

The data in Kr and Xe are new. As with Pd, the atomic transitions for Pt in Ar and Kr can be correlated reasonably well with the gas-phase transitions.¹⁶ However, anomalous behavior is observed in Xe, resulting in an amonotonic order of matrix-induced frequency shifts, Xe > Ar > Kr, analogous to the situation described for Pd.

Discussion

It would appear to be generally accepted that the changes in the energy levels of the various atomic states of matrix-isolated atoms result from weak interactions between the metal atom and its surrounding matrix cage. Whether the actual system is described in terms of van der Waals interactions or weak complex formation would seem to be a matter of semantics. Whatever the case, matrix interactions will induce frequency shifts away from the respective gas-phase values and will generally be different for different matrix supports. Moreover, the various atomic states of the metal will experience different perturbations from the electronic wave functions of the surrounding matrix cage which will be responsible for the different shifts observed for different atomic transitions. In this context the amonotonic trends observed for the matrix-induced frequency shifts for Pd and Pt in noble gas matrices

Xe > Ar > Kr

compared to the more normal, monotonic trend for Ni

Ar > Kr > Xe

could be taken to indicate a substantial metal atom-matrix interaction. This would be expected to be most pronounced for the most highly polarizable metals, Pd and Pt (soft, in the Pearson notation), with the most highly polarizable matrix material Xe. One is tempted to speculate that Pd and Pt can,

in a qualitative sense, be considered to be forming a "weak complex" with Xe (i.e., a specific guest-host interaction). To confirm this proposal further experimental and theoretical studies will be required.

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Registry No. Ni, 7440-02-0; Pd, 7440-05-3; Pt, 7440-06-4; Pd(N₂), 57031-38-6; Pd(N₂)₂, 40810-27-3.

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Preparation of Dealuminized Mordenite

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A two-step method is described for the dealuminization of H mordenite: the zeolite is first dealuminized in the presence of steam at 538°C and then refluxed in hydrochloric acid to solubilize the removed aluminum. Unlike previous methods which either employed concentrated mineral acids below 100°C or high-temperature heating and acid extraction, the use of steam facilitates the hydrolysis and the migration of aluminum from the anionic framework to cation positions. This ion-exchange reaction serves to regulate and limit the degree of dealuminization during steaming. By repeating this two-step treatment, framework aluminum has been progressively hydrolyzed and removed to yield products having silica to alumina molal ratios above 100. These highly siliceous products retain the mordenite structure and the hydrocarbon sorption capacity; however, they are hydrophobic. Their hydrophobicity indicates the absence of intracrystalline silanol groups and suggests that structural rearrangement forming new ≡Si—O—Si≡ bonds takes place during steaming.

Introduction

The removal of framework aluminum from clinoptilolite, a siliceous zeolite, by leaching with boiling hydrochloric acid was first reported by Barrer and Makki in 1964.¹ Similar treatment on mordenite was reported by Dubinin and his co-workers^{2,3} and Eberly et al.⁴ Dealuminized mordenite with molal SiO₂:Al₂O₃ ratios as high as 69 was obtained from a 9.7 SiO₂:Al₂O₃ mordenite after leaching at 100°C for 84 h with 11 N hydrochloric acid. However partial breakdown of

the crystal lattice and amorphization of the zeolite under these conditions were noted.³

An alternative procedure using a combination of thermal and acid treatments was reported by Sand and his co-workers.^{5,6} Nearly all of the aluminum was removed (SiO₂:Al₂O₃ > 1200) from a 12.5 SiO₂:Al₂O₃ mordenite and the mordenite crystal structure was retained. The ease with which aluminum was removed by acid leaching after heating the sample to 700°C and holding there for 2 h in a dry nitrogen purge suggests that at least part of the framework aluminum was expelled from the structure during the thermal treatment. However, possibly because the procedure does not distinguish

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Table I. Composition of Na and H Mordenites

	Wt %		
	BG-11 Na mordenite	BG-10 H mordenite	AG-5 H mordenite
SiO ₂	79.7	84.6	89.5
Al ₂ O ₃	11.9	13.1	10.4
Na ₂ O	7.0	0.4	<0.1
CaO	0.6	0.6	<0.1
MgO	0.4	0.2	
Fe	0.4	0.4	

the aluminum expulsion step from the aluminum solubilization step, their data showed that a controlled degree of dealuminization was not achieved. Mishin et al.⁷ using a similar procedure studied the effect of preheating temperature (150–700°C for 5 h) on the degree of dealuminization and concluded that preheating temperature and the concentration of acid are the principal factors governing the dealuminization process. Examination of their data obtained by using a dilute (2 N) acid indicates that the degree of aluminization when a dilute acid is used is determined primarily by the rate of aluminum expulsion during the preheating treatment and suggests that it may be possible to obtain a controlled degree of dealuminization by uncoupling the aluminum expulsion step from the solubilization step.

Described in this paper is a two-step dealuminization method. In the first step, a structurally aluminum-deficient zeolite is created by treating mordenite with high-temperature steam, and in the second step, the expelled aluminum is solubilized and removed from the zeolite by refluxing with an acid solution.

Experimental Section

Three batches of synthetic mordenite (Zeolon) were obtained from the Norton Co. in the form of a fine crystalline powder having a crystalline size in the range of 1–5 μ. The Na mordenite (Lot No. BG-11) as received had a silica to alumina ratio of 11.4. The H mordenite samples as received had silica to alumina ratios of 11.0 (Lot No. BG-10) and 14.6 (Lot No. Ag-5), respectively. Their chemical compositions are shown in Table I.

To facilitate solid handling, the powdered samples were pressed without using any binder into 1/2-in. diameter, 3/16-in. thick pellets before chemical treatments.

In a typical steaming experiment, 200 g of pelleted sample was placed in the center of a "Vycor" tube inside a tube furnace. The furnace temperature was quickly brought up to the set point while saturated steam at 15 psig was preheated to the reaction temperature and passed over the zeolite at a rate of 2–400 cm³/min for a preset duration. The reactor was then cooled in a flowing stream of helium to room temperature. The steamed sample was extracted in hydrochloric acid by placing the sample in the solution and heating the acid solution to refluxing temperature for a preset duration. The acid-extracted sample was washed with water till chloride free. In the case of multistage experiments, a portion of the acid-extracted sample after each cycle was retained, while the remaining sample was subjected to further treatments.

Standard physical and chemical analyses of the sample were done by the analytical laboratory of Mobil Research and Development Corp., Paulsboro Laboratory.

In the determination of the relative crystallinity of dealuminized samples, the sum total of all the observed x-ray diffraction lines of each of the starting materials was arbitrarily assigned a value of 100, and the data on the dealuminized samples were compared and reported as percent crystallinity relative to the starting material.

Results

1. High-Temperature Steaming. Steaming H mordenite (SiO₂:Al₂O₃ = 11) at 538°C for 2–16 h resulted in a substantial hydrolysis of the zeolite. No evidence of hydrolysis was found when similar treatment was applied to Na mordenite. After extraction with 2 N HCl for 4 h, we obtain the results shown in Table II.

The extent of hydrolysis of H mordenite as a function of

Table II. Effect of Duration of Steaming of H and Na Mordenite at 538°C

Duration, h	SiO ₂ :Al ₂ O ₃ after acid extraction	% Al removal
(a) H Mordenite		
0	16.0	28
1/4	16.4	30
2	27.0	56
16	29.0	59
(b) Na Mordenite		
0	15.6	27
2	15.2	25

Table III. Effect of Temperature on Hydrolysis of H Mordenite

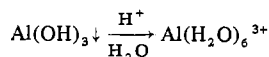
Temp, °C	SiO ₂ :Al ₂ O ₃ after acid extraction	% Al removal
315	15.4	26
538	27.0	56
700	28.8	58

Table IV. Effect of Acid Concentration on Aluminum Removal

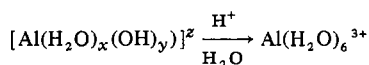
Normality of acid soln	SiO ₂ :Al ₂ O ₃ after acid extraction	% Al removal	% crystallinity of product
0.5	14.1	20	100
1	14.1	20	94
2	18.1	36	90
5	14.0	19	89
10	19.2	39	72

steam temperature was studied over a temperature range of 315–700°C at a fixed steaming duration of 2 h. Results as shown in Table III indicate negligible hydrolysis at 315°C and little additional hydrolysis at 700°C over that at 538°C. Based on these results, steaming at 538°C for 2 h was selected as the standard conditions for the multistage experiments.

2. Acid Extraction. The solubilization of aluminum salts in acid solution probably proceeds according to the following equation to form soluble aluminum aquo complex ions



or more generally



where x and y vary between 0 and 6 and z varies between 3+ and 3-. The soluble aluminum aquo complex ions would be expected to compete with H₃O⁺ ions for cationic positions in the zeolite.

Refluxing H mordenite for 4 h with HCl solution of 0.5–10 N concentration effects partial dealuminization. In the following experiments, the volume of acid solution was kept constant at 20 ml/g of zeolite. The results are shown in Table IV. The partial amorphization of the zeolite with 10 N acid confirms the observation of Dubinin et al.³ The hydrolysis of framework aluminum required a large excess of acid. A plausible explanation for this is that excess acid shifts the zeolite ion-exchange equilibrium between the soluble aluminum-aquo complex ions and H₃O⁺ toward the latter permitting further hydrolysis to take place.

The rate of dealuminization was checked by another set of experiments with H mordenite in 2 N HCl solution refluxing for 1 and 16 h, respectively. The results showed that the reaction was essentially completed in 4 h.

3. Multistage High-Temperature Steaming and Acid Extraction. Hydrogen mordenite (Lot BG-10) was put through cycles of steaming at 538°C for 2 h followed by refluxing in 2 N HCl (~46 inequiv of H⁺/g) for 4 h. After nine cycles,

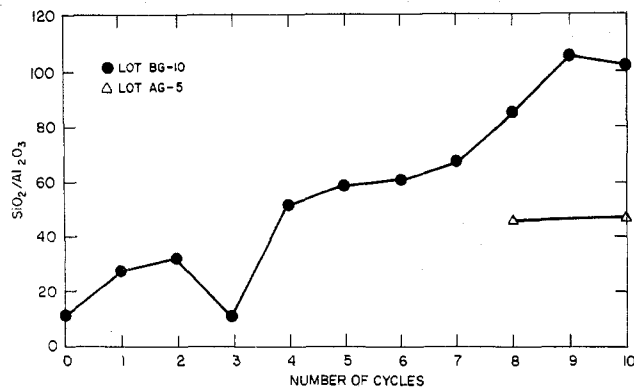


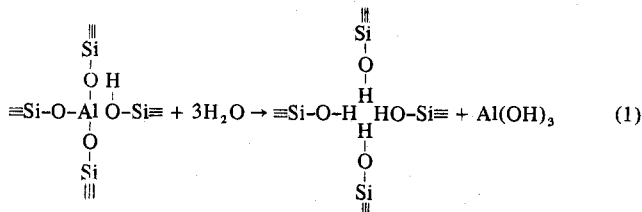
Figure 1. Increasing the silica:alumina ratio of a mordenite by alternating cycles of high-temperature hydrolysis and acid extraction.

the SiO₂:Al₂O₃ ratio was greater than 100. The amount of alumina in mordenite was reduced from 13.4% to 1.6% corresponding to 88% removal of the framework aluminum in the starting material. However during the first three cycles, the SiO₂:Al₂O₃ ratio rose first to 32 and then fell to 11 indicating simultaneous loss of both aluminum and silicon. The change of SiO₂:Al₂O₃ as a function of the number of steam and acid cycles is shown in Figure 1. X-ray diffraction data showed that the crystallinity of all samples after acid extraction was within $\pm 10\%$ of the starting material. Coincidental to the reversal in SiO₂:Al₂O₃ ratio on the third cycle, the diffraction pattern of samples after the third cycle showed the peaks shifted to larger angles indicating a shrinkage of the unit cell. Similar observations were made by Dubinin et al.³ and Eberly et al.⁸

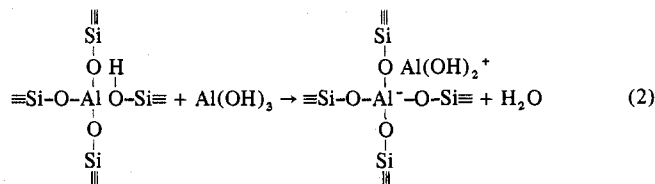
The reproducibility of this method is fairly good on the same lot of mordenite sample. However, the rate of hydrolysis appeared to vary with different lots of mordenite samples supplied by the Norton Co. For example, with Lot AG-5, we were not able to dealuminize beyond a SiO₂:Al₂O₃ ratio of 47 with the standard procedure. Further dealuminization may be possible by selecting a more severe steaming condition. Nevertheless our results clearly show that the rate of hydrolysis depends not only on the steaming condition but also on the concentration of aluminum in the starting material and other yet undefined structural variables possibly relating to the specific location of the aluminum in the framework structure of the zeolite.

Discussion

The two-step dealuminization method described in this paper was an attempt to demonstrate that the aluminum hydrolysis reaction can be facilitated and controlled by the use of water vapor. Kerr⁹ showed that hydrogen zeolite Y at 700–800°C in the presence of water vapor undergoes structural rearrangement to form a stabilized Y. In this stable Y, approximately 25% of the alumina is present in the cationic form derived from tetrahedrally coordinated aluminum that is initially in the anionic zeolite framework. He proposed the mechanism given by eq 1 and 2 to explain the role of chemical



water and the formation of cationic aluminum. Reaction 1 yields an alumina-deficient structure which is the same as the



structure of dealuminized mordenite after acid extraction proposed by Barrer and Peterson.¹⁰ Reaction 2 describes the neutralization or ion-exchange reaction between a hydroxy-aluminum ion, Al(OH)_x^y, and the remaining proton or hydronium ion present in the zeolite.

On the basis that only those framework aluminum atoms associated with protons are hydrolyzable, the degree of dealuminization in a single steaming step would depend on the relative rate of hydrolysis vs. that of neutralization and the effective charge of the hydroxyaluminum ion. If we assume that the neutralization reaction is much faster than the hydrolysis reaction and since hydroxyaluminum ion can have a 1+ up to a 3+ charge, a range of 16.7–50% can be calculated as the maximum degree of dealuminization in one steaming step. From Figure 1, with the exception of cycle 1 and cycle 4, the average amount of dealuminization per cycle was found to be about 10–15%, which is close to the maximum degree of dealuminization calculated for the case of monovalent hydroxyaluminum ions.

In cycle 1 and cycle 4, the starting material had a low silica to alumina ratio of 11, and the degree of dealuminization was above 50%. A significant portion of the removed aluminum in these low silica to alumina samples was shown to be removable at 100°C with 2 N HCl solution; thus hydrogen mordenite of low SiO₂:Al₂O₃ contains at least two types of structural aluminum, different in their reactivity toward acid.

The reversal in SiO₂:Al₂O₃ of Lot BG-10 during the third cycle showed that when >60% of the aluminum was removed from this particular sample, silica began to be expelled from the framework, and the structure reverted back to a low SiO₂:Al₂O₃ zeolite, suggesting strongly that structural reformation had taken place during the steaming process. A recent study¹¹ on the sorption properties of zeolites showed that dealuminized mordenite prepared by our two-step method retains its hydrocarbon sorption capacity but is truly hydrophobic. The hydrophobicity of the intracrystalline siliceous surface indicates the absence of silanol groups which were proposed by earlier investigators¹ using the acid extraction method. The absence of intracrystalline silanol groups adds further evidence for the occurrence of structural reformation, possibly involving the formation of new $\equiv\text{Si}-\text{O}-\text{Si}(\text{Al})\equiv$ bonds during steaming.

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