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Poisoning of Zeolite Catalyst with Ammonia

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In the acid-catalyzed reactions of hydrocarbons such as isomerization,[1] alkylation[2,3] and cracking,[4] the catalytic activity of zeolite increased with the amount of adsorbed water, which was controlled by thermal treatment of zeolite prior to being brought to catalysis. The activation energies of these reactions were, however, almost independent of the water content in zeolite.[1,2] The result suggests that the catalytically active surface of zeolite is regarded as homogeneous, while the existence of several different OH groups in the lattice was confirmed by IR measurements.[5] This work was carried out to confirm the homogeneity of the active surface of zeolite catalyst by means of partial poisoning with ammonia.

The reaction apparatus and its procedure were similar to those given in previous work.[6] Cumene cracking was chosen for the activity test of zeolite. The reaction was carried out at 350°C under a constant pressure of ammonia in order to measure the activity of zeolite at an equilibrium state of ammonia adsorption. The partial pressure of cumene was maintained constant (36 mmHg). Dried hydrogen was used as a carrier gas. Pretreatment of zeolite was done in a stream of hydrogen for two hours at a desired temperature and the resulting weight change was measured with a thermobalance. CaY Zeolite used in this work was prepared by the ion exchange of Linde Molecular Sieves (SK-40). The ion exchange level,

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[1] H. Matsumoto and Y. Morita, *Bull. Jap. Petroleum Inst.*, **11**, 40 (1969).

[2] H. Matsumoto and Y. Morita, unpublished data.

[3] P. B. Venuto, L. A. Hamilton and P. S. Landis, *J. Catal.*, **5**, 484 (1966).

[4] P. D. Hopkins, *ibid.*, **12**, 325 (1968).

[5] C. L. Angell and P. C. Schaffer, *J. Phys. Chem.*, **69**, 3463 (1965). J. B. Uytterhoven, R. Schonheydt, B. V. Lingme and W. K. Hall, *J. Catal.*, **13**, 425 (1969).

[6] H. Matsumoto, K. Yasui and Y. Morita, *J. Catal.*, **12**, 84 (1968).

Table 1. Cracking activity of CaY pretreated at various temperatures

Pretreatment temperature (°C)	350	400	450	500	550
Amount of adsorbed water (mg/g)	11.4	8.9	6.7	5.2	4.1
Cracking rate[a] (g/g hr)	0.982	1.080	0.809	0.657	0.558

a) Initial rate determined by first order kinetics.

defined as the percentage of the original sodium ion replaced, was determined to be 70.

The cracking activity of CaY zeolite pretreated at various temperatures is shown in Table 1 in comparison with the amount of adsorbed water. Water content and catalytic activity of CaY decreased with the rise of pretreatment temperature. The active protonic sites of zeolite may be produced by the adsorption of water.[7] A low activity of CaY pretreated at 350°C was due presumably to poisoning by the adsorption of excessive water on the active surface.

The catalytic activity of CaY zeolite considerably decreased by the addition of ammonia to the reaction system. The relation between the cumene conversion and the on-stream period is shown in Fig. 1. CaY pretreated at 450°C was brought to 350°C in a stream of hydrogen and then a continuous flow of cumene was started. During this period 40% of the conversion was observed. On the introduction of 8.23 mmHg of ammonia to the system, the conversion decreased sharply and reached the stationary value of 16% within 10 min. Cumene conversion decreased with the increase of ammonia pressure in the system. When the pressure of ammonia decreased, the conversion again increased. In this series of runs, the same conversion was obtained under the same partial pressure of ammonia. Thus, the poisoning of CaY with ammonia was completely reversible and the establishment of equilibrium was expected between the ammonia in the gas phase and that adsorbed on the active surace of zeolite.

If we postulate that the decrease in the activity of zeolite depends in first order on the amount of adsorbed ammonia, the initial rate of the reaction, r, will be expressed by the equation

$$r = r_0(1-\theta),$$

where r_0 stands for the initial rate in the absence of ammonia and θ for the fraction of the active surface occupied by ammonia. The poisoning effect of ammonia may be expressed as a function of ammonia pressure in the system (P_{NH_3}), postulating the establishment of the Langmuir assumption for the effective adsorption of ammonia on the active

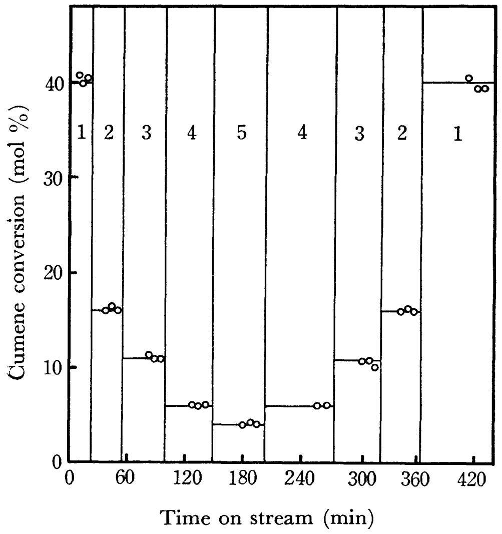

Fig. 1. Reversible poisoning of CaY with ammonia.

Pressure of ammonia;
1 0 mmHg
2 11.5
3 16.4
4 31.9
5 42.3

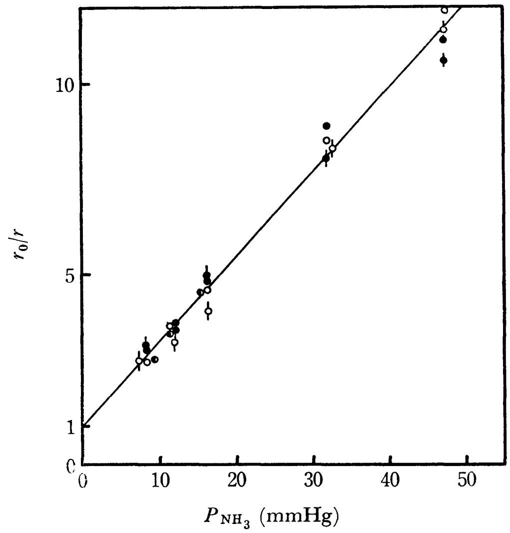

Fig. 2. Pressure dependence of ammonia poisoning of CaY pretreated at various temperatures.

CaY pretreated at
● 350°C
○ 400
○ 450
● 500
◑ 550

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[7] J. W. Ward, *J. Catal.*, **10**, 34 (1968); H. Hattori and T. Shiba, *ibid.*, **12**, 111 (1968).

surface of zeolite. Thus, the ratio of these initial rates, r_0/r, was evaluated by the simple relation under a constant pressure of the reactant

$$r_0/r = 1 + K \cdot P_{NH_3},$$

where K represents the constant of ammonia adsorption effective for the catalysis.

In accordance with this equation, plots of the ratio of initial rates against the pressure of ammonia should be linear. Such plots for CaY zeolite pretreated at various temperatures have been obtained in Fig. 2, where the initial rate of cumene cracking was determined by first order kinetics.[6] The data evidently satisfy the above equation. As evident from Fig. 2, the adsorption constant K was approximately independent of the pretreatment temperature (or the water content) of the zeolite, on which the catalytic activity strongly depends. This probably indicates that the catalytically active surface of CaY is nearly homogeneous.