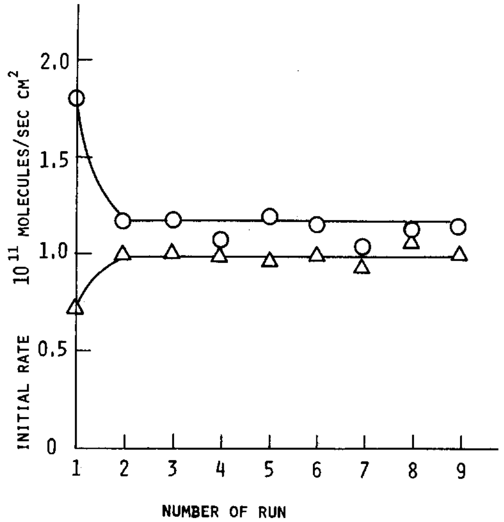

FIG. 1. Change in the initial rate. (○) Initial rate over NH_4-Y zeolite calcined at 550°C; (△) initial rate over NH_4-Y zeolite calcined at 260°C.

reaction to minimize the pressure change of the reacting gases caused by the change of the temperature.

The initial rate obtained in the first run showed an unsteady value and the rates in the subsequent runs showed steady ones as shown in Fig. 1. The subsequent run was carried out after 1 min evacuation of the reacting gases of the previous run at the reaction temperature, 250°C. The rate in the first run was higher than those in the subsequent runs over the zeolite calcined at a higher temperature (550°C). The rates in the first runs were lower than those in the subsequent runs over the zeolites calcined at lower temperatures (260–450°C). We have no ideas yet about the cause for the decrease or the increase of rates in the second runs over the zeolites calcined at the higher temperature or at the lower temperatures, respectively. The initial rates obtained in the first runs and the initial rates in the subsequent runs (steady rates) were plotted against the calcination temperatures of the zeolite as shown in Fig. 2. The rates were obtained with 20 Torr initial pressure of chlorine and with 10 Torr initial pressure of nitric oxide. The amount of the Lewis acid sites obtained by the adsorption of pyridine (*3*) or trinitrobenzene (*4*) increases as the temperature of the calcination is higher, but the amount of the Brönsted acid sites decreases (*3*). The catalytic activities obtained here are correlated better with the amount of the Lewis acid sites than that of the Brönsted acid sites of the zeolite.

The dependency of the steady initial rate on the initial pressure of nitric oxide was investigated over the zeolite calcined at 450°C. The initial rate obtained under a constant initial pressure of chlorine (18.8 Torr) was proportional to the initial pressure of nitric oxide ($P_{NO} \leqslant 20$ Torr). The steady initial rates obtained under a constant initial pressure of nitric oxide (7.8 Torr) were plotted against the initial pressure of chlorine as shown in Fig. 3. The rate may, therefore, be expressed as:

$$r_0 = kP_{NO}\frac{KP_{Cl_2}}{1 + KP_{Cl_2}}, \qquad (2)$$

where k and K are constants and P_{NO} and P_{Cl_2} are the initial pressures of nitric oxide and chlorine, respectively. Over H-mordenite which is also crystalline aluminosilicate, the rate determining step of the reaction expressed in Eq. (1) was concluded to

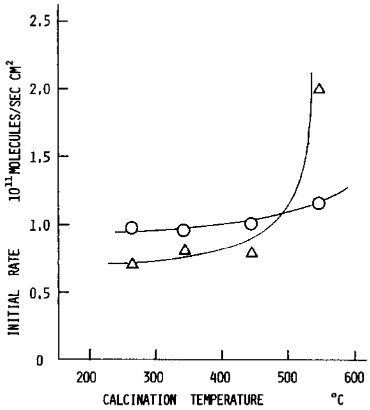

FIG. 2. Change in the initial rate is a function of calcination temperature of NH_4-Y zeolite. (△) Rate in the first run; (○) rate in the subsequent runs.

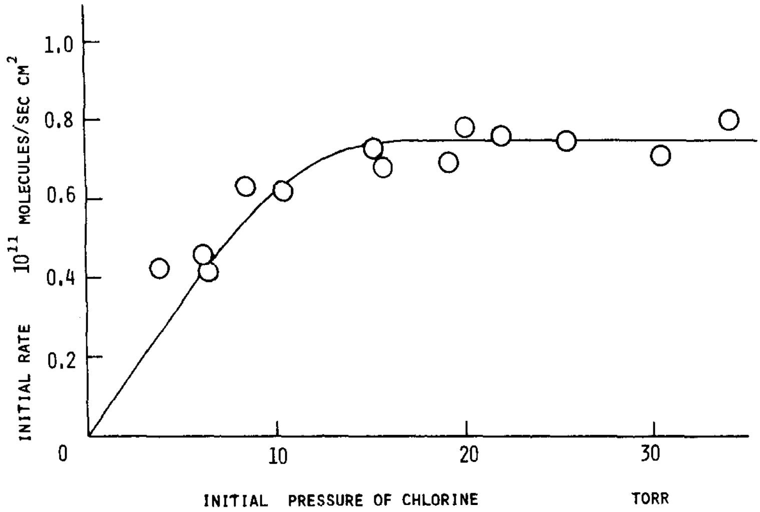

FIG. 3. Initial rate as a function of initial pressure of chlorine at 250°C over NH_4-Y zeolite calcined at 450°C. Initial pressure of chlorine, 7.8 Torr.

be the surface reaction of adsorbed nitric oxide and adsorbed chlorine (5):

$$NO(a) + Cl_2(a) \rightarrow NOCl(a) + Cl(a), \quad (3)$$

where NO(a), $Cl_2(a)$, NOCl(a) and Cl(a) are those adsorbed species. The initial rate of the reaction over H-mordenite at 250°C was also expressed in Eq. (2), and the rate determining step of the reaction over the zeolite may, therefore, be concluded to be the surface reaction as expressed in Eq. (3). The initial rate shown in Fig. 2 is proportional to the constant k in Eq. (2) under the experimental condition ($P_{NO} = 10$ Torr and $P_{Cl_2} = 20$ Torr). The constant k is written as the product of the rate constant of the surface reaction (3) and the adsorption equilibrium constant for the adsorption of nitric oxide (5). The constant k is, therefore, written as;

$$k = k_0 \exp\{-(\Delta E_a - H_a)/RT\}, \quad (4)$$

where ΔE_a is the activation energy of the reaction expressed in Eq. (3) and ΔH_a is the heat of the adsorption of nitric oxide. The heat of the adsorption ΔH_a leads to reduction of the apparent activation energy of the overall reaction written in Eq. (1). The rate shown in Fig. 2 may, therefore, show that the adsorption sites (Lewis acid sites), with large heat of the adsorption of nitric oxide, increased as the calcination temperature of the zeolite was high.

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