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Dealuminated Faujasite-Type Structures with SiO_2/Al_2O_3 Ratios over 100

Calcination of ammonium-exchanged Y zeolites at high temperatures in the presence of steam results in the migration of part of the framework aluminum into nonframework positions (*1–4*). Moreover, under these conditions, a structural rearrangement occurs in the zeolitic framework, leading to the elimination of vacancies left by dealumination (*4–6*). The result is an ultrastable Y zeolite, characterized by higher thermal and hydrothermal stability, lower unit cell size, and lower ion exchange capacity as compared to the original Y zeolite.

The nonframework aluminum can be removed by treating the zeolite with solutions of caustic (*2, 7, 8*), mineral acid (*9*), or salts (*10, 11*). When caustic solutions are used, about 30% of the total aluminum is removed (*8*). A similar degree of dealumination was achieved by treating ammonium Y with EDTA (*12*). With dilute HCl solutions (less than 0.1 *N*), 50 and 60% of the total aluminum can be removed from the ultrastable zeolite (*9*). The resulting dealuminated zeolite has a molar SiO_2/Al_2O_3 ratio near 12.

It has been claimed that steaming of ammonium Y zeolites at 760°C for 24 hr followed by acid treatment results in alumina-free faujasite (*13*). However, our attempts to confirm that claim were unsuccessful.

We have found that stable, high-crystallinity faujasite-type structures with an advanced degree of dealumination can be obtained by submitting ammonium Y zeolites to one or several aluminum extractions combined with one or several hydrothermal treatments. The aluminum extraction can be done by using a suitable acid. The hydrothermal treatment consists in calcination under self-steaming conditions (calcination of the wet zeolite in a static atmosphere) or calcination under a flow of steam. The calcination can be done at temperatures varying from 500 to 870°C, depending upon the composition and the type of material desired.

We have used two types of Y zeolites as starting materials in these preparations. Both were obtained from NaY by ammonium exchange. One of the starting materials had one hydrothermal treatment and the other one had two such treatments prior to acid extraction. The first of these materials was an ultrastable Y zeolite, type A (USY-A), prepared by calcining at 760°C for 3 hr under self-steaming conditions, a partially ammonium-exchanged Y zeolite that contained about 3 wt% Na_2O. The calcined material was again ammonium exchanged, to reduce the soda content to 0.2 wt% Na_2O or less. This low-soda ultrastable Y zeolite (USY-A) was used in the preparation of stable, dealuminated structures, as described in procedure A.

Another starting material used in the preparation of dealuminated faujasite-type structures was an ultrastable Y zeolite, type B (USY-B). This zeolite was obtained by submitting a USY-A zeolite (with about 0.2 wt% Na_2O) to an additional hydrothermal treatment at 815°C for 3 hr under self-steaming conditions. The two hydrothermal treatments (at 760° and 815°C)

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TABLE 1

Preparation and Properties of Dealuminated Faujasite-type Structures[a]

Number	Acid treatment			Properties of product			
	Acid	Concn	Treatment at 90°C (hr)	Al_2O_3 (wt%)	SiO_2/Al_2O_3 mole ratio	SA, m^2/g at 540°C for 2 hr	SA, m^2/g at 1040°C for 2 hr
1	HCl	2 *N*	0.5	1.63	102	846	597
2	HCl	2 *N*	1	1.55	108	836	555
3	HCl	2 *N*	2	0.85	198	830	516
4	HCl	2 *N*	4	0.80	211	800	509
5	HCl	3 *N*	1	1.26	133	806	689
6	HCl	3 *N*	2	0.95	177	832	624
7	HCl	3 *N*	4	0.89	189	809	600
8	HCl	5 *N*	1	1.14	147	826	699
9	HCl	5 *N*	2	0.94	179	806	672
10	HCl	5 *N*	4	0.87	192	800	655
11	HNO_3	3 *N*	1	1.26	133	784	689
12	HNO_3	3 *N*	2	0.96	175	782	668
13	HNO_3	3 *N*	4	0.93	181	783	656

[a] Starting material: USY-B; $SiO_2/Al_2O_3 = 5.2$; $Na_2O = 0.16$ wt%; SA = 775 m^2/g; U.C. = 24.35 Å.

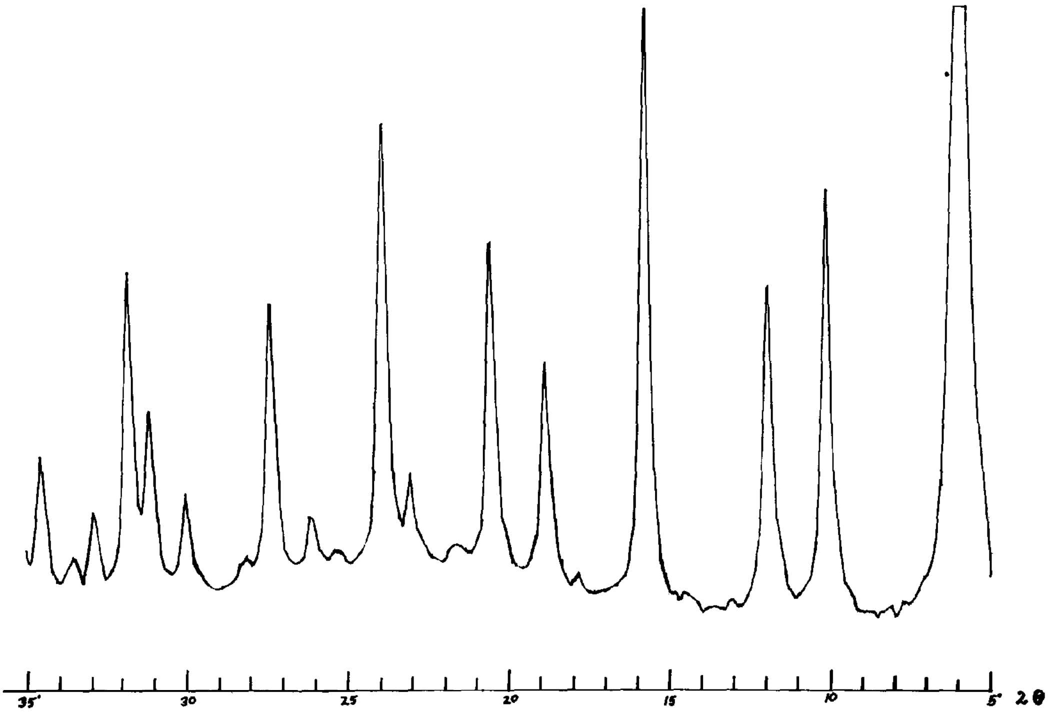

Fig. 1. X-ray powder diffractogram of dealuminated, faujasite-type structure with molar SiO_2/Al_2O_3 ratio of 192, after drying at 110°C for 2 hr.

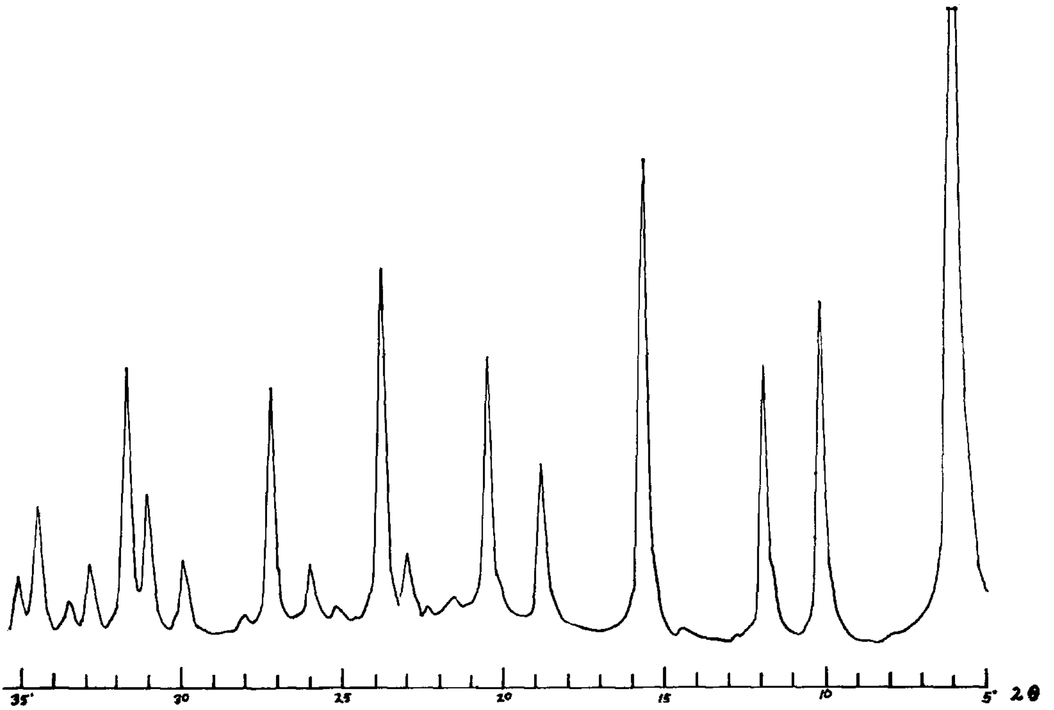

FIG. 2. X-ray diffractogram of dealuminated, faujasite-type structure, after calcination at 1150°C for 2 hr (surface area: 600 m^2/g; SiO_2/Al_2O_3 = 192).

led to an advanced degree of migration of aluminum from the framework into nonframework positions and an increased stability of the zeolite framework. A material with similar properties was obtained by carrying out the first calcination at 540°C rather than 760°C and the second calcination between 815° and 870°C (*14*). These ultrastable Y zeolites (USY-B) were used in the preparation of dealuminated structures, as described in procedure B.

Procedure A. The low-soda USY-A zeolite was treated with solutions of hydrochloric acid at 90°C and then calcined at 540°C under steam or self-steaming conditions. The process was repeated several times, progressively increasing the concentration of the HCl solution from 0.2 to 5 *N*. When this procedure was used, a series of dealuminated faujasite-type zeolites was obtained with molar SiO_2/AlO_{23} ratios less than 100. For example, when the USY zeolite was treated consecutively with solutions of 0.2, 0.5 and 5.0 *N* HCl at 90°C for 2 hr each and when each acid treatment was alternated with steaming at 540°C for 3 hr, a crystalline product resulted with a molar SiO_2/Al_2O_3 ratio of 50.

The materials obtained by this procedure have good crystallinity and high thermal stability, similar to the initial USY zeolite.

Procedure B. Portions of USY-B zeolite were treated with mineral acids (HCl or HNO_3) of different concentrations at 90°C for up to 4 hr. The resulting materials had very good crystallinity. The molar SiO_2/Al_2O_3 ratio of the materials prepared was between 100 and 200, indicating a removal of up to about 98% of the initial alumina content of the zeolite. Many of the materials prepared contain less than 1 wt% Al_2O_3. This procedure allows the preparation of stable structures with less alumina than those obtained by procedure A. Data concerning the preparation and properties of these highly dealuminated, faujasite-type structures are summarized in Table 1. The X-ray diffractograms of such materials are shown in Figs. 1 and 2.

The materials described were again submitted to calcination at 760°C for 3 hr under self-steaming conditions and treated with acid. The molar SiO_2/Al_2O_3 ratio further increased in some instances. In other cases, however, the molar SiO_2/Al_2O_3 ratio decreased during the second acid treatment, on account of partial silica leaching by the strongly acidic solution. A similar phenomenon has been observed during the dealumination of mordenite (*15*).

Milder acid treatment of USY-B zeolites results in materials with molar SiO_2/Al_2O_3 ratios less than 100.

The dealuminated structures prepared by combining acid leaching and hydrothermal treatment have very good crystallinity, as reflected by their high BET surface areas and by the X-ray diffractograms. The materials with $SiO_2/Al_2O_3 > 100$ have unit cell sizes that vary from $d = 24.18$ to 24.27 Å, depending upon calcination conditions. They have exceptionally high thermal stability, as shown by their BET surface area after calcination at 1040°C and by their high crystallinity after calcination at 1150°C for 2 hr. (Fig. 2). Their thermal stability surpasses that of ultrastable Y zeolites. Evidently their stability toward acids is also high. Excellent crystallinity is maintained even after boiling in concentrated hydrochloric acid for several hours.

The materials prepared prove that stable, dealuminated, faujasite-type structures can be obtained in the absence of cationic aluminum species or any other ionic species. Moreover, their stability is higher than that of any known cationic form of faujasite-type zeolites. Since most of these materials contain over 99 wt% SiO_2, practically they can be considered a new, highly porous form of silica with a faujasite-type structure (faujasite–silica).

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JULIUS SCHERZER[1]

W. R. Grace & Co.
Davison Chemical Division
Washington Research Center
7379 Rt. 32
Columbia, Maryland 21044

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[1] Present address: Filtrol Corporation, 3200 E. Washington Boulevard, Los Angeles, California 90023.