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The Effect of Ion Exchange on the 1,2-Epoxybutane-Isomerization Activity[1,2]

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Synopsis. The isomerization of 1,2-epoxybutane was studied over NaA-type zeolite and its zinc-exchanged forms in a flow system. The catalytic activity increased from 31 to 92% upon the replacement of Na^+ by Zn^{2+}. This increase may be the consequence of the enlargement of the zeolite pore size and the increase in the surface acidity.

We reported previously that the synthetic A-type zeolites exchanged with various cations are effective as catalysts in 1,2-epoxybutane (EB) isomerization.[1] It was shown that the catalytic activity depends upon the surface acidity, which varies with the kind of cation. It may, then, be expected that the degree of ion exchange also has an influence on the acidity and activity.

In this paper we will deal with the effects of the degree of ion exchange on the EB isomerization activity and on acidity of zinc-exchanged A-type zeolite.

Table 1 shows various properties of A-type zeolites exchanged with the zinc ion. The X-ray diffraction patterns and specific surface areas of all the catalysts (ZnA=sample II-VIII) were similar to those of the original Linde 4A(NaA=sample I) and showed ZnA to be highly crystalline.

The products of the EB isomerization reaction were BA, CA_c, CA_t, EMK, and a small amount of *n*-butyl alcohol (NB). Sample I showed no catalytic activity under the conditions studied here. Figure 1 shows the correlation between the catalytic activity and the extent of zinc ion exchanged on ZnA. As is evident from Fig. 1, ZnA begins to show the catalytic activity slightly when the extent of exchange exceeds 30%, the activity increases rapidly as the extent of exchange exceeds 50%, and then becomes almost constant in the range above 80%. This suggests that any comparison of the catalytic activity among zeolites exchanged with various cations, which are of widely differing degrees of ion exchange, should be done with extra care. The order of activity of cation-exchanged A-type zeolites will be effective only when the degree of ion exchange is either the same or $\geq 80\%$.

Many authors have already reported on the influence of the degree of ion exchange on the activity of zeolite catalysts.[4-6] All of their studies, however, have been of X- and Y-type zeolites. Type-A zeolites have hardly been investigated at all.[7] X- and Y-type zeolites with large pores (9—10 Å) also show an activity change with the degree of ion exchange similar to that described above. Those zeolites have three kinds of cation sites.[6] When the replacement of cations at inactive sites is achieved, *i.e.*, when the degree of ion exchange exceeds *ca.* 50%, the activity increases suddenly.

In the case of the A-type, however, the effective pore size of zeolite should be considered aside from the above interpretation, because the cation sites of the A-type differ from those of the X- and Y-types and the size of the reactant molecule is close to the pore size. The molecular size of EB** is larger than the effective pore size of NaA(4.2 Å). The reactant molecules cannot, therefore, pass the pore and are not adsorbed on the internal surface(cavity of zeolite). Consequently, Samples I, II, III, and IV, which are Na-rich forms, are inactive for isomerization. The effective pore size of the A-type is determined by the number and species of cations at the 8-membered oxygen-ring sites, as has been pointed out by Breck *et al.*[8] and Takaishi and Yusa.[9] Takaishi and Yusa have proposed cation-exchange scheme as below to account for the adsorption phenomena of ZnA. The A-type zeolite has two types of cation sites; that is, there are 3 of the 8-membered oxygen ring sites and 8 of the 6-membered oxygen ring sites per unit cell. A total of 12 mon ovalent cations per unit cell are distributed among those sites (see Ref. 9). When 2 Zn ions are introduced (*i.e.*, when the Na ions at the 8-ring sites and the 2 Na ions at the 6-ring sites are replaced (4/12=33%)), the effective pore size becomes 5 Å since 2 Zn ions are located at the 6-ring sites and one of the 8-ring sites is vacant, and the adsorption of *n*-butane begins to occur.[10] At a point corresponding to the replacement of 4 Zn ions for 8 Na ions(8/12=67%) all the 8-ring sites become vacant and molecules of about 5Å size can freely

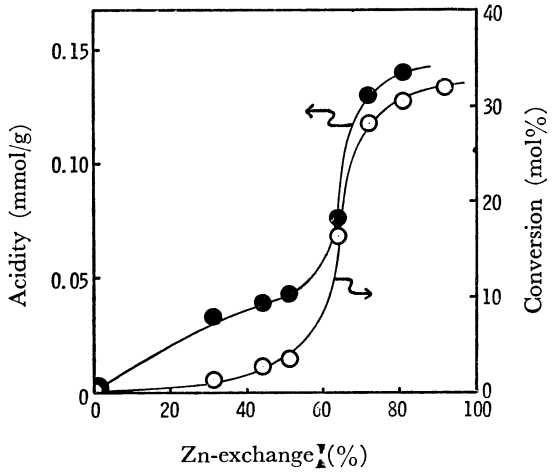

Fig. 1. Change of catalytic activity and acidity with degree of ion exchange.
○: Conversion of EB, ●: Acid amount at $H_0 \leqq +4.8$

* In our paper the "4A" zeolite, which contains only sodium as a cation, is designated as NaA, while forms in which sodium has been exchanged to even a slight degree with the zinc ion are designated "ZnA,"

** About 4.9 Å; estimated from *n*-butane: 4.89 Å; tehane: 4.2 Å; ethylene oxide: 4.2 Å.

Table 1. Various properties of ZnA type zeolites

Sample	Zn-exchanged (%)	Surface area (m^2/g)	Diffraction peak intensity[b]	ΔE_a[c] (kcal/mol)	Selectivity (BA+CA)/EMK	Acid strength[d] (H_0)
I	0	659[a]	144	0	—	$>+4.8$
II	31	—	128	11.2	39.2	-5.6
III	44	—	133	23.6	37.5	-5.6
IV	51	643	—	22.1	40.0	-5.6
V	64	—	119	—	36.5	-5.6
VI	72	—	—	—	38.0	-5.6
VII	81	619[e]	121	31.6	41.2	-5.6
VIII	92	631	124	—	42.3	-5.6

a) Using O_2; b) Sum of peak heights for (311), (321) and (410, 322) planes; c) Apparent activation energy; Reaction temp.: 180—240 °C; d) Maximum value which the catalyst shows; e) After reaction.

go in and out of the cavity. Thus, the catalytic activity of Samples V and VI increases. Beyond this point Zn ions occupy the 8-ring sites, but do not disturb the passage of molecules since one of the 8-ring sites is still vacant and since the Zn ion(ionic radius, 0.74Å) is smaller than the Na ion (0.97 Å); hence, Samples VII and VIII are highly active, much like V and VI.

The constitution of the products is almost the same in all the catalysts except I. The selectivity, (BA+CA)/EMK, is about 40; this indicates that BA is preferentially produced. This implies that the "molecular sieve action" characteristic of A-type zeolite does not change with the degree of ion exchange for this reaction.

The acidic character of the catalysts is given in Table 1. Sample I has no acidity at $H_0 \leqq 4.8$. It is known from the results of spectroscopic study that the Na-forms in X- and Y-type zeolites are also nonacidic.[11] As may be seen in Table 1, the strong acid sites as $H_0 = -5.6$ appear rapidly, as the degree of ion exchange is about 30%. When the degree of exchange rises, the total amount of acid sites increase, although the strength of the acid sites does not change further. A previous study clarified that those acid sites are the active sites for EB isomerization.[1] The inertness of Sample I (NaA) is due to both the absence of acid sites and the small pore size. The rise in activity with the growing zinc content can be explained as an increase in the total amount of acid sites and an enlargement of the effective pore size. On the low-exchanged ZnA(II, III, IV) the activity is considerably smaller than that expected from the amount of acid, as is shown in Fig. 1. This is due to the diffusion hindrance, as has been mentioned above.

The apparent activation energy changes are shown in Table 1. The apparent activation energy of EB isomerization over low-exchanged ZnA(II, III, IV) was smaller than that of the high-exchanged sample, VII. A similar dependence of the activation energy was noted by Balandin *et al.* for A-type zeolite (CoA) in a 1-butanol dehydration study.[7] The low activation energy may be a result of diffusion hindrance because of the small effective pore size; this would be in agreement with the conclusion of Balandin.

Experimental

Materials. The original sodium-form zeolite(NaA)* was Linde Molecular Sieves 4A, which is in a binder-free powder form. The zinc chloride used for ion-exchange was of a guaranteed grade. The EB was of an extra pure grade, and the heart-cut after distillation was chromatographically pure. The nitrogen deoxygenated and dehydrated was used as a carrier gas.

Ion-exchange. The ion-exchange experiment was carried out at 85 °C ±1 for 5 hr in a thermostat.

The NaA was treated as has been described in Part II.

The degree of ion exchange was determined by flame photometry after dissolution in dilute hydrochloric acid.

The X-ray powder diffraction patterns of the hydrated samples were obtained using filtered copper K_α radiation. The specific surface areas of the samples were measured by the BET method using N_2 and O_2. The crystallinity of the ion-exchanged zeolites was judged by a comparison of these results.

Reaction and Analysis. For estimating the catalytic activity, a flow reactor was used.[1] The zeolite catalysts were heat-treated at 400 °C for 3 hr in a reactor. The reaction was carried out at 220 °C in a nitrogen carrier. The activity of the catalyst was given in terms of EB conversion. The selectivity of the catalyst was expressed in terms of the mole ratio of butyraldehyde (BA) and crotyl alcohol (*cis*=CA_c, *trans*=CA_t) to ethyl methyl ketone(EMK).

Acidity. The acidic properties of the catalysts, which were heated at 400 °C for 3 hr in air, were determined by the titration method with *n*-butylamine and using a series of Hammett indicators.[3]

References

1) Studies of the Catalytic Properties of Synthetic A-Type Zeolite. Part III. Part II: M. Nitta, S. Matsumoto, and K. Aomura, *Nippon Kagaku Kaishi*, **1973**, 1839.

2) Presented at the Summer Meeting of the Hokkaido Branch of the Chemical Society of Japan, Hakodate, July, 1973.

3) O. Johnson, *J. Phys. Chem.*, **59**, 827 (1955).

4) G. M. Schwab and R. Sieb, *Z. Naturforsch, A*, **18**, 164 (1963).

5) H. Otouma and H. Ukihashi, This Bulletin, **42**, 2449 (1969).

6) K. Tsutsumi and H. Takahashi, *J. Catal.*, **24**, 1 (1972).

7) Z. V. Gryajnova, M. M. Ermilova, A. A. Balandin, G. V. Tsitsishvili, and V. I. Bashin, "Proc. 4th Internat. Congr. Catalysis,,' (Moscow, 1968), Paper 58.

8) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Read, and T. L. Thomas, *J. Amer. Chem. Soc.*, **78**, 5963 (1956); *ibid.*, **78**, 5972 (1956).

9) T. Takaishi and A. Yusa, *Shokubai*, **13**, 149 (1971).

10) T. Takaishi, A. Yusa, and Y. Yatsurugi, The 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971; Preprint **B**. 12342.

11) J. W. Ward, *J. Catal.*, **11**, 238 (1968).