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Communications

Systematic Synthesis of Zeolites That Contain Cubic and Hexagonal Stackings of Faujasite Sheets

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Introduction

Synthetic cubic faujasite (FAU) has been known for several decades,[1] and it is one of the most studied and commercially important zeolites.[2] Recently, the hexagonal polytype of faujasite has been synthesized by Delprato et al.[3] We have subsequently confirmed the synthesis procedures used to crystallize this new zeolite and have compared some of its physicochemical properties to those of FAU.[4] Also, we have shown that the hexagonal polytype of faujasite (for our purposes denoted as hex) can be dealuminated by contact with $SiCl_4$ vapor[5] in a manner similar to that used for the dealumination of FAU. The existence of the cubic and hexagonal polytypes of faujasite leads one to speculate on whether zeolites can be synthesized as intergrowths between these two end members at any ratio of two polytype contents. ZSM-20 is an intergrowth of cubic and hexagonal stackings of faujasite sheets,[6] and ZSM-2,[7] ZSM-3,[8] and ZSM-10[9] may also be intergrowths.

The purpose of our work is to explore the possibility of synthesizing zeolites that are comprised of intergrowths of cubic and hexagonal stackings of faujasite sheets and vary in the ratio of cubic/hexagonal content. From Delprato et al., pure hex and FAU can be synthesized from the reaction mixture $R \cdot 2.4Na_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 140H_2O$, where R is 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) and 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5), respectively. Thus, in this work we use the reaction mixture $(1 - x)R_1 \cdot xR_2 \cdot 2.4Na_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 140H_2O$, where R_1 = 18-crown-6, R_2 = 15-crown-5, and x is varied as $0 \leq x \leq 1$.

Experimental Section

Samples. The following procedure is used to crystallize all the samples for this study. To 77.6 g of H_2O add 7.26 g of sodium aluminate (VWR Scientific), 7.48 g of aqueous NaOH (50% wt, Fisher), and the appropriate amount of crown ethers, e.g., for $x = 0$, 8.81 g of 18-crown-6. Stir vigorously until all the components are completely dissolved. Next add 20 g of amorphous SiO_2 (Syloid 74, Davidson) and blend at room temperature for 24 h. The reaction mixture is statically heated to 110 °C for 12 days at autogenous pressure in Teflon-lined autoclaves (the reaction mixture remains amorphous for 9 days). The solid products are obtained by filtration.

Prior to X-ray analysis, all of the samples were treated as described below in order to exchange them into their acid form. Each sample was heated from ambient to 500 °C in air at 2 °C/min and maintained at 500 °C for an additional 30 min before cooling to room temperature. These calcined samples were refluxed in 1 N NH_4Cl (200 g of liquid/g of solid) for 4 h and then heated again at the conditions mentioned previously.

Analysis. X-ray powder diffraction data were collected on a Scintag XDS 2000 θ–θ diffractometer using Cu Kα radiation. Argon adsorption isotherms were measured at liquid argon temperature on an Omnisorp 100 analyzer. Thermogravimetric analyses (TGA) were performed in air on a Du Pont 951 thermogravimetric analyzer. Scanning electron micrographs were obtained on a Cambridge Instruments Stereoscan 200 microscope. Magic angle spinning ^{29}Si NMR spectra were recorded on a Bruker MSL 300 spectrometer.

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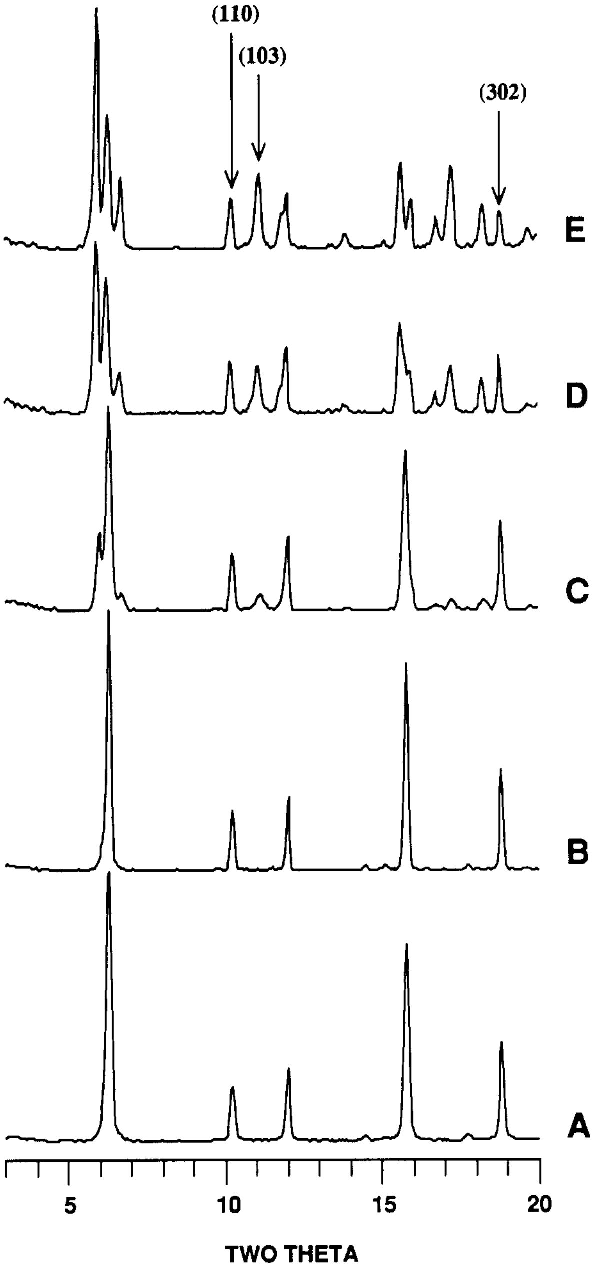

Figure 1. X-ray powder diffraction patterns of samples: (A) $x = 1$, (B) $x = 0.75$, (C) $x = 0.50$, (D) $x = 0.25$, (E) $x = 0$.

Results and Discussion

Figure 1 shows the X-ray powder diffraction patterns of the zeolites obtained from syntheses where $x = 1, 0.75, 0.5, 0.25, 0$. The samples prepared with $x = 0$ and $x = 1$ are easily identified as hex and FAU, respectively.[3,4] The X-ray powder diffraction pattern from the zeolite synthesized with $x = 0.75$ is the same as FAU, i.e., $x = 1$. However, notice that the X-ray powder diffraction patterns from the samples synthesized with $x = 0.5$ and $x = 0.25$ are significantly different from FAU. In the region $5° \leq 2\theta \leq 7°$, three peaks appear in the samples prepared with $x = 0.5, 0.25, 0$. These peaks are indexed as the 100, 002, and the 101 reflections of hex. The position of the 002 reflection coincides with the 111 reflection of FAU. The peak at approximately 18.8° 2θ is the 302 or 511 reflection if indexed on a hexagonal or cubic cell, respectively. Also, in the region $10° \leq 2\theta \leq 12°$ there are three major lines that correspond to the 110, 103, and 112 reflections of hex. The unresolved shoulder on the 112 reflection is the 200 peak. FAU has no observable reflection that occurs at the position of the 103 peak of hex. Thus, the samples prepared with $x = 0.5$ and 0.25 are either intergrowths of cubic and hexagonal stacking of faujasite (with a greater density of hexagonal stackings for $x = 0.25$ than for $x = 0.5$) or physical mixtures of hex and FAU crystals. The key observation is the 103 and 302 reflections. Notice that the 103 reflection has approximately the same width as the 110 and 302 reflections of hex (see Table I). Thus, a physical mixture of hex and FAU would give a 103 reflection with a width similar to hex. Such is not the case for the 103 reflections from the samples prepared with $x = 0.5$ and 0.25. In fact, the X-ray powder diffraction pattern of the sample with $x = 0.5$ is essentially that of ZSM-20 (a known intergrowth of cubic and hexagonal stackings of faujasite). In Table I are listed the full width at half-maximums (fwhm) for the 110, 103, and 302 reflections from the X-ray patterns illustrated in Figure 1. The fwhm's for the 110 are listed to give an indication of the experimental peak broadening from the zeolites. Notice that the 110 fwhm's are essentially the same from all samples. If for some reason the crystal size of the sample dramatically decreased in a given direction, then peak broadening could occur from particle size effects. If such is the case for the broadening in the 103 reflection, then the 302 reflection will be broadened as well. From the data listed in Table I, the fwhm of the 302 reflection is that of the 110 reflection. Thus, particle size effects are ruled out. Warren[10] provides an analysis for the intergrowth of cubic and hexagonal materials and gives a generalized derivation that explains the results of stacking faults on the X-ray powder diffraction pattern. According to his derivation, the 103 reflection is broadened proportional to 3 times the fault probability, whereas the 302 is not affected. Our data are in agreement with his analysis and therefore indicate that our samples are in fact true intergrowth structures.

Table I. Physicochemical Properties of Samples

sample	fwhm[a] 110	fwhm[a] 103	fwhm[a] 302	T_{max},[b] °C	ads capacity, g/g[c]
$x = 0$	0.15	0.19	0.16	318	0.34
$x = 0.25$	0.16	0.23	0.15	278	0.37
$x = 0.50$	0.18	0.45	0.21	262	0.35
$x = 0.75$	0.13		0.14	249	0.32
$x = 1.0$	0.16		0.17	247	0.36

[a] Full width at half-maximum of specified X-ray reflection. [b] Temperature at which maximum rate of weight loss occurs. [c] Grams of argon/grams of dry solid at $P/P_0 = 0.17$ and T = 87 K.

We have shown previously that the temperature at which the maximum rate of weight loss occurs for the combustion of the crown ethers from hex and FAU with the same Si/Al is quite different.[4] Here, all samples are found to have Si/Al = 3.6 ± 0.2 by ^{29}Si NMR analyses. Table I gives the temperature at which the maximum rate of weight loss occurs (from TGA, sample size ~8 mg, heating rate = 10 °C/min) for the samples studied here. The values listed for $x = 0$ and 1 correspond well to those observed previously from hex and FAU, respectively.[4] Notice that the samples with $x = 1$ and 0.75 give similar results. Also, the T_{max} increases as x decreases. A 50 wt %–50 wt % physical mixture of hex and FAU gives T_{max} = 257 °C. Thus, the TGA results are consistent with the premise that the samples with $x = 0.5$ and 0.25 are true intergrowths and not just physical mixtures.

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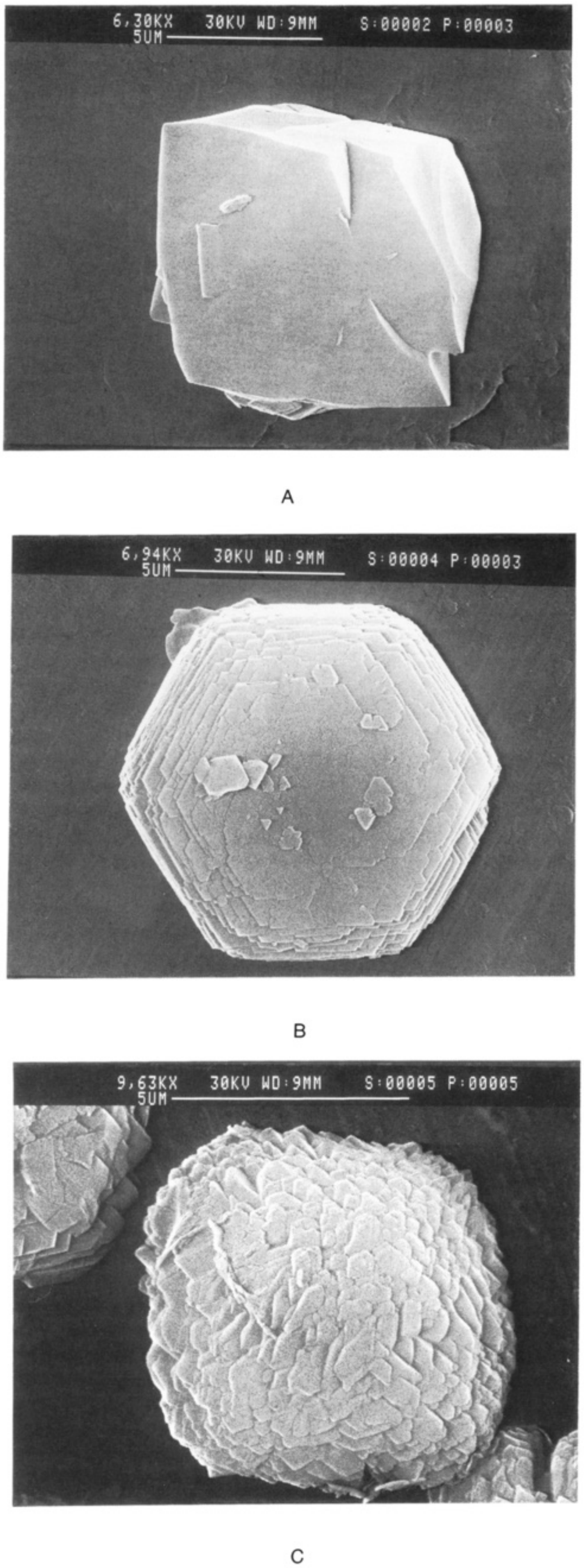

Figure 2. Scanning electron micrographs of samples: (A) $x = 1$, (B) $x = 0$, (C) $x = 0.5$. Space bar = 5 μm.

The argon adsorption data from all the samples show essentially the same isotherm in the range $10^{-5} \leq P/P_0 \leq 10^{-2}$, and the microporous adsorption capacities are listed in Table I. From these data, it is clear that there is no significant loss in adsorption capacity, indicating that there is no blocked access to portions of the crystal interiors for the intergrowth samples ($x = 0.5$ and 0.25).

Figure 2 shows scanning electron micrographs of the samples with $x = 1$, 0, and 0.5. The hex ($x = 0$) and FAU ($x = 1$) samples possess hexagonal and octahedral morphologies, respectively, as have been previously reported.[3,4] Notice that for the sample where $x = 0.5$, the particles are approximately 8-μm aggregates. This morphology is distinctly different from that of ZSM-20, hex, and FAU. Again, this sample does not appear to be a physical mixture of hex and FAU. Taken in total, the above data lead to the conclusion that zeolites comprised of intergrowths of cubic and hexagonal stackings of faujasite sheets can be synthesized by using mixtures of 18-crown-6 and 15-crown-5. A sample synthesized with $x = 0.62$ reveals an X-ray powder diffraction pattern similar to that shown for $x = 0.75$, while a sample synthesized with $x = 0.37$ gives a pattern intermediate between $x = 0.25$ and $x = 0.5$. Thus, by X-ray powder diffraction we can observe systematic changes in the hexagonal/cubic content for $0 \leq x \leq 0.5$. Variations in the hexagonal/cubic content may also occur for $x > 0.5$, but they are not observable by the techniques employed here. The use of transmission electron microscopy would certainly be advantageous in studying these materials (see Newsam et al.[6] for an example of how TEM was used to assist the structure solution of ZSM-20) and will be necessary to define domain sizes and homogeneities.

Our results are the first to show that a systematic design of intergrowth structures can occur for the faujasite system. Thus, the zeolite sample can be "tuned" to have a specific property by adjusting the synthesis conditions. It will be interesting to see if this principle can be applied to other zeolites such as zeolite beta.[11] At present, polymorphs A and B must be synthesized before this principle can be tested with zeolite-β.

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Synthesis of a Rotaxane via the Template Method

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In recent years, there has been a rapid development in the area of synthesis of compounds with interesting topologies. Among these compounds, catenanes, rotaxanes, and polyrotaxanes have attracted much attention (Figure 1). The study not only reveals some interesting and im-

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