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Differences between Properties of (Na,Ca)-A Zeolites Treated in Deep-bed and Shallow-bed

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Properties of (Na,Ca)-A zeolites treated in a deep-bed and shallow-bed were compared with each other. Adsorptive capacities for water linearly increased with increasing of a Ca content in the deep-bed zeolites but not in the shallow-bed zeolites. Thermal stabilities of the zeolites were lowered by the deep-bed treatment but not by the shallow-bed one. Differences in the properties of both zeolites were related to rearrangement of Ca^{2+} ions.

It is known that zeolites treated in deep-bed (abbreviated as DB) conditions and shallow-bed (SB) ones have different properties with each other. An essential difference between the DB and SB conditions is in a difference of steaming effect, that is, the zeolites are exposed to high temperature steam in the DB conditions, but scarcely exposed in the SB conditions. Effects of the treatments upon the properties have been widely studied on zeolite Y[1-3] but not on zeolite A. In a previous paper,[4] adsorptive properties of DB- and SB-(Na,Mn)-A zeolites were studied, and it was found that an adsorptive capacity for water depended linearly upon a Mn content in the DB-zeolite but, in the SB-zeolite, showed a minimum at a composition of ca. 60% Mn content. The purposes of the present study are to investigate whether the adsorptive properties mentioned above are characteristic to (Na,Mn)-A zeolites or not, and why the adsorptive capacity of the SB-zeolite becomes minimum at the composition of ca. 60% Mn content.

In the present experiments, the DB- and SB-zeolites were respectively defined as; the zeolite which is heated in a test tube of glass at 473 K for 12 h in the atmosphere and then evacuated at 673 K for 12 h in a high vacuum. apparatus, and the zeolite which is gradually heated, in order to minimize a steaming effect, in the vacuum apparatus and ultimately heated at 673 K for 12 h. We studied the effects of the treatments upon the properties of (Na,Ca)-A zeolites, since distributions of Ca^{2+} ion in zeolite A have been investigated in detail.[5,6]

The starting material, $Na_{11.8}(AlO_2)_{11.8}(SiO_2)_{12.2} \cdot nH_2O$ (abbreviated as $Na_{11.8}$-A), was washed with distilled water for several times and ion-exchanged with 0.1 mol dm^{-3} solution of $(CH_3COO)_2Ca$ at 353 K for 2 days. The ion-exchange solution was analyzed by EDTA-titration and a composition, $Na_{11.8-2x}Ca_x$-A, of the zeolite after ion-exchange was determined from material balance. The zeolite was dried at 353 K in an oven dryer and stored for 3 days or more in a desiccator containing saturated NH_4Cl solution in order to saturate adsorbed water. The zeolite was pelletized under a pressure of ca. 6×10^7 Pa. This zeolite is named an untreated one. The zeolite was treated in the DB (SB) conditions and a DB (SB) zeolite was obtained. The treated zeolite was dehydrated in the vacuum apparatus and its weight was measured with McBain type quartz spring balance. The zeolite was stored in the desiccator for 3 days or more and its weight was measured with microbalance.

Sorption capacities for water are illustrated in Fig. 1, which were determined from differences of the weights of dehydrated and fully hydrated zeolites. The capacity of the DB-zeolite showed linear dependence upon the composition x and that of the SB-zeolite a minimum at ca. x=3. The dependences of the capacities upon the composition are respectively quite similar to those observed in the DB- and SB-(Na,Mn)-A zeolites.[4] The facts show that such relationships between the adsorptive capacity and the composition are common to Na-A zeolite containing divalent cations, i.e., the adsorptive capacity of DB-

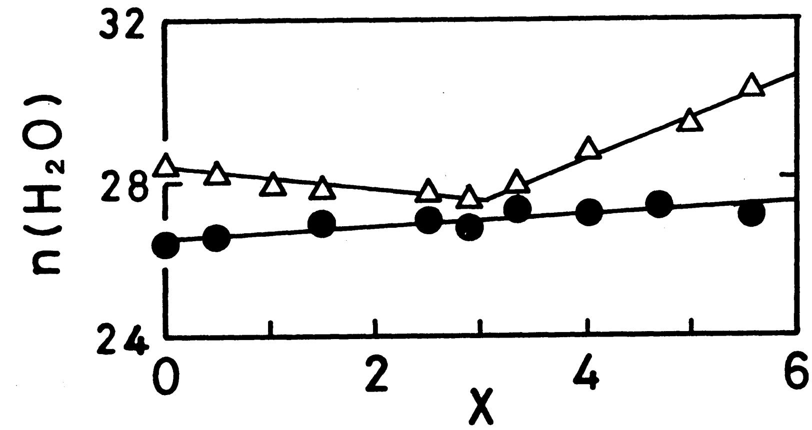

Fig. 1. Adsorption capacities for water.
(●), DB-zeolite;
(△), SB-zeolite.
$n(H_2O)$, water molecule adsorbed in unit cell; x, composition of zeolite $Na_{11.8-2x}Ca_x$-A.

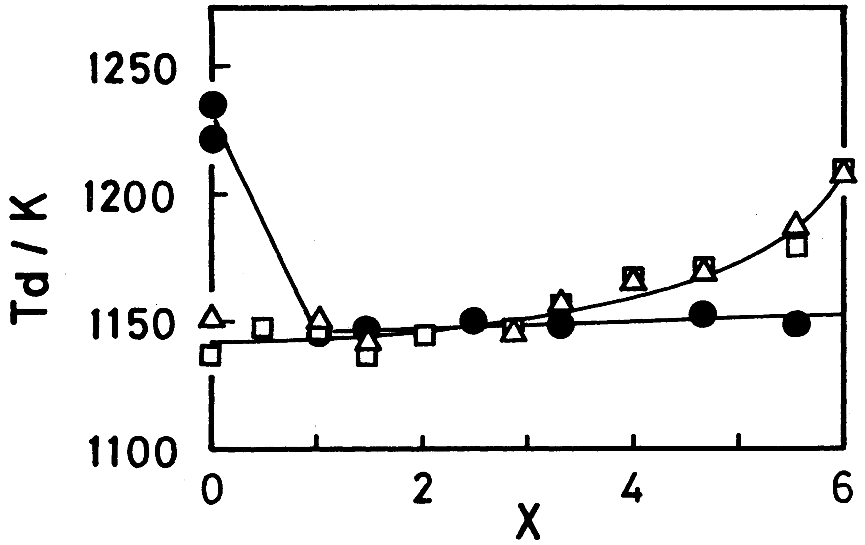

Fig. 2. Decomposition temperatures. (●), DB-zeolite; (△), SB-zeolite; (□), untreated zeolite. T_d, decomposition temperature; x, composition of zeolite $Na_{11.8-2x}Ca_x$-A.

(Na,M^{II})-A zeolite linearly increases with increasing of the M^{II} content and the capacity of SB-(Na,M^{II})-A zeolite becomes minimum at the composition of $3<x<4$, where M^{II} denotes a divalent cation. X-ray diffractions of the DB-, SB- ,and untreated zeolites were measured, in order to examine the effects of the treatments upon crystallinity. The patterns showed no disintegration of the crystals of the treated zeolites. Thermal stabilities of the treated and untreated zeolites were measured by DTA, and decomposition temperatures7) are illustrated in Fig. 2. In a range of $0 < x < 1$, the thermal stability of the DB-zeolite remarkably changed. Special behaviors in the range have frequently been observed in zeolite A,4,8,9) and may be related to Na^+ ion on a 4-membered oxygen ring. The figure shows that the thermal stability of the zeolite is not affected by the SB treatment but lowered by the DB treatment, except for the composition of $0 < x < 1$.

Let us consider the differences between the properties of the DB- and SB-zeolites. Two possibilities are considered as causes of the differences. One is re-arrangements of cations, and another is de-alumination from the framework. However, the latter possibility is discarded from followings. According to studies on zeolite Y, de-alumination by steaming occurs only when the zeolite is heated above 673 K in a presence of ammonia.10) Similar conditions may be required for de-alumination in zeolite A. However, such sever conditions were not realized in the present zeolites. Thus the differences in the properties of both zeolites are attributed to a difference of re-arrangements of cations. Calcium ion in fully calcium exchanged zeolite A migrates from a large cage to a sodalite cage by a heat treatment.11) Such migration of Ca^{2+} ion must be promoted by the DB treatment. Hence we think that the differences between the properties of the DB- and SB- zeolites are caused by followings; Ca^{2+} ion migrates into the sodalite cage by the DB treatment, distorts the cage, and lowers the thermal stability of the zeolite.

The break of sorption capacity of the SB-zeolite at $3<x<4$ is related to a distribution of divalent cations. Calcium (manganese) ions, up to the fourth, introduced into the zeolite occupy sites of 6-membered oxygen rings4-6) and tightly bond to the sites.12,13) The ions beyond the fourth occupy other sites and weakly bond to the sites. Thus the cations on the 6-ring site weakly bond to adsorbate molecules more than the cations on the other sites. Hence the sorption property of the SB-zeolite changes in the vicinity of $x = 4$.

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