February, 1982] © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 581—586 (1982) 581

Preparation and Properties of Dealuminated Y Type Zeolite

Akira Yoshida,* Hiromi Nakamoto,** Kazuhito Okanishi,** Tatsuro Tsuru,**
and Hiroshi Takahashi**
Mineral Resources Division, National Industrial Research Institute of Kyushu, Shukumachi, Tosu, Saga 841
***Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106*

(Received May 25, 1981)

The removal of aluminium cations from Y type zeolite, faujasite, was studied by means of three methods of treatment, *i.e.*, acetic acid–sodium acetate buffer treatment, acetate buffer–Na_2H_2EDTA treatment and H_4EDTA treatment. It was confirmed from the results that the reagent for dealumination of faujasite should have two functions, *i.e.* weakly acidic and chelating ability with aluminium cations. When more than 23 aluminium cations were extracted from 53 aluminium atoms in a unit cell, lattice was seriously destroyed. But the analysis of the adsorption isotherms suggested that more than 66% of α-cages remained even in a nearly amorphous sample obtained after dealumination as far as 75%. The differential heat of immersion of the dealuminated Y type zeolite in water showed that the acid strength of the surface increased slightly by dealumination.

Since Kerr[1—3] showed that the tetracoordinate aluminum atoms of faujasite were readily extracted by ethylenediaminetetraacetic acid (H_4EDTA) treatment or by the ion exchange in deep bed method followed by extraction with a sodium hydroxide solution, dealumination of faujasite has been reported by may investigators.[1—12] Beaumont and Barthomeuf[4—6] showed that aluminium atoms could be removed from faujasite with organic solvent such as acetylacetone. They also examined to treat faujasite with diethylenetriaminepeantaacetic acid and 1,2-cyclohexanediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid. Miecznikowski *et al.*[7] showed the dealumination of faujasite by the treatment with aqueous tartaric acid solution. Garwood *et al.*[8] reported the partial dealumination of faujasite by chromium salt solution.

The stability of the crystallographic structure of faujasite through dealumination process was mainly related to the silica/alimina molar ratio of starting zeolite. Kerr[2] indicated that the silica/alumina molar ratio should be more than 5.0. Tsutsumi *et al.*[9] attempted dealumination of faujasite whose silica/alumina molar ratio was 4.8 and noted that about 50% of the aluminium atoms was removed by H_4EDTA treatment successfully without collapse of the crystallographic structure. Kerr *et al.*[10] recently reported the technique to remove more than 80% of tetracoordinate aluminium atoms from Y type zeolite retaining 60—70% of the crystallinity. Sherzer[11] produced highly siliceous faujasite with silica/alumina molar ratio over 100 from the starting material whose silica/alumina molar ratio was 5.2.

These reports put focuses on the high crystalline structure retained through the dealumination processes. But, when the starting materials with the silica/alumina molar ratio smaller than 4.8 are dealuminated, the loss of crystallinity is inevitable. This study concerns the amorphous structure of dealuminated faujasite and its properties which were examined by X-ray diffraction analysis, SEM observation, N_2 adsorption, and the measurement of heat of immersion into water.

Experimental

Y type zeolite ($NaY_{4.73}$) used in this work was obtained from Shokubai Kasei Co. Ltd., whose silica/alumina molar ratio

Table 1. Conditions of preparing the samples

Treatment	Sample No.	pH Initial	pH Final	Amount of EDTA g/g zeolite	Reaction time h	V[a)] cm^3
Acetic acid–sodium acetate	A-1	4.05	4.18	0	20	
	A-2	3.61	3.77	0	20	
	A-3	3.02	3.30	0	20	
	A-4	0.47	1.95	0	20	
Acetic acid–sodium acetate–Na_2H_2EDTA	AE-1	3.61	4.21	1	20	
	AE-2	3.45	4.08	1	20	
	AE-3	3.21	3.64	1	20	
H_4EDTA with Soxhlet extractor	CS-1			0.36	120	20
	CS-2			0.39	240	20
	CS-3			0.47	216	20
	CS-4			0.55	240	20
	CS-5			0.58	264	20
	CS-6			0.66	576	20
	CS-7			0.75	624	7

a) V is the amount of refluxing water poured into the flask at a time.

was 4.73. As the first experiment, $NaY_{4.73}$ (10 g) was mixed only with acetate buffer solution at pH 0.47—4.05 (100 cm^3) in a 300 cm^3 eggplant type flask, and heated at the boiling temperature of the slurry for 20 h. In the second treatment, chelating agent, ten grams of ethylenediamineteraacetic acid disodium salt (Na_2H_2EDTA), was added to the acetate buffer solution to check the role of the chelating agent on the dealumination. The third H_4EDTA treatment was performed with a modified Soxhlet extractor containing 20 g of faujasite and 200 cm^3 of distilled water in the flask of extractor and different amount of H_4EDTA in the extraction room. The conditions of preparing the samples were summarized in Table 1. The amount of refluxing water poured at a time into the flask was controlled by using glass beads between the filter paper thimble and the extraction room to decrease the volume of the extraction room.

The crystallinity of the dealuminated sample was studied by X-ray diffraction analysis. The lattice constant was determined from the interplaner spacing of (533) and (642) with reference to anatase as a standard. The crystallite size was determined from the X-ray line-profile of (533) using silicon as a standard. The appearence of pseudomorphic particles of the sample were observed by MINI SEM of Hitachi-Akashi Co., Ltd. Nitrogen adsorption was measured at −196 °C with Orr Surface-Area Pore-Volume Analyzer 2100D. Heat of immersion was measured in a twin isothermal type calorimeter of Tokyo Rico Co., Ltd. Before measurement, each sample was pretreated at 400 °C under 10^{-5} Torr[†] for 5 h. The total weight of sample, quartz wool stopper, glass ampule and glass manifold which connected with a vacuum line and a water vapor chamber through glass cocks and joints was measured before and after the pretreatment. Then the different amount of water vapor was injected to the ampule and was adsorbed on the sample. After this adsorption, the amount of water adsorbed was weighed.

Results and Discussion

Dealumination of Faujasite. The properties of the dealuminated Y type zeolite were comparatively studied. Figure 1 shows the correlation between unit cell constants and the average intensities of (111), (533), and (642) peaks of the dealuminated samples treated with the different three methods. The lattice of faujasite is known to contract through dealumination,[9,12] but the treatment with acetic acid–sodium acetate solution brought about only the collapse of the crystallographic structure without successful dealumination. When Na_2H_2EDTA was added to the acetate buffer solution, a little amount of aluminium was extracted. Na_2H_2EDTA, as described by Kerr,[2] could not react with sodium zeolite by itself. By the treatment with H_4EDTA, about 40% of tetracoordinate aluminium of $NaY_{4.73}$ was removed retaining 80% of the crystallinity. These results coincided with the mechanism of dealumination reaction proposed by Kerr.[2] That is, the first step of dealumination reaction is decationization by weak acid, forming basic aluminium hydroxide which is neutralized by Brönsted acid sites, and the second step is the formation of a chelate, NaAlEDTA. The second step of the reaction was not attained by the treatment with acetate buffer solution. The removal of aluminium cations by the chelating agent seems to ensure the partial migration of silicon atoms into the vacant sites by aluminium removal.[12] But this silicon migration did not cause the destruction of the structure of zeolite in H_4EDTA treatment. The limit of dealumination keeping high crystallinity seems to depend on the silica/alumina molar ratio in the starting material.[2,6] The silica/alumina molar ratio of the sample used by Kerr[2] was 5.25, and 37 among 53 aluminium atoms per unit cell were extracted. Barthomeuf *et al.*[6] succeeded to remove 29 aluminium atoms from a unit cell containing 56 aluminium atoms. In our study, the silica/alumina molar ratio of the starting material was 4.73, and 23 among 57 aluminium atoms were extracted with the retention of high crystallinity. The probability of collapse of lattice due to the removal of aluminium atoms seems to increase steeply with the increasing number of the aluminium atoms per unit cell of the starting material. Dealumination and formation of amorphous part from Y type zeolite progressed without noticeable destruction of the shape and the reduction of the size of pseudomorphic particles (Fig. 2). Figure 3 shows the correlation between the ratio of dealumination and the apparent crystallite size determined from the X-ray line-profile of (533). The diameter of pseudomorphic particles of the starting material were between 1000—8000 Å, and their average crystallite size was about 2200 Å. It means that a pseudomorphic particle consists of one or several crystallites. Probably, almost all of the crystallites could be contracted with the dealuminating solution containing H_4EDTA. The process of the formation of amorphous state by dealumination and destruction of the crystal structure of zeolite is schematically described by a model in Fig. 4-a, and is further simplified to the model illustrated in Fig. 4-b. The calculated crystallite sizes from this model are shown in Fig. 3 with dotted line. In this model, $r/r_0=(I/I_0)$,[3] where r and r_0 are the crystallite sizes and I and I_0 are the X-ray diffraction intensities of the dealuminated and original particles,

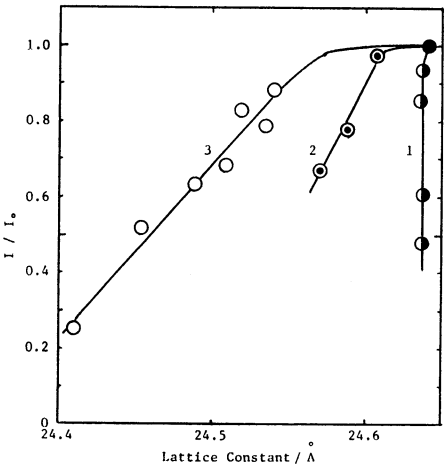
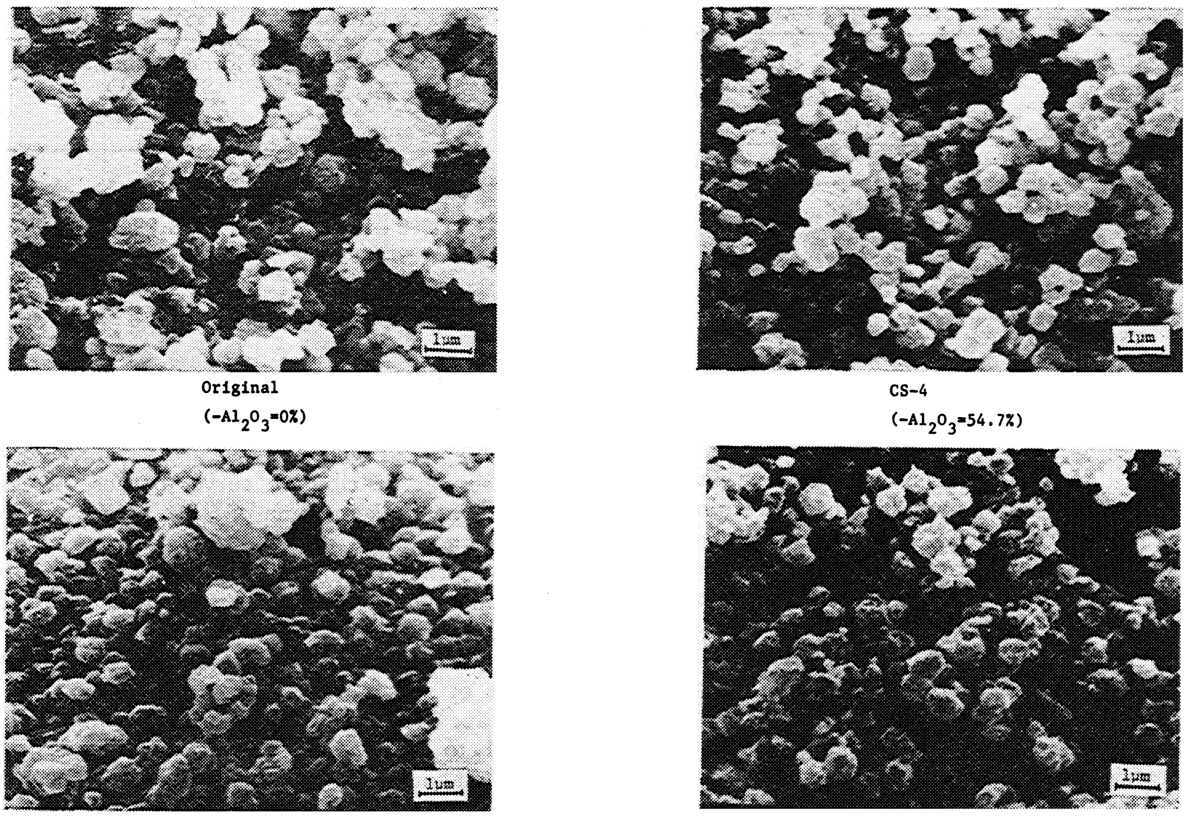


Fig. 1. Correlation between lattice constant and I/I_0.
I: Peak intensity of dealuminated Y type zeolite, I_0: peak intensity of starting material.
1: CH_3COOH-CH_3COONa, 2: CH_3COOH-CH_3COONa-Na_2H_2EDTA, 3: H_4EDTA.

[†] 1 Torr≈133.32 Pa.



Original
($-Al_2O_3=0\%$)

CS-4
($-Al_2O_3=54.7\%$)

CS-1
($-Al_2O_3=34.3\%$)

CS-6
($-Al_2O_3=65.4\%$)

Fig. 2. Electron micrographs of dealuminated Y type zeolite.

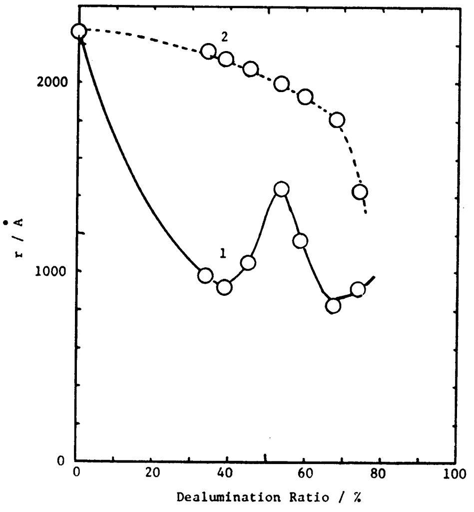


Fig. 3. Changes of apparent crystallite sizes by dealumination.
1: Calculated from line profile of (533), 2: calculated from following equation.
$r/r_0=(I/I_0)^{1/3}$, r,r_0=crystallite sizes of dealuminated and original zeolite, respectively.

respectively. From this calculation, crystallite size of the sample whose dealumination ratio was about 65% should have decreased to 80% of that of the starting material. However, the calculated values did not agree with those observed. Another unexpected phenomenon is the increase of crystallite size after first decrease.

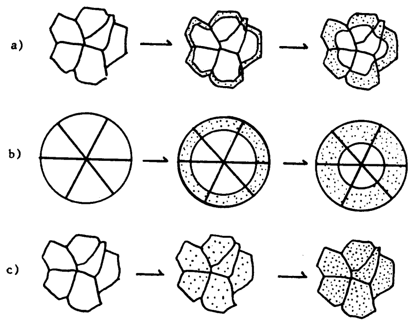


Fig. 4. Models of dealumination and formation of amorphous state.
a): Formation of amorphous state, b): approximation of amorphous state for calculation, c): dealumination.

Since the lattice constant is affected by the silica/alumina molar ratio as described in Fig. 1, the difference of silica/alumina molar ratio in the different crystallites would cause the increase of the half width of X-ray diffraction peak. The first decrease of apparent crystaleite size would be attributed to the heterogeneity of the silica/alumina molar ratio. After the partial dealumination, some part became more siliceous and had extended stability in acid media. Then, the unreacted part of zeolite would be attacked by H_4EDTA. In such a manner, Y type zeolite would be dealuminated nearly homogeneously (Fig. 4-c).

On the assumption that the formation of amorphous state had only negligible effect on the decrease of

Table 2. The molar ratio of faujasite crystal and solid phase of dealuminated Y type zeolite

Sample No.	Dealumination $-Al_2O_3$%	X-Ray analysis $2\theta_{533}$/°	$d2\theta_{533}$/°	SiO_2/Al_2O_3 (Faujasite)	Chemical analysis SiO_2/Al_2O_3 (Solid phase)
CS-0[a)]	0	23.652	0	4.73	4.73
CS-1	34.3	23.755	0.040	7.3—8.8	7.74
CS-2	38.1	23.775	0.039	8.0—9.8	8.29
CS-3	46.5	23.760	0.033	7.7—8.9	9.74
CS-4	54.7	23.787	0.016	8.9—9.8	11.7
CS-5	57.5	23.807	0.027	9.7—11.3	12.5
CS-6	65.4	23.844	0.054	—	15.6
CS-7	74.2	23.880	0.043	—	21.3

a) CS-0 means the starting zeolite.

crystallite size, the heterogeneity of the silica/alumina molar ratio of the sample was calculated from the increase of half width of (533). The correlation between the silica/alumina molar ratio of faujasite crystal and the unit cell constant was previously reported by Tsutsumi *et al.*[9)] On the basis of their results, the silica/alumina molar ratio of the crystalline fraction, and that of the solid phase from the results of chemical analysis, are shown in Table 2. This table shows that in the range of 0 to 38.1% of dealumination, the silica/alumina ratios of faujasite and of the solid phase were similar. The silica/alumina ratio of faujasite in the sample of CS-3 was lower than that of CS-2. In the preparation of CS-1-7, the extent of dealumination was controlled by reaction time and reaction rate. For dealumination to higher extent, the reaction rate must be kept slow to prevent the lattice from destruction, and for this purpose, the more amount of refluxing water was used. In the preparation of CS-3, however, the same amount of refluxing water with and more amount of H_4EDTA than those of CS-2 were used, resulting in the similar reaction time. The rapid dealumination seems to lead to the different silica/alumina molar ratios in faujasite fraction and amorphous fraction. As for CS-6 and CS-7, the lattice constant to be referred to has not been reported. The sample dealuminated at more than 50% of tetracoordinate aluminium have slightly different silica/alumina molar ratios in the faujasite crystal fraction and amorphous fraction. Aluminium atoms in the amorphous state would be extracted easily compared to those in faujasite crystal. The dispersion of silica/alumina molar ratio of faujasite was in the range of 0.9 to 1.8, and the difference of silica/alumina molar ratio between crystalline part and solid phase was in the range of 0 to 2.4.

Changes in Pore Size Distribution. The external forms of particles were not destroyed by acidic H_4EDTA treatment, but their crystallinity decreased to 25%. The change of the pore size distribution due to the treatment was studied next by means of nitrogen adsorption at −196 °C. Figures, 5, 6, and 7 show the pore size distribution curves obtained from the analysis of nitrogen adsorption isotherms in Cranston-Inkley method.[13)] For samples CS-1 to CS-4, a large peak of the distribution curves were observed in the range of 12 to 50 Å diameter, and the pores with the larger diameter than 100 Å was negligible. CS-2 has the almost similar distribution curve to those of CS-1, 3 and 4. The peak maxima of these curves are in very narrow range of 14 to 18 Å, and the peak shapes are similar to that of the starting material, CS-0. For CS-5 and CS-6, the pore size distributed to 100—150 Å, and the several peaks lie around 12—120 Å. The pore size seems to distribute over a broader range with the progress of dealumination. But in case of CS-7, the peak shape of the distribution curve is similar to those of CS-1 to CS-4, though the pore size distribution extend to about 100 Å. This would be the result of very slow dealumination, because CS-7 was prepared by the treatment using one third of refluxing water poured at a time than the other samples and the dealumination took 26 d.

The micro pore volume was evaluated by deducing the volume of transitional pores with the diameter of 12—300 Å from the total volume of pores observed as the volume of adsorbed nitrogen at relative pressure of 0.931. At this relative pressure, all pores smaller than 300 Å have been filled by capillary condensation. The wall of pores larger than 300 Å and the external

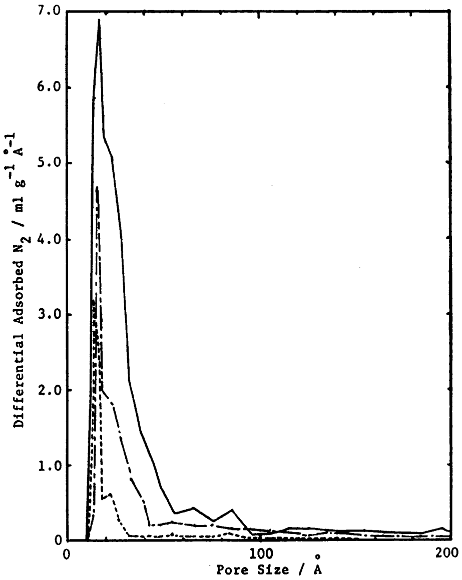


Fig. 5. Pore size distribution of dealuminated Y type zeolite.
----: Starting material, —-—: CS-1($-Al_2O_3$=34.3%), ——: CS-7($-Al_2O_3$=74.2%).

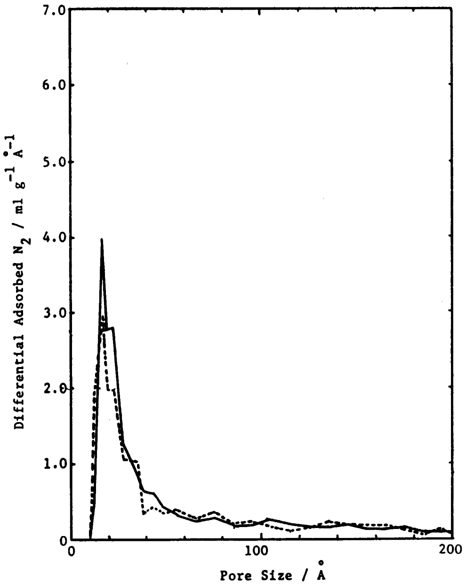


Fig. 6. Pore size distribution of dealuminated Y type zolite.
——: CS-3($-Al_2O_3$=46.5%), ------: CS-4($-Al_2O_3$=54.7%).

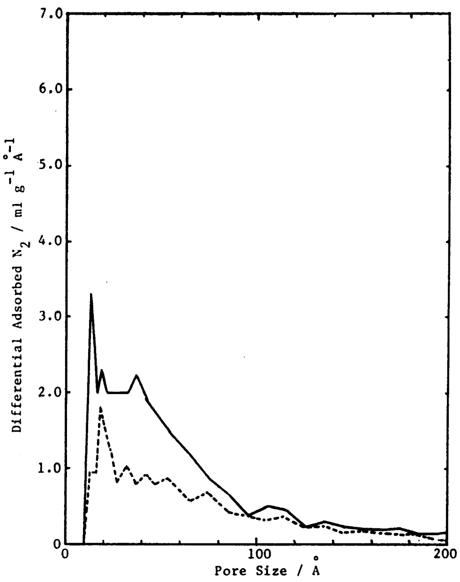


Fig. 7. Pore size distribution of dealuminated Y type zeolite.
------: CS-5($-Al_2O_3$=57.5%), ——: CS-6($-Al_2O_3$=65.4%).

surface were assumed to be negligible. The result are shown in Fig. 8. In these calculations, the specific gravity of nitrogen adsorbed on the solid surface at −196 °C assumed to be that of liquid nitrogen at same temperature. For CS-0, the volume of micro pores is about 0.281 cm^3/g. M. M. Dubinin[14] calculated the total void volume of sodium X type zeolite from the known crystal structure to be 0.322 cm^3/g. The void volume of faujasite consists of two kinds of cavities, *i.e.* α-cages and β-cages. The ratio of void volume of α-cages to that of β-cages in a unit cell is 6700 $Å^3$/1200 $Å^3$. So, the void volume of α-cages calculated is about 0.271 cm^3/g, and this value is slightly lower than the observed micro pore volume of CS-0. Breck *et al.*[15] reported the void volume of α-cages of X type zeolite to be 0.291 cm^3/g, which was determined from the adsorption of water. This value is slightly larger than the micro pore volume of CS-0. From these values, it would be considered that the micro pore volume consists mainly of α-cages, or most of α-cages would be evaluated as the micro pores, and the change of micro pore volume would be affected mainly by the decrease of α-cages through dealumination. By dealumination, the volume of α-cages seems to decrease slightly, but even in CS-6 and CS-7, the volume only decreased to 58.1 and 66.2% of the original volume, respectively. The rate of dealumination seems to have an influence on the retention of α-cages. The slow rate of dealumination changes the shapes of α-cages partly, but not the pore size essentially.

Calorimetric Study. To make clear the properties of remaining cationic sites, new structural hydroxyl groups and transitional pores of zeolite after dealumination, immersional heats into water of the dealuminated samples were examined. The results are shown in Fig. 9. The initial immersional heat seems to be related to the acidity at the remaining cationic sites. The initial heat of immersion on the starting material was in the range of 31.8 to 32.6 kJ/mol, and those on the dealuminated samples were slightly larger, *i.e.* 32.6—33.9 kJ/mol. The amounts of water adsorbed in the range of 31.8 to 33.9 kJ/mol of immersional heat seem to correspond to the amounts of water adsorbed on the cationic sites of the samples, and were 3.7, 3.0, and 1.8 mmol/g for the starting material, CS-1 and CS-5, respectively. The amounts of cationic sites calculated from sodium contents of these samples were 4.0, 3.0, and 1.8 mmol/g, and the amounts of cationic sites

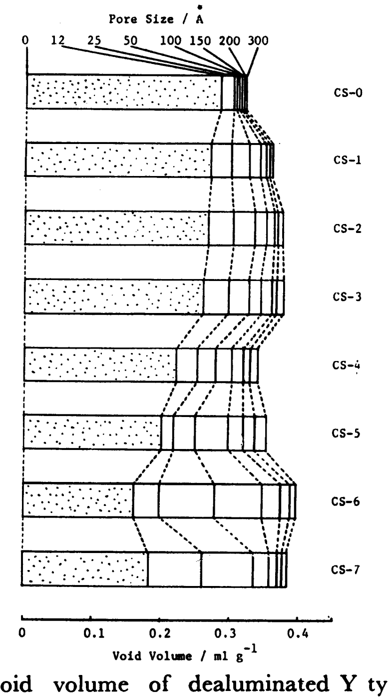


Fig. 8. Void volume of dealuminated Y type zeolite calculated from the amount of N_2 adsorbed using Cranston-Inkley method.

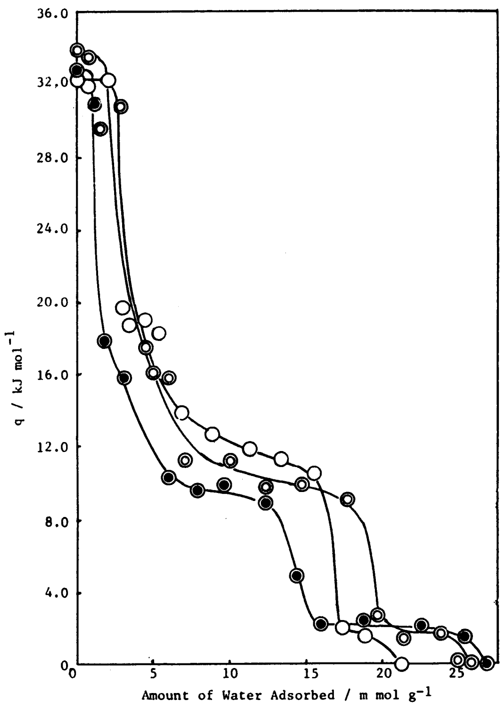


Fig. 9. Differential heat of immersion of dealuminated Y type zeolite.
○: CS-0, ◎: CD-1, ⊙: CS-5.

calculated from aluminium contents were 4.5, 3.2, and 2.2 mmol/g, respectively. After immersion of one water molecule per one sodium ion, the immersional heats of the samples into water decreased sharply to about 11.7 kJ/mol. Each curve of differential heat of immersion has two shoulders at about 10.0—12.5 kJ/mol and at about 1.55—2.51 kJ/mol. The first shoulders seem to be due to the immersion of water molecules in α-cages, partially modified α-cages and β-cages. On the assumption that the volumes of micro pores smaller than 12 Å are nearly equal to the volumes of α-cages and partially modified α-cages of the samples, the amounts of water with different heat of immersion were compared with the pore volumes calculated by Cranston-Inkley method. As for CS-1 and CS-5, it was assumed that the destruction of α-cages accompanied the equivalent collapse of β-cages, and the ratio of the volume of α-cages to that of β-cages in the dealuminated sample was similar to that of the starting material, *i.e.* 6700 Å^3/1200 Å^3, because each silicon or aluminium atom at T site in faujasite belongs to β-cage as well as α-cage. The volume of micro pores smaller than 12 Å in the starting material was 0.281 cm^3/g, and this value corresponds to 0.331 cm^3/g for α-cages and β-cages. The amount of water immersed with the heat larger than 8.37 kJ/mol was about 0.32—0.35 cm^3/g assuming the density of immersed water is the same with that of water at 25 °C. For CS-1, the volume of micro pores smaller than 12 Å was about 0.270 cm^3/g, which leads 0.318 cm^3/g for both cages. The total volume of α-cages, β-cages, and the transitional pores smaller than 25 Å in diameter was about 0.352 cm^3/g which accorded with the amount of water immersed with the heat larger than 8.37 kJ/mol, 0.35—0.39 cm^3/g. For CS-5, the micro pore volume was 0.200 cm^3/g which means 0.235 cm^3/g for both cages. The total volume of pores smaller than 25 Å was 0.254 cm^3/g and the amount of water immersed with the heat larger than 8.37 kJ/mol was about 0.25—0.29 cm^3/g. The electrostatic field of the cationic sites of the starting material seems to affected only the water molecules immersed in both cages, even though in the dealuminated samples the electrostatic field of remaining cationic sites seems to affect the water molecules immersed in the pores smaller than 25 Å. The transitional pores in the starting material would be produced by coagulation of pseudomorphic particles and there would be no cationic site on the wall of transitional pore, but the transitional pores in the dealuminated samples were formed by the partial destruction of α-cages and have some remaining cationic sites and dealuminated sites on the wall. Second shoulder at about 1.55—2.51 kJ/mol seems to correspond to the water molecules immersed in the transitional pores larger than 25 Å. The average immersional heat of water in the large transitional pores seems not to be affected by the dealumination.

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