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The Catalytic Activity of the Zeolite–Hydrogen Chloride System

HIROSHIGE MATSUMOTO, KIYOSHI YASUI, AND YOSHIRO MORITA

From the Department of Applied Chemistry, School of Science and Engineering,
Waseda University, Nishiokubo Shinjuku-ku, Tokyo, Japan

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The catalytic action of the zeolite–hydrogen chloride system in cumene cracking was investigated using a flow apparatus. Though sodium faujasite (Linde Y) was completely inactive for the reaction at temperatures ranging from 250° to 350°C, its activity was reversibly induced by the introduction of hydrogen chloride to the reaction system.

Assuming the Langmuir adsorption of hydrogen chloride on zeolite in the reaction system, the reaction rate of cumene cracking was proportional to the coverage of hydrogen chloride. The hydrogen chloride effect on calcium faujasite could be treated in a similar manner to the case of sodium faujasite. The activation energy by the former was about two-thirds of that by the latter.

INTRODUCTION

On addition of hydrogen chloride, rare earth zeolites have attained high activity levels for reactions via carbonium ion intermediates, such as alkylation of benzene (*1*), isomerization of xylene (*2*), and disproportionation of toluene (*3*). These phenomena were due to the "promotive" action of hydrogen chloride, as the zeolites in rare earth form had considerable activity even in the absence of hydrogen chloride. In the present work, the "inductive" action of hydrogen chloride for inactive sodium faujasite (NaY) was studied in the dealkylation of cumene at low temperatures.

There are some difficulties in establishing the relationship between the catalytic activity of the zeolite and the amount of adsorbed hydrogen chloride on the zeolite. As the adsorption of hydrogen chloride effective for the reaction seems to be reversible, a constant activity cannot be obtained by a preliminary treatment of the zeolite with hydrogen chloride. In this work, therefore, the dealkylation of cumene was carried out under constant pressures of hydrogen chloride, in order to measure the activities at equilibrium states of adsorption. Another difficulty is that methods for measuring adsorbed amounts of hydrogen chloride in the working state are unknown. Therefore, this relation was obtained using the assumptions that the effective adsorption of hydrogen chloride on zeolite proceeds in accordance with the Langmuir equation, and that the activity of the catalyst can be shown by the initial rate of the reaction calculated from pseudo first order kinetics.

EXPERIMENTAL

The flow apparatus used for the dealkylation of cumene is shown schematically in Fig. 1. The carrier gas (hydrogen) from a high pressure cylinder was passed through a purification train of Pd and 5A Molecular Sieve to remove oxygen and water contaminants. The dried cumene and hydrogen chloride were pumped to the hydrogen stream at constant velocities from two gas-tight syringes driven with synchronous motors. The gases were premixed in the desired ratios and heated to reaction temperature prior to the catalysis. The reactor was constructed from a 7-mm diameter silica tube of 40-cm length with a constriction near the middle to hold a catalyst basket. Prior to the reaction, 0.1–0.6 g of the catalyst (zeolite) was treated in the hydrogen stream at 450°C for 2 hr. The partial pressure of cumene was maintained constant (36 mm Hg) in all the experiments. Through a six way cock, the reactor effluent mixture was led to a gas-chromatographic column for analysis. The reaction was carried out with the fresh zeolite in each case. The reaction product from cumene mainly consisted of benzene and propylene. Though a small amount of diisopropylbenzene, probably a disproportionation product of cumene, was formed at low reaction temperature under a high pressure of the reactant, the formation of this material was negligible when the reaction was carried out above 250°C and below 0.05 atm of cumene pressure.

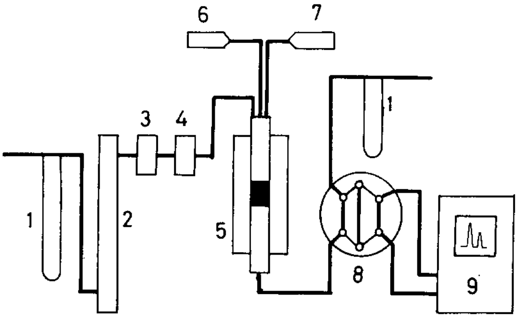

Fig. 1. Schematic diagram of reaction apparatus: 1, manometer; 2, flow meter; 3, Deoxo unit; 4, drier; 5, reactor; 6, microfeeder (HCl); 7, microfeeder (cumene); 8, 6-way cock; 9, gas chromatograph.

The amount of adsorbed hydrogen chloride on the zeolite was measured by a silica spring thermobalance. After similar pretreatment as in the case of the reaction, a hydrogen chloride–hydrogen mixture at a constant ratio was led to the zeolite sample suspended by the spring and then the stretch of the spring was measured.

The zeolite (NaY) was Linde Molecular Sieve Type Y and CaY was prepared by ion-exchanging NaY with a calcium nitrate solution. The remaining sodium ion content of CaY obtained was 20% equivalent.* Before use, commercial guaranteed grade cumene was dehydrated with metallic sodium, distilled, and passed through a silica gel column.

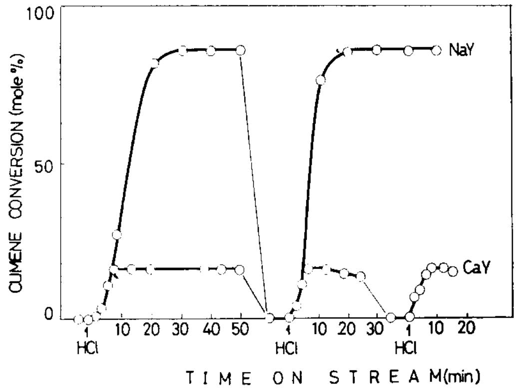

Fig. 2. Reversible action of hydrogen chloride for NaY and CaY. NaY: 350°, P_{cumene} = 36 mmHg, P_{HCl} = 51.4 mmHg, LHSV = 1.5 hr^{-1}. CaY: 250°, P_{cumene} = 36 mmHg, P_{HCl} = 51.4 mmHg, LHSV = 4 hr^{-1}.

RESULTS

Many workers have reported that sodium faujasite was completely inactive for the acid-catalyzed reactions of aromatic hydrocarbons. The catalytic activity for dealkylation of cumene was, however, strongly induced in this catalyst (NaY) by treatment with hydrogen chloride. The features of the hydrogen chloride effect on NaY are shown in Fig. 2, as the relation between the cumene conversion and the on stream period. The pretreated NaY was brought to 350°C in a stream of dried hydrogen and then a continuous flow of cumene was started. During this period no conversion of cumene was observed. On the introduction of hydrogen chloride to the reaction system, the conversion increased remarkably and reached a stationary value in 20 min. On interrupting the injection of hydrogen chloride to the system, the conversion fell and NaY again became inactive in an hour. On reintroduction of hydrogen chloride to the system, the same level of activity of NaY was regained. Thus, the catalytic activity of NaY was reversibly induced by hydrogen chloride. A similar reversible effect of hydrogen chloride was also observed in the case of calcium zeolite (CaY), as also shown in Fig. 2. On the other hand, both before and after treatment with hydrogen chloride under similar conditions, silica gel was inactive for cumene cracking. There-

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* The structure formula of the sodium zeolite used in this work was $\mathrm{Na_{57}(AlO_2)_{57}(SiO_2)_{135}}$.

fore, the activity enhancement of the zeolite–hydrogen chloride system cannot have resulted from the catalytic action of hydrogen chloride by itself, but is due to an interaction between zeolite and hydrogen chloride.

Several experiments were carried out under various hydrogen chloride pressures (P_{HCl}) to determine the activity dependence of NaY and CaY on the amount of hydrogen chloride. In Fig. 3, the cumene conversion is plotted against the P_{HCl} examined. The activities of both catalysts increased with the increase of P_{HCl} in the system.

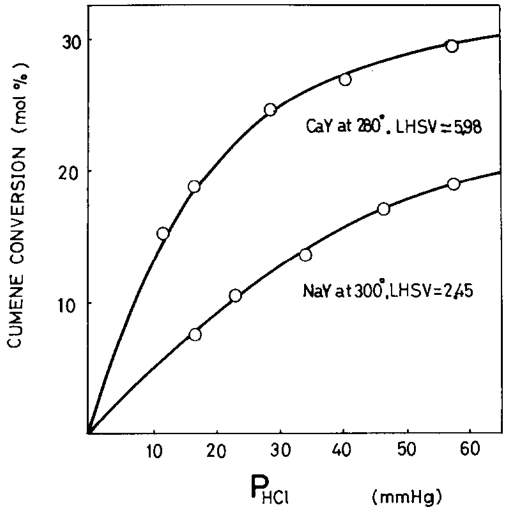

FIG. 3. Activities of NaY-HCl and CaY-HCl under various pressures of hydrogen chloride.

The pseudo first order character of cumene cracking was confirmed in the flow experiment over the zeolite–hydrogen chloride catalyst system. The rate of the cracking (r) is assumed at a constant pressure of cumene to be given by

$$r = \frac{dX}{d(W/F)} = k_f(1 - X) + k_b X \qquad (1)$$

where X, W, F, k_f, and k_b represent fractional conversion (mole %), amount of zeolite catalyst (g), flow velocity of cumene (g/hr), the constant for the cracking, and the constant for the back reaction, respectively. Using the value of equilibrium conversion (X_e),

$$k_f = \frac{F}{W} X_e \ln \frac{1}{1 - (X/X_e)} \qquad (2)$$

To test the equation, the conversion of cumene was observed over various weights of catalyst (NaY) at various velocities of cumene under a constant pressure of hydrogen chloride (9 mmHg) and at a constant temperature (330°C). When W/F was plotted against

$$\ln \frac{1}{1 - (X/X_e)}$$

a straight line resulted (Fig. 4). From this result, the effect of external diffusion was able to be neglected. Similar results were also obtained at other temperatures. When r_0 [r at $X = 0$ in Eq. (1)] is taken as the initial rate of cumene cracking, the value of r_0 is equal to that of the constant k_f.

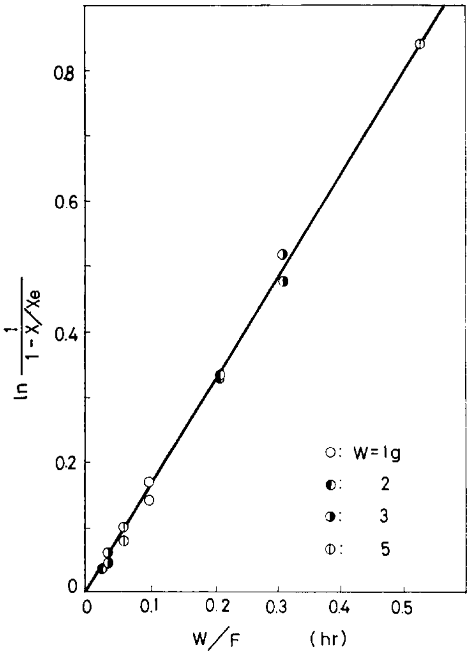

FIG. 4. Pseudo first order plot of cumene cracking with NaY-HCl at 330°C. P_{cumene} = 36 mmHg, P_{HCl} = 9 mmHg.

If it can be postulated that the action of hydrogen chloride on zeolite contributes to the formation of the active protonic acid sites, a direct relationship is expected between the activity and the amount of hydrogen chloride adsorbed on the surface. It is, however, difficult to measure the amount of adsorbed hydrogen chloride in the reaction system. Hence we treated the experimental

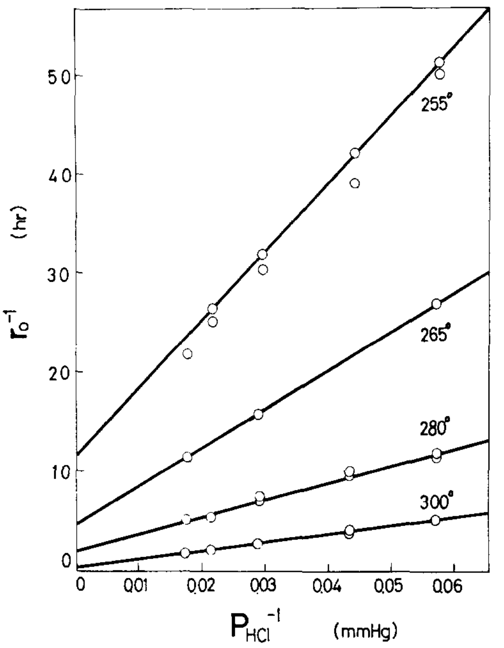

FIG. 5. Dependence of the reciprocal initial rate on the reciprocal pressure of hydrogen chloride (NaY-HCl).

results by two assumptions. One of these is the first order dependence of the initial rate of cumene cracking on the amount of the adsorbed hydrogen chloride on zeolite, the other is the Langumir adsorption of hydrogen chloride in the working state. Therefore, at a constant pressure of cumene

$$r_0 = k_{HCl}\theta = k_{HCl}\frac{AP_{HCl}}{1 + AP_{HCl}} \qquad (3)$$

where k_{HCl} and A are constants, and θ is the fraction of the surface occupied by hydrogen chloride. In accordance with Eq. (3), plots of the reciprocal initial rates against the reciprocal pressure of hydrogen chloride should be linear. Such plots for NaY and CaY at various temperatures have been obtained in Figs. 5 and 6, respectively. It is evident that the initial rates agree well with Eq. (3). In these plots, their intercepts of the vertical axis should provide the various k_{HCl}. Figure 7 shows the Arrhenius plots of k_{HCl} for NaY and CaY. The activation effect of hydrogen chloride for CaY seems to be more pronounced than for NaY. Furthermore, the apparent activation energy of the CaY-saturated hydrogen chloride system is about two-thirds of that of the NaY-saturated hydrogen chloride system.

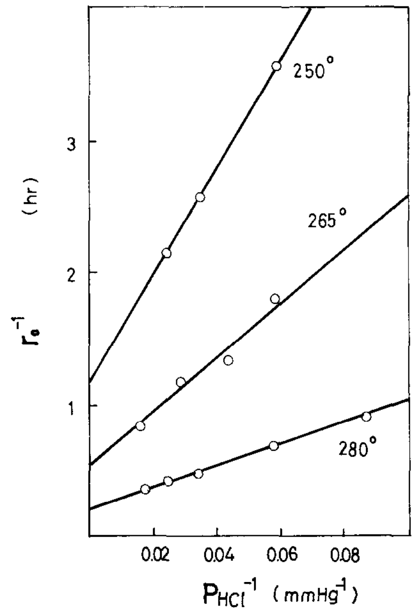

FIG. 6. Dependence of the reciprocal initial rate on the reciprocal pressure of hydrogen chloride (CaY-HCl).

DISCUSSION

The induction of catalytic activity upon introduction of a proton donor, such as

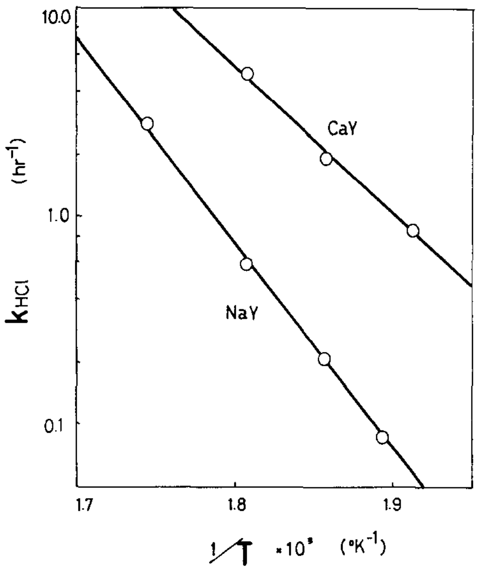

FIG. 7. Arrhenius plots showing temperature dependence of k_{HCl}.

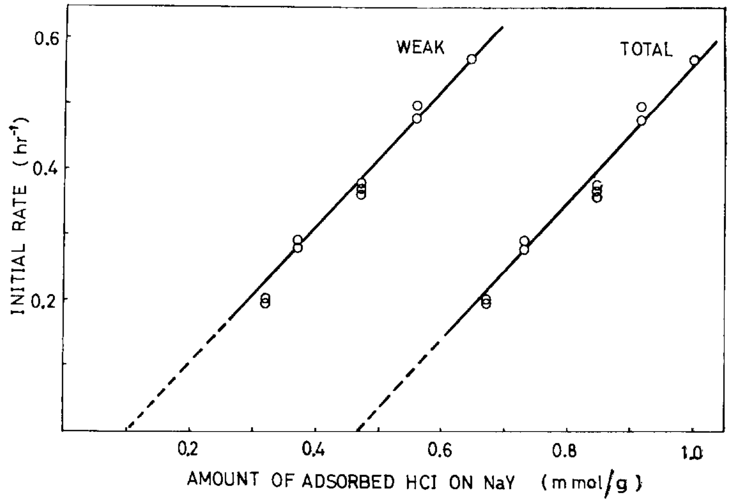

FIG. 8. The relation between initial rate and amounts of hydrogen chloride on NaY measured in the absence of cumene.

hydrogen chloride, suggests the role of protons in the reaction of cumene cracking. As described in many works, (1) the sites active for the decomposition of cumene to benzene and propylene should be the protonic acid sites.

Furthermore, inactive sodium zeolite attained a high level of cumene conversion by hydrogen chloride treatment and its catalytic activity seemed to be proportional to the amount of adsorbed hydrogen chloride. (2) The active sites may be formed by the adsorption of hydrogen chloride on zeolite.

It has been reported (*4*) that the catalytic activity of alumina was irreversibly promoted by a treatment with halogen compounds. This phenomenon appeared to depend on an exchange of halogen atom for oxygen atom or hydroxyl group on the surface. On the other hand, as the action of hydrogen chloride for zeolite was reversible, it is reasonable to consider that (3) hydrogen chloride seems to interact with the sodium cation rather than with the aluminosilicate framework of zeolite.

From these considerations, the active sites of the NaY–hydrogen chloride system may be formed by the reversible interaction between hydrogen chloride and the zeolite cation. As an example, the model of the sites is shown, as follows:

$$\underline{Na^+ \qquad Z^-} + HCl \rightleftarrows \underline{\overset{\overset{Cl^{\delta-}}{\downarrow}}{Na^{\delta+}} \qquad \overset{H^+ \text{ (active)}}{Z^-}}$$

where Z^- represents the anionic framework of zeolite. The interaction between CaY and hydrogen chloride also could be considered in a similar manner. By the X-ray examination, NaY almost maintained its crystallinity under these reaction conditions, while the lattice was destroyed when it was exposed in the stream of hydrogen chloride during a long period at an elevated temperature. Bertsch and Habgood (*5*) have suggested an analogous interaction of water with the cation by the IR study of water adsorbed on NaX. An activation energy difference between CaY and NaY (Fig. 7) is probably due to the activity difference of the protons which are formed by the interactions of hydrogen chloride with sodium ion and with calcium ion.

Now, the rates of cumene cracking by the NaY–hydrogen chloride system and the amounts of adsorbed hydrogen chloride on NaY in the absence of cumene were independently measured at the same temperature (300°C). As the hydrogen chloride effect was reversible in the reaction, we also measured the amount of the weak adsorption which was able to be desorbed at 300°C within 10 hr. These results are shown in Fig. 8 as the relation between the amounts of adsorption (weak and total) and the rates of cumene cracking. If the same value of the amount adsorbed could be expected both in the reactor and in the thermobalance under a constant pressure of hydrogen chloride, the cracking rate should be proportional to the amount of adsorbed hydrogen chloride within a restricted region of the amount. From this point of view, about 0.45 mmole/g in total adsorption or 0.1 mmole/g in the weak adsorption should be ineffective for the catalysis (from the intercept of the horizontal axis). Furthermore, as the curve of rate–weak adsorption was parallel to that of rate–total adsorption, the effective adsorption of hydrogen chloride may be involved in the weak adsorption and the hydrogen chloride strongly adsorbed on zeolite may be ineffective for the reaction. This consideration seems to be consistent with the reversibility of the hydrogen chloride effect (Fig. 2). However, the reason for the discrepancy of the rate–adsorption line from the origin is still obscure. This discrepancy seems to be due not only to an ineffective adsorption of hydrogen chloride but to a disturbance of the adsorption by the cumene molecule in the activity test, since aromatic hydrocarbon (π-base) may be influencing the sorption dynamics.

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