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Effects of Cation Exchange on the Acidity and the Catalytic Activity of Type A Zeolite

It is well known that the catalytic properties of zeolites are markedly affected by the particular cation present, which is required to balance the negative framework charge. The studies on the catalytic activity and the active site of Type X and Y zeolites exchanged with various cations are too numerous to mention. However, that of Type A zeolite is not sufficient. Recently, the indirect investigations such as spectroscopy (*1*) and sorption property (*2,3*) give a clue to know the positions of cations in zeolites A and to understand the catalysis of zeolites A better. In the present work, we studied the changes in the surface acidity and ethanol dehydration activity of zeolites A containing Ca^{2+} and Zn^{2+} as cations, and attempted to gain information on Zn^{2+} positions in zeolite A and the active sites for dehydration.

The starting material was powdery Linde molecular sieves 5A, which contains Ca^{2+} (76%) and Na^+ (24%) as cations. The ion exchange was carried out 85°C for 10 hr by immersing the 5A in a solution of $CaCl_2$ to prepare complete Ca-form and by immersing the Ca-form in a solution of $CaCl_2 + ZnCl_2$ to prepare the zinc-exchanged zeolites A (Ca–Zn–A). After exchanging and drying for 10 hr at 120°C, the sample was stored over saturated ammonium chloride solution to ensure a constant of zeolitic water. The degree of ion exchange was determined by chemical analysis and flame photometry. Retention of crystal structure, after ion exchange and heat treatment, was confirmed by X-ray diffraction pattern and the BET surface area measurements. The acidic property of the sample preheated at 400 and 600°C in air was determined by a usual Hammett indicator method (*4*).

The catalytic activity for the dehydration of ethanol was estimated from reaction in a pulse microreactor connected to a gas chromatograph. The catalyst sample was preheated for 3 hr at 400 and 600°C in air before use. The reaction temperature was set at 350°C. The conversion of ethanol was taken as the activity.

Table 1 shows the physical and chemical properties of Ca–Zn–A. The surface area and X-ray diffraction patterns of all the samples did not change, even after heat treatment at 700°C, compared with those of the original 5A. This indicates that the zinc-exchanged zeolites are stable, in contrast to the earlier conclusion by Barrer and Meier (*5*). The maximum acid strength of surface sites of Ca–Zn–A was -5.6 in terms of H_0 unit, and it did not vary with the zinc content. The total amount of acid sites of $H_0 \leqq +4.8$ increased with the degree of exchange. The acid sites on Ca–A and Zn–A preheated at 400°C are Brönsted sites, as has been reported by the authors (*6*). It is, therefore, suggested that the active sites are the Brönsted acid sites. Ward (*7*) has reported that the Brönsted acid sites of Type Y zeolites increase with increasing electrostatic field (e/r_i), where r_i is ionic radius of cation exchanged. Here r_i of Zn^{2+} is smaller than that of Ca^{2+}. Therefore, Zn^{2+} ions dissociate water molecules coordinated to them and form protons more than Ca^{2+} ions do, and it would result in an increase of the Brönsted acid sites.

On the other hand, zeolite A has three kinds of cation sites (*8*): site I (SI) is near the centers of the six-oxygen rings, site II (SII) is near the centers of the eight-oxygen rings and site III (SIII) is near a four-oxygen ring; it was shown that Ca^{2+}

TABLE 1

PHYSICAL AND CHEMICAL PROPERTIES OF ZEOLITES A EXCHANGED WITH Ca^{2+} AND Zn^{2+}

% Exchanged Zn/(Ca + Zn)	Surface area[a] (m^2/g)	X-Ray peak intensity[b]	Maximum acid strength,[a] H_0	Acid amount[c] (mmol/g)	
				400°C[d]	600°C[d]
0	673	133	−5.6	0.038	0.020
6.3	—	—	−5.6	—	—
30	639	111	−5.6	0.065	0.032
41	—	—	−5.6	—	—
64	618	112	−5.6	0.10	0.051
86	—	—	−5.6	0.14	—
98	631	112[e] 118	−5.6	0.15	0.070

[a] Preheated at 400°C. The original 5A: 676 m^2/g.

[b] Uncalcined and hydrated samples. Sum of peak heights for (311), (321) and (410, 322) planes. 5A: 146.

[c] $H_0 \leqq +4.8$.

[d] Preheating temperature.

[e] Hydrated after preheated at 700°C.

ions strongly prefer SI sites by X-ray crystallography (*9*) and molecular sieving properties (*2,10*). Mn^{2+} and Co^{2+} ions are also found in SI sites in a recent investigation (*11*). From the analogy to those divalent cations, it would be reasonable that Zn^{2+} ions occupy SI sites preferably. The site selectivity of Zn^{2+} is supported by the result of the activity presented below.

Figure 1 shows the catalytic activity of Ca–Zn–A for ethanol dehydration, and it contains also the results of Type Y zeolites for comparison (*12,13*). The activity of Ca–Zn–A preheated at 400°C increased linearly with the degree of ion exchange. There is a good correlation between the increase of the activity and that of the acid amount. Therefore, it may be concluded that the Brönsted acid sites could very well be responsible for dehydration activity. Bryant and Kranich (*14*) have reported the result of ethanol dehydration on zeolites A exchanged with various cations, but they have not revealed the active sites. When Ca–Zn–A preheated at 600°C was used as catalyst, the dehydration activity was decreased. This is due to the decrease in the acid amount. The decrease in activity more than the decrease in acid amount may be due to the loss of stronger acid sites, such as $H_0 = -5.6$ and -3.0. At the same time, a small amount of acetaldehyde was detected in the products. As has been ascertained elsewhere (*6*), the zeolites A preheated at 600°C have a small amount of Lewis acid sites in addition to a remaining small amount of Brönsted sites. The formation of acetaldehyde may be due to the Lewis acid sites.

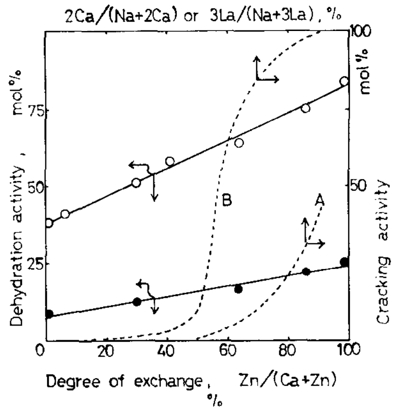

FIG. 1. Change of catalytic activity with degree of ion exchange. (○) Preheated at 400°C; (●) preheated at 600°C; (A) hexane cracking by Na–La–Y at 350°C, Ref. (*12*); (B) cumene cracking by Na–Ca–Y at 450°C, Ref. (*13*).

In the studies of cation-exchanged zeolites, the linear relationship between the catalytic activity and the degree of ion exchange is not found in literature. It is generally known that Type Y zeolites exhibit an activity change with the degree of exchange as shown by broken lines in Fig. 1, i.e., when the replacement of Na^+ ions by Ca^{2+} or La^{3+} ions exceeds ca. 60%, the catalytic activity is set up sharply. The behavior was well explained by Tung and McInich (*12*) and Tsutsumi and Takahashi (*13*). Briefly, the nonlinear change indicates that cations occupy two kinds of sites which are accessible and inaccessible to reactant molecules.

In the present case, if Zn^{2+} ions occupy SII sites in zeolite A different from Ca^{2+} ions, the activity curve of Ca–Zn–A should be nonlinear and bend at a cartain degree of ion exchange. Because the Zn^{2+} ions entered SII sites make the effective pore size of zeolite A smaller and consequently bring about a diffusion hindrance to reactant molecules. However, such a fact was not present in Fig. 1. This supports that Zn^{2+} ions in zeolite A are situated in SI sites which Ca^{2+} ions occupied, as analogized above.

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