Reviews

Zeolite and Molecular Sieve Synthesis

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Received March 31, 1992. Revised Manuscript Received June 5, 1992

Zeolite and molecular sieve syntheses are reviewed. The synthesis of aluminum-rich zeolites, high-silica zeolites, and phosphate-based molecular sieves are evaluated. Unresolved mechanistic issues are outlined, and areas for exploration suggested. The ability to plan zeolite and molecular sieve syntheses is discussed and a strategy for synthesizing a chiral zeolite is used to demonstrate the current limitations in "designing" new molecular sieves.

Introduction

Zeolites and molecular sieves are finding widespread application in diverse areas. No longer are they of interest to only those working in ion exchange, separations, and catalysis. The close connection between the microscopic structure and the macroscopic properties of these materials allows one to use molecular sieves to recognize, discriminate, and organize molecules with precisions that can be less than 1 Å. As a result, molecular sieves are drawing attention in all fields of molecular recognition phenomena. There are extensive references on zeolites and molecular sieves.[1-5] Additionally, a short general review[6] and overviews of the methods used to characterize zeolites and molecular sieves[4,5,7,8] are available.

This review is intended to evaluate data from zeolite and molecular sieve syntheses, to identify significant trends, and to comment on the plausibility of rationally designing the synthesis of molecular sieves. We hope that the information provided will stimulate further fundamental work in this area. Ultimately, the crystallization mechanisms of molecular sieves must be understood in order to perform synthesis by a priori design.

Background

In 1756, the Swedish mineralogist A. F. Cronstedt heated an unidentified silicate mineral and observed that it fused readily in a blowpipe flame with marked intumescence. This result led him to call minerals that behaved in this manner zeolites (derived from the Greek words "zeo" (to boil) and "lithos" (stone)). Since then, approximately 40 natural zeolites have been discovered. Zeolites are hydrated, crystalline tectoaluminosilicates that are constructed from TO_4 tetrahedra (T = tetrahedral atom, e.g., Si, Al); each apical oxygen atom is shared between two adjacent tetrahedra (Figure 1) giving a framework ratio of $O/T = 2$. (The term tectoaluminosilicate designates that all the oxygen atoms bridge two tetrahedral atoms.) Pure silicate materials (SiO_2) do not contain framework charge since silicon is tetravalent. However, aluminosilicates have negatively charged oxide frameworks (one charge per framework Al^{3+}) that require balancing, extraframework positive ions. Typical cations in natural zeolites are alkali metal, e.g., Na^+, K^+, and alkaline earth, e.g., Ca^{2+}, Ba^{2+}, ions. In addition to natural zeolites, there are both synthetic analogues of natural zeolites and synthetic zeolites with no natural counterparts. (The large-scale synthesis of zeolites for use as adsorbents for separations and purifications initiated molecular sieve technology in 1954.) Unlike natural zeolites, synthetic zeolites may contain both inorganic and organic cations, e.g., Na^+, quaternary ammonium ions, and protons. In all, there are approximately 75 molecular sieve structures.[9] The Structure Commission of the International Zeolite Association assigns a three-letter code to each framework topology. The designations are based on the connectivity of the tetrahedral atoms using the maximum topological symmetry, regardless of the changes in unit cell size and symmetry that may result from differences in chemical composition. These codes are especially useful when there are many names for the same topology (there are 21 different names for molecular sieves with the MFI (Mobil number five: ZSM-5) topology.) Here, we will use the most common name of the material and the three-letter code afterwards if deemed necessary. Molecular sieve nomenclature is discussed in greater detail elsewhere.[9] Figure 1 illustrates typical framework projections and various ring (pore) sizes for molecular sieves. The unique properties of zeolites and molecular sieves arise from their uniformity in pore size (due to their crystalline nature) and because the pore sizes are about the same size as small molecules. These properties allow molecular sieves to recognize, discriminate, and organize molecules with precisions that can be less than 1 Å.

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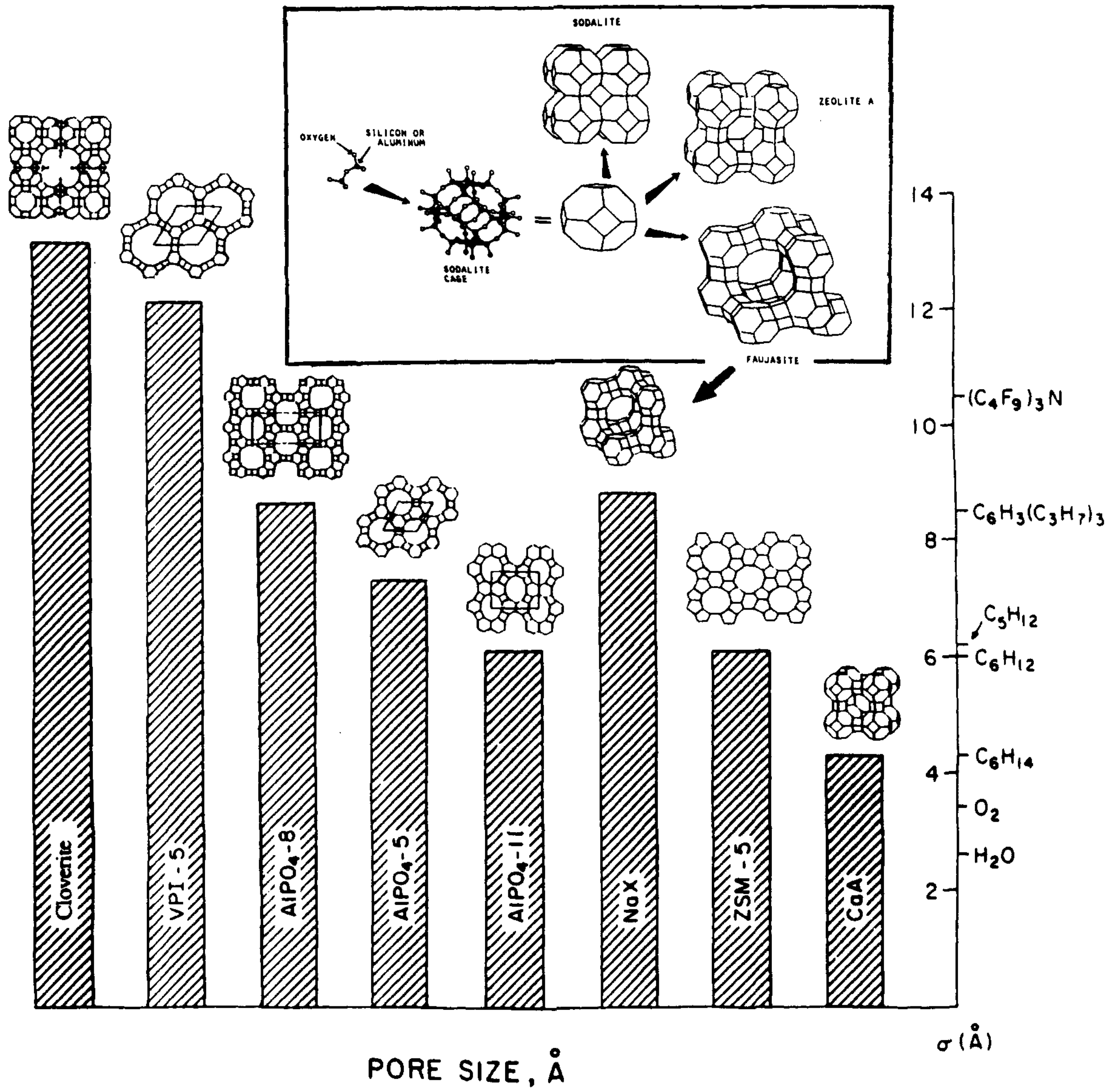

Figure 1. Correlation between pore size of molecular sieves and the diameter (σ) of various molecules. Inset: schematic of zeolite frameworks. The synthetic faujasites are zeolites NaX (Si/Al = ~1.1) and NaY (Si/Al = ~2.4).

Strictly speaking, a zeolite is an aluminosilicate. Molecular sieves with framework T atoms other than silicon and aluminum are not zeolites. For example, a neutral $AlPO_4$ framework is obtained from the connection of Al^{3+} and P^{5+} oxide tetrahedra in strict alternation (Al/P = 1). The $AlPO_4$ framework is the "3–5" analogue of the "4–4" pure SiO_2. Additional elements can be partially substituted into the $AlPO_4$ framework resulting in an anionic framework, e.g., substitution of Si^{4+} for P^{5+}[10] or Co^{2+} for Al^{3+}.[11] $AlPO_4$'s[12] and element-substituted $AlPO_4$'s[13] have been reviewed.

Zeolites and phosphate-based molecular sieves are microporous solids with a broad range of physicochemical properties (Table I). The commercial success of molecular sieves is due largely to the continual discovery of new materials whose diverse properties have allowed process improvements and the development of new technologies. Thus, the ability to control the materials properties through synthetic efforts has been and will continue to be of paramount importance.

Table I. Physicochemical Properties of Zeolites and Molecular Sieves

property	range
pore size	~4–13 Å
pore shape	circular, elliptical
dimensionality of pore system	1-D, 2-D, 3-D
pore configuration	channels, cages
surface properties	hydrophilic, hydrophobic (high silica)
void volume	less than ~50%
framework oxide composition	Si, Al, P, Ga, Ge, B, Be, Zn: major Ti, Fe, Co, Cr, V, Mg, Mn: minor

The first synthetic zeolites were aluminum-rich or low silicon to aluminum ratio.[14] Aluminum-rich zeolites can contain aluminum concentrations equivalent to silicon. However, Al–O–Al linkages have not been observed in zeolites. (Nonzeolitic (condensed) forms of the sodalite

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Table II. Compositions of Zeolites and Molecular Sieves

$\mathrm{Si/Al} \le 2$ low-silica	$2 < \mathrm{Si/Al} \le 5$ intermediate silica	$5 < \mathrm{Si/Al}$ high-silica	phosphate
ABW, Li-A(BW)	BHP, linde Q	BEA, zeolite beta	AEI, AlPO$_4$-18
AFG, afghanite[a]	BOG, boggsite[a]	DDR, decadodecasil 3R	AEL, AlPO$_4$-11
ANA, analcime[a]	BRE, brewsterite[a]	DOH, dodecasil 1H	AET, AlPO$_4$-8
BIK, bikitaite[a]	CAS, Cs-aluminosilicate	EUO, EU-1	AFI, AlPO$_4$-5
CAN, cancrinite[a]	CHA, chabazite[a]	FER, ferrierite	AFO, AlPO$_4$-41
EDI, edingtonite[a]	CHI, chiavennite[b]	LEV, NU-3	AFS, MAPSO-46
FAU, NaX	DAC, dachiardite[a]	MEL, ZSM-11	AFT, AlPO$_4$-52
GIS, gismondine[a]	EAB, EAB	MEP, melanophlogite	AFY, CoAPO-50
GME, gmelinite[a]	EMT, hexagonal faujasite	MFI, ZSM-5	APC, AlPO$_4$-C
JBW, NaJ	EPI, epistilbite[a]	MFS, ZSM-57	APD, AlPO$_4$-D
LAU, laumontite[a]	ERI, erionite[a]	MTN, dodecasil 3C	AST, AlPO$_4$-16
LEV, levyne[a]	FAU, faujasite,[a] NaY	MTT, ZSM-23	ATF, AlPO$_4$-25
LIO, liottite[a]	FER, ferrierite[a]	MTW, ZSM-12	ATN, MAPO-39
LOS, losod	GOO, Goosecreekite[a]	NON, nonasil	ATS, MAPO-36
LTN, NaZ-21	HEU, heulandite[a]	SGT, sigma-2	ATT, AlPO$_4$-12 TAMU
NAT, natrolite[a]	KFI, ZK-5	SOD, sodalite	ATV, AlPO$_4$-25
PAR, partheite[a]	LOV, lovdarite[b]	TON, theta-1	AWW, AlPO$_4$-22
PHI, phillipsite[a]	LTA, ZK-4	ZSM-48	BPH, beryllophosphate-H
ROG, roggianite[a]	LTL, linde L		CAN, tiptopite[a]
SOD, sodalite	MAZ, mazzite[a]		CHA, SAPO-47
THO, thomsonite[a]	MEI, ZSM-18		CLO, cloverite
WEN, wenkite[a]	MER, merlinoite[a]		ERI, AlPO$_4$-17
	MON, montasommaite[a]		FAU, SAPO-37
	MOR, mordenite[a]		GIS, MgAPO-43
	OFF, offretite[a]		RHO, pahasapaite[a]
	PAU, paulingite[a]		SOD, AlPO$_4$-20
	RHO, rho		VFI, VPI-5
	SOD, sodalite		
	STI, stilbite[a]		
	YUG, yugawaralite[a]		

[a] Natural materials. [b] Beryllosilicates (natural).

framework (SOD) such as $Ca_4(Al_6O_{12})$[15] and bicchulite $Ca_4(Si_2Al_4O_{12})OH_4$[16] are known and do contain Al–O–Al linkages.) Loewenstein first rationalized the absence of Al–O–Al linkages in tectoaluminosilicates on the basis that clusters of negative charge are less stable than isolated negative charges.[17] Thus, if aluminum atoms do not have aluminum atoms in their second coordination sphere, then $\mathrm{Si/Al} \ge 1$. According to Flanigen's notation[14] low-silica zeolites are defined as having $1 \le \mathrm{Si/Al} < 2$, while intermediate Si/Al zeolites contain $2 < \mathrm{Si/Al} \le 5$. A number of molecular sieve structures and representative materials are listed in Table II according to their Si/Al ratio. In the late 1960s and early 1970s high-silica zeolites with $\mathrm{Si/Al} > 5$ were synthesized. As the Si/Al ratio increases the properties of the zeolite are significantly altered. At higher Si/Al ratios the crystals are hydrophobic. For example, essentially aluminum-free ZSM-5 adsorbs less than 1 wt % water at 20 Torr and 25 °C (adsorbs 0.18 cm^3 hexane/g) and even floats on water. In the early 1980s silica-free molecular sieves were synthesized. To date, a very broad spectrum of phosphate-based molecular sieves have been reported.[12,13,18,19]

Hundreds of molecular sieves, corresponding to the nearly 75 structures, are known. Given this broad spectrum of reported materials and physicochemical properties, the question arises of whether new structures and properties are still desired. The answer is yes. For example, zeolites with pores comprised of 12, 10, and 8 T atoms (large-, medium-, and small-pore materials, respectively) are known. These pores may extend in one, two, or all three spatial dimensions of the crystal. Although intersecting 12–8 and 10–8 pore systems exist, an intersecting 12–10 pore system that would likely be useful in hydrocarbon transformation reactions has not yet been synthesized. (NU-87 possesses an intersecting 12–10 pore system, but access to the interior of the crystals is through the 10 rings alone.[20]) A material with such a pore system does exist, Boggsite (BOG).[21] However, only a very limited amount of this material exists. A synthetic analogue of Boggsite (Table II) would give the first zeolite with an intersecting 12–10 pore system with access via the 12 rings. The current limit on void volume is approximately 50%. Crystals with larger void volumes would be useful for a variety of confinement, adsorption, and catalytic applications. Theoretical predictions suggest that the presence of three T-atom rings in the framework could have the potential to dramatically increase the void volume of molecular sieves.[22,23] Chiral frameworks could be used in asymmetric synthesis and the separation of enantiomers. (We will close our review with a discussion of this problem.) The point is that there are still many new synthetic targets that are most likely to be accomplished through rationally designing the synthesis of molecular sieves. Historically, the synthesis of new zeolites has occurred mainly through Edisonian-type efforts. Today there are guidelines for certain types of syntheses, although mechanistic understanding of the crystallization process is still not available. The lack of fundamental understanding is due to the high complexity of these systems that does not make them readily amenable to in situ investigations and also to the apparent lack of a universal crystallization mechanism (rather there appear to be several mechanisms in each subclass of materials, e.g., high-silica, low-silica, and the mechanisms can vary from subclass to subclass). The

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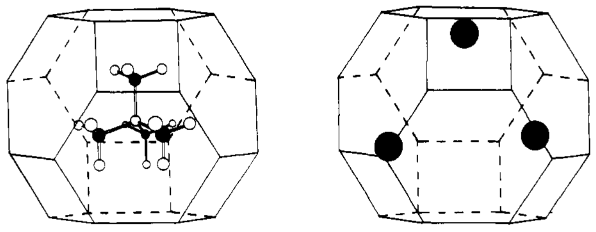
synthesis of aluminum-rich zeolites, high-silica zeolites, and aluminophosphates will be discussed in three different sections. For each subclass, the synthesis process and some of the unsolved issues will be evaluated. Finally, a discussion concerning the feasibility of rationally designing the synthesis of new molecular sieves will be presented using the particularly important example of synthesizing a chiral zeolite.

Evolution in Zeolite and Molecular Sieve Synthesis

The first natural zeolite was discovered in 1756, and efforts to synthesize zeolites can be traced back to 1862.[24] Early attempts of zeolite synthesis centered around mimicking geologic conditions that involve high temperatures ($T > 200$ °C) and pressures ($P > 100$ bar). Since the 1940's, systematic synthetic studies have been disclosed. In 1948, the first synthesis of a zeolite that did not have a natural counterpart was accomplished by Barrer.[25] However, zeolite technology was initiated in the late 1940s by the large-scale, synthetic methodologies of Milton and co-workers, who developed hydrothermal zeolite syntheses using reactive alkali-metal aluminosilicate gels at low temperatures (~100 °C) and pressures (autogenous). This type of crystallization may involve the structure-directing effects of hydrated alkali-metal cations that organize zeolite structural subunits and solution-mediated crystallization of the amorphous gel. That is, the amorphous solid formed in the reaction mixture serves as a source of reactants that are then dissolved into the liquid phase and transported to nucleation centers. The concept that nucleation centers are critically sized entities (at this time the structure of these nuclei remains unknown) that allow spontaneous growth by lowering the free energy of the solutions is speculated to be true for zeolite synthesis. Using alkali-metal hydroxides, "reactive" forms of silica (sodium silicate, colloidal silica, fumed silica, amorphous silica) and alumina (sodium aluminate, aluminum hydroxide, aluminum sulfate) and water to form the gels, aluminum-rich zeolites such as zeolites A (LTA) and X (FAU) can be crystallized at temperatures below ~100 °C (pH typically greater than 12).[26]

The next advance in zeolite synthesis was again due to Barrer. In 1961, Barrer and Denny reported a zeolite synthesis using alkylammonium cations, namely, an intermediate-silica analogue of zeolite A using tetramethylammonium (TMA^+) cations.[27] They noted that the addition of alkylammonium ions to sodium aluminosilicate gels increased the framework Si/Al ratio. (At about the same time, G. Kerr at Mobil Oil Company began using organic molecules in zeolite synthesis.) This effect has been observed for zeolites that contain sodalite cages, e.g., zeolites A, X, Y (FAU), and sodalite (SOD). The zeolite sodalite is comprised entirely of sodalite cages. For the sodalite structure, there are six T atoms per sodalite cage and three anionic charges per cage when Si/Al = 1 (one per Al^{3+}). Thus, three extraframework sodium ions per cage are necessary to balance the framework charge (Figure 2). If an aluminosilicate gel is formed with TMAOH in the absence of alkali cations, sodalite with Si/Al = 5 is obtained.[28] Since only one TMA^+ ion can be accommodated in the sodalite cage, the Si/Al ratio is forced to 5 (Figure 2). From Figure 2 it is clear that TMA^+ cannot diffuse into and out of the sodalite cage. Therefore, the cage must crystallize around the TMA^+. TMA^+ has a particularly strong affinity for the creation of sodalite cages. In fact, the word "template" has been applied to the "organizing ability" of TMA^+ toward sodalite cage formation. We will discuss the issue of structure direction versus templating below.



TMA-Sodalite

Si/Al = 5

Na-Sodalite

Si/Al = 1

Figure 2. Schematic illustrations of cations in sodalite cages.

The use of organic materials in zeolite syntheses was quickly expanded after the initial work of Barrer and Denny. Many new high-silica zeolites were crystallized using organic molecules with aluminosilicate gels at 100–200 °C. For example, zeolites β (BEA), ZSM-5, and ZSM-11 (MEL) are synthesized using tetraethylammonium, tetrapropylammonium, and tetrabutylammonium ions, respectively (pHs generally greater than 10). Alkali-metal ions, in addition to the organic materials, are normally used in the crystallization of high-silica zeolites except for ZSM-5, ZSM-11, and ZSM-48.

In 1982, Wilson et al. reported the synthesis of aluminophosphate molecular sieves.[29] $AlPO_4$ syntheses differ from zeolite syntheses in that they involve acidic or mildly basic conditions and no alkali-metal ions. A typical $AlPO_4$ synthesis mixture is prepared from alumina, H_3PO_4, water, and an organic material. In addition to quaternary ammonium ions, amines are frequently used in $AlPO_4$ syntheses (amines will protonate to become water soluble in the acidic gel). The reactions are conducted at 100–200 °C. The partial substitution of other framework elements is accomplished by inclusion of the appropriate precursor compounds into the reaction mixture, e.g., cobalt acetate, silica. In general, alkali-metal cations have a detrimental effect on the synthesis of $AlPO_4$ molecular sieves. However, there are a few examples in which alkali-metal cations can be used in phosphate gels, e.g., in the synthesis of a silicoaluminophosphate with the sodalite structure[10b] and the low-temperature synthesis of hydrated zinco- and beryllophosphate molecular sieves.[18]

Synthesis of Zeolites and Molecular Sieves

The mechanisms of zeolite formation are very complex due to the plethora of chemical reactions, equilibria, and solubility variations that occur throughout the heterogeneous synthesis mixture during the crystallization process. One can idealize the time evolution of the process by considering that the reaction mixture proceeds from an initially random state to one with microscopic order (nucleation sites), then to the final state where long-range order is apparent (observation of crystals). At the two extremes of the proposed mechanism for zeolite synthesis are (i) the solution-mediated transport mechanism and (ii) the solid-phase transformation mechanism. The solu-

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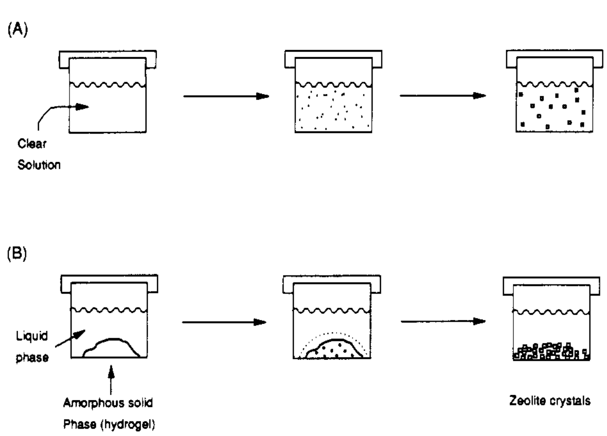

Figure 3. Schematic illustrations of the (A) solution-mediated transport and the (B) solid-hydrogen transformation crystallization mechanisms.

tion-mediated transport mechanism involves the diffusion of aluminate, silicate, and/or aluminosilicate species from the liquid phase to the nucleation site for crystal growth. There are many examples of solution-mediated transport in the crystallization of aluminum-rich zeolites. However, the best example of this process is from Ueda et al.[30] Zeolites Y, S (GME), and P (GIS) were synthesized from *clear* solutions, i.e., no hydrogel (solid phase) was present. The solid-phase transformation mechanism suggests that the solid hydrogel reorganizes in forming the zeolite structure. An example of this process is illustrated by the synthesis of ZSM-35 (FER) and ZSM-5 from nonaqueous reaction mixtures by Xu et al.[31] After dehydration of an aluminosilicate gel at 550 °C, the reaction mixture was formed by adding this solid to liquid triethylamine and ethylenediamine and heated to ~160 °C. No aluminate or silicate species were observed in the liquid phase during the course of the reaction. Clearly, in these cases, a solid-phase transformation mechanism is occurring. Iton et al. have shown by small-angle neutron scattering that ZSM-5 can be crystallized by either of these two general routes and that the route is dependent on the source of silica (sodium silicate yields a solid–hydrogel transformation while colloidal silica, e.g., Ludox, gives liquid-phase transport).[32] Finally, Bodart et al. compare the crystallization mechanisms of zeolites Y, mordenite (MOR) and ZSM-5.[33] Mordenite is crystallized via solution-mediated transport while ZSM-5 can be crystallized by either the solution-mediated transport mechanism or the solid–hydrogen transformation mechanism depending upon the reaction conditions. Also, zeolite Y was found to crystallize by a combination of the two mechanisms (Figure 3).[33] Since a particular structure can be formed via different crystallization processes, extreme caution is necessary when attempting to generalize conclusions from one zeolite to a class of zeolites or molecular sieves.

Aluminum-Rich Zeolites. Aluminum-rich zeolites, e.g., zeolite A, X, P, sodalite, chabazite (CHA), and edingtonite (EDI) have pore volumes in the range ~0.4–0.5 cm^3 void/cm^3 of crystal and are formed near 100 °C. In general, the higher the synthesis temperature, the lower the water content and the lower the intracrystalline void volumes in zeolites. The aluminum-rich zeolites are at the high end of the porosity scale for zeolites. Flanigen in her synthesis review that covered 1969–1973 suggests two roles of the alkali-metal cations in the synthesis of zeolites: (i) the source of hydroxyl ions (alkali-metal hydroxides commonly used in zeolites synthesis) and (ii) a limited structure-directing role.[34] In basic media, the solubility of silica increases roughly exponentially with alkali-metal ion concentration (solubility of silica is very low below pH 10) and a plethora of silicate anions appear due to oligomerization.[35] However, at high pH, aluminum species exists as $Al(OH)_4^-$. Basic conditions facilitate mixing of reactants that then lead to nucleation and crystal growth. Structure-direction by the hydrated alkali-metal cations is proposed to involve the ordering of water around the cations with subsequent displacement by silicate and aluminate species to form regions of microorganization (leading to nucleation centers). More recently, Dutta et al. have proposed that cation–water complexes stabilize small aluminosilicate anions that are responsible for forming unique zeolite structures primarily through electrostatic and steric factors.[36] (McCormick and Bell have shown via ^{29}Si NMR that alkali-metal cations influence the distribution of silicate species in aqueous solutions.[35]) Using identical aluminosilicate solids and hydroxide concentrations, Dutta et al. show that the variation of the alkali-metal cation in the series Na^+, K^+, Cs^+ gave zeolite A, chabazite, and edingtonite, respectively. All of these zeolites are constructed from rings that contain four T-atoms. Regardless of the mechanism of structure-direction, it is clear that alkali-metal cations exhibit this property in the synthesis of aluminum-rich zeolites. Further in situ spectroscopic studies of zeolite crystallizations, e.g., ^{23}Na or ^{113}Cs NMR would be most helpful in investigating the mechanistic role of the hydrated cations.

For aluminum-rich zeolites: (i) the greater the concentration of alkali-metal cations, the smaller tends to be the Si/Al ratio (lower limit is 1.0), (ii) the framework Si/Al ratio increases to greater than 1 if the gel Si/Al ratio is less than 1, and (iii) the framework Si/Al ratio can be lower than that of the gel Si/Al ratio leaving a siliceous solution.[37] Thus, the possibilities for manipulating alkali-metal aluminosilicate synthesis mixtures to yield aluminum-rich zeolites is somewhat limited. However, two largely unexplored avenues exist. First, the use of cations other than alkali-metal ions has not been investigated in depth. In 1978 Robson suggested that alkaline-earth-metal cations would play an important role in future synthesis.[38] This has not been the case. Although work in the early 1960s with Ca^{2+}, Sr^{2+}, and Ba^{2+} by Roy and Barrer produced synthetic counterparts of natural zeolites like heulandite (HEU), yugawaralite (YUG), and harmotone (PHI), respectively, there is much room for study. Since aluminum-rich zeolites contain a large number of framework charge and are hydrophilic, the use of ions with high charge-to-diameter ratio should be likely candidates for structure-direction. However, the relatively low solubilities of these ions in aqueous media severely limits the composition ranges that are achievable, e.g., $Ca(OH)_2$ is less soluble than alkali metal hydroxides. The shape of the hydrated alkali-metal ions and alkaline-earth-metal cations is spherical. Thus, one is not able to manipulate the shape of the cations. The use of organic and organometallic

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cations allows one the option of size and shape "design" of the cations (vide infra).[39] There have been very few studies involving organometallic cations in molecular sieve synthesis. We have investigated this area of synthesis and have found that in most cases the organometallic cations are not sufficiently robust to withstand the high temperatures and pH conditions necessary for molecular sieve synthesis.[40] Second, most if not all studies on the synthesis of aluminum-rich zeolites suggest that the crystallization process involves a solution-mediated transport mechanism although recent evidence from small-angle X-ray scattering suggests that this may not be true for the synthesis of zeolite A.[41] If the synthesis conditions were altered such that a solid-hydrogel transformation could occur, then novel materials may result. Recently, the zincosilicate VPI-7 was synthesized.[42] Since zinc is a divalent ion, its incorporation into a silicate framework yields two anionic charges per framework zinc ion. Because of the double charge per zinc ion, the charge density in VPI-7 is similar to aluminum-rich zeolites. VPI-7 likely is synthesized via a solid-hydrogen transformation[43,44] and shows that molecular sieves with high charge density can be synthesized by a solid-hydrogel transformation route. Further work in forcing the crystallization of aluminum-rich zeolites by a solid-hydrogel transformation, e.g., by restricted water environments and nonaqueous solvents, may lead to novel materials.

Zeolites are thermodynamically metastable phases. In general, Ostwald's law of successive reactions is followed in zeolite synthesis. This law states that the first phase produced is consumed and replaced by a thermodynamically more stable second phase and so on until the most stable phase is formed, e.g., quartz with SiO_2. The formation of zeolites cannot be rationalized on a thermodynamic basis alone, and kinetics must be considered as well. While a particular structure may be thermodynamically unfavorable, it may crystallize at conditions where the energy barrier for the transformation to a more thermodynamically stable phase is high, and therefore the structure may not be rapidly converted to another product. When synthesizing aluminum-rich zeolites from alkali-metal aluminosilicate gels, Ostwald's law is observed. For example, zeolite A (framework density = FD = number of T atoms/nm^3 = 12.9) and zeolite X (FD = 12.7) dissolve to form sodalite (FD = 17.2) and zeolite P (FD = 15.4), respectively. The increase in FD is observed unless an additional component is added to the system. For example, if TMA^+ is added to the synthesis of zeolite Y, instead of dissolving and forming zeolite P, zeolite Y dissolves and forms zeolite ZSM-4 (MAZ) (also called zeolite omega) via the effects of the TMA^+. In fact, the trend in increasing FD can be altered by the addition of organic components. For example, Zones and co-workers have shown that zeolite P (FD = 15.4) can be converted to a variety of zeolites by the inclusion of organic compounds.[45] With *N*,*N*,*N*-trimethyladamantammonium, zeolite P is converted to SSZ-13 (high-silica zeolite with chabazite structure (FD = 14.6)). The organic compounds may act as structure-directing agents to determine the ultimate phase formed during the synthesis. (In the section on high silica zeolites we will discuss in detail structure-direction with organic compounds.) These transformations are not topotatic. Rather the initial phase is dissolved and serves as a source of nutrients for the next phase to form. These results, in addition to the consensus that the synthesis mechanism involves solution-mediated transport, lead to questions about the nature of the participating aluminosilicate species.

Much work has focused on the role of small oxide clusters, secondary building units (e.g., double six-membered rings for faujasite, etc.)[9] and other spectroscopically (Raman,[36] IR, NMR[35]) observable entities as the major participating species in the synthesis of zeolite structures. For example, in the synthesis of aluminum-rich zeolites, Dutta and co-workers have identified rings containing four T atoms in the amorphous aluminosilicate solid by Raman spectroscopy.[36,46] However, no building blocks such as secondary building units for specific zeolite structures could be observed. Additionally, species such as three-membered rings (cyclic trimeric silicic acid) are commonly observed in silicate solutions by liquid ^{29}Si NMR studies,[35,41] yet three-membered rings are not observed in zeolites except in ZSM-18 where the formation of three-membered rings appears to be controlled by the organic template. Thus, the relationships between the species observed by NMR and/or Raman spectroscopy and the final zeolite structures formed have not been developed.

Recently, Vaughan has suggested that extended sheet and columnar substructures are important building units when using sodium and potassium aluminosilicate gels, respectively.[47] Sodium aluminosilicate gels with additional Li^+, Na^+, K^+, Rb^+, and Cs^+ ions produced ZSM-3, faujasite, platelet faujasite, platelet faujasite, and CSZ-1, respectively, at 100 °C. These zeolites are comprised of FAU sheets. Thus, Vaughan proposes that sodium structure-directs the formation of FAU sheets. Additionally, the fact that intergrowths of cubic and hexagonal faujasite (EMT) can be synthesized at various degrees of each polymorph[48,49] in a systematic fashion[48] supports Vaughan's view. Also, Vaughan observes further evidence for sheet substructures by the formation of mazzite (MAZ), mordenite, and ECR-1 at 150 °C. When using potassium aluminosilicate gels, Vaughan synthesized zeolites that contain chains of four membered T-atom rings, e.g., zeolite L (LTL), offretite (OFF), and erionite (ERI). Thus, growth by columnar substructures is proposed. Finally, a striking transmission electron micrograph is given by Vaughan that shows what appears to be a small rectangular structure consisting of approximately 3 by 10, 12-membered T-atom rings that has been observed in the early stages of the synthesis of a 12-ring zeolite.[47]

The above results suggest that emphasis should be placed on understanding the formation and structure of nucleation sites and on probing synthesis processes at length scales larger than those obtained from Raman and NMR spectroscopies. It is likely that the structures of the nucleation centers determine the structures of the zeolites formed. Also, it is hard to envision crystals forming from the condensation of small species of the type observable by Raman or NMR spectroscopy. More likely, these

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species react to form extended structures of medium-range order (as suggested by Vaughan) not observable by probes of short-range order (Raman, IR, NMR). These extended structures then react to form the long-range order in the crystals. Analogy can be drawn to the formation of a protein structure. The tertiary structure of a protein is not formed immediately upon the chemical linking of the amino acids (formation of the peptide bond). Rather, the amino acids condense to form the primary structure afterwhich folding occurs to generate secondary and tertiary structure. In zeolite formation, the small structures observed by Raman and NMR spectroscopies may not be directly incorporated into a growing crystal but instead form extended structures. These extended structures then participate in the formation of long-range order whether they participate via a solution transport mechanism, a solid–hydrogel reorganization, or a combination of both. Wijnen et al. observe via small-angle X-ray scattering that during the synthesis of zeolite A, changes in gel morphology occur before crystalline zeolite formation is observed by the onset of Bragg reflections in the powder X-ray diffraction pattern.[41] These results illustrate the importance of "microordering" prior to the formation of long-range order. Thus, to rationalize the effects of alkali-metal ions and organic cations on the ultimate zeolite products formed, it appears that the cations create local order which then produces "microordered states". Alkali metal and organic ions can act in concert to order silicate species.[50] However, it is not clear whether these small species can condense to form extended structures that vary in structure as the cations are changed.

Elucidation of the information described in the previous paragraph will open new avenues for controlling the crystallization of zeolites. Since the sizes and shapes of inorganic cations in aqueous solution are limited, there is little flexibility for the rational "design" of synthesis conditions for aluminum-rich zeolites. The use of organic reagents greatly expands the ability to direct the synthesis of zeolites.

High-Silica Zeolites. The synthesis of high-silica zeolites requires the addition of organic molecules into the reaction mixture (an exception is ZSM-5 which can by synthesized without the use of organic reagents in a very narrow range of Na^+ and aluminum concentrations[51]) and the reaction temperatures are normally higher (~100–200 °C) than those used to crystallize aluminum-rich zeolites. The organic species can balance the framework charge. However, for siliceous zeolites, the organic species can be found in amounts greater than is necessary for framework charge compensation (suggesting roles other than charge balance). The term templating has been frequently used in the context of synthesizing high-silica zeolites. Templating has been defined as "the phenomenon occurring during either the gelation or the nucleation process whereby the organic species organizes oxide tetrahedra into a particular geometric topology around itself and thus provides the initial building block for a particular structure type."[13,52] Additionally, Rollmann stated that a true templating effect would occur with a reaction mixture if the organic reagent causes a different structure to form or a molecular sieve to crystallize from a reaction mixture that otherwise would remain amorphous.[53] We believe that neither of these definitions are really appropriate. If the term templating is used in a manner similar to that employed in biological templating and template polymerization, then the zeolite structure must adopt the geometric and electronic configurations that are unique to the templating molecule. In general this is not true for high-silica zeolites. Thus, we suggest the aforementioned definitions apply to the term structure-direction rather than a strict templating action. Organic guest molecules can act as (i) space-filling species, (ii) structure-directing agents, or (iii) templates. Organic species can fill the void space of high-silica zeolites. Since the surface of a forming high-silica crystal will be hydrophobic, the organic species will partition into these regions from the aqueous reaction mixture. By packing into the cages and channels, the organic species can increase the thermodynamic stability of the organic-framework composite over the stability (or more correctly metastability) of the framework alone. If structure-direction is occurring, then it should affect the nucleation process and ultimately the crystal structure that is formed. It is the question of the specificity of a particular structure to a particular organic that allows the distinction of structure-direction. For example, at least 22 and 13 different organic molecules can be used to synthesize ZSM-5 and ZSM-48, respectively.[54] Clearly, in these cases the organics are not acting as structure-directing agents but rather as space-fillers. Structure-direction implies that a specific structure is synthesized via a single organic species. There are true cases of structure-direction in the synthesis of zeolites. Two examples of structure-direction are (i) *N,N,N*-trimethylammonium derivative of 1-adamantanamine in the synthesis of SSZ-24[55] and (ii) 1,4,7,10,13,16-hexaoxacyclooctane (18-crown-6) in the synthesis of hexagonal faujasite.[48,49,56,57] Additionally, we believe that there may only be one example in all the literature on zeolites and molecular sieves that qualifies as true templating. A specific $C_{18}H_{36}N^+$ triquaternary amine (tri-quat) is necessary for the synthesis of ZSM-18.[58,59] This tri-quat has D_{3h} point symmetry (bending of the nitrogen atoms in the five-membered rings about the plane of the central aromatic ring is ignored).[59] Using the geometry obtained from the crystal structure of the pure tri-quat,[60] we placed the tri-quat molecule into the cage of ZSM-18 (framework structure from Lawton and Rohrbaugh[59]) and performed energy minimization calculations that allowed for atomic displacements of the tri-quat molecule. Interestingly, the minimum energy configuration occurs when the center of the tri-quat molecule resides at a position in the ZSM-18 cage that has the C_{3h} symmetry (suggested by Lawton and Rohrbaugh). The position of the tri-quat in the ZSM-18 cage that gives the lowest energy is schematically illustrated in Figure 4. The ZSM-18 cage that hosts the tri-quat has the same 3-fold rotational symmetry as the organic molecule. However, the guest–host interaction is sufficient not to allow rotations of the tri-quat[61] (many cases of clathration exist, e.g., TMA^+ in sodalite (Figure 2) so inhibition of translation from cage to cage is common but elimination of rotation is rare). This is not the case

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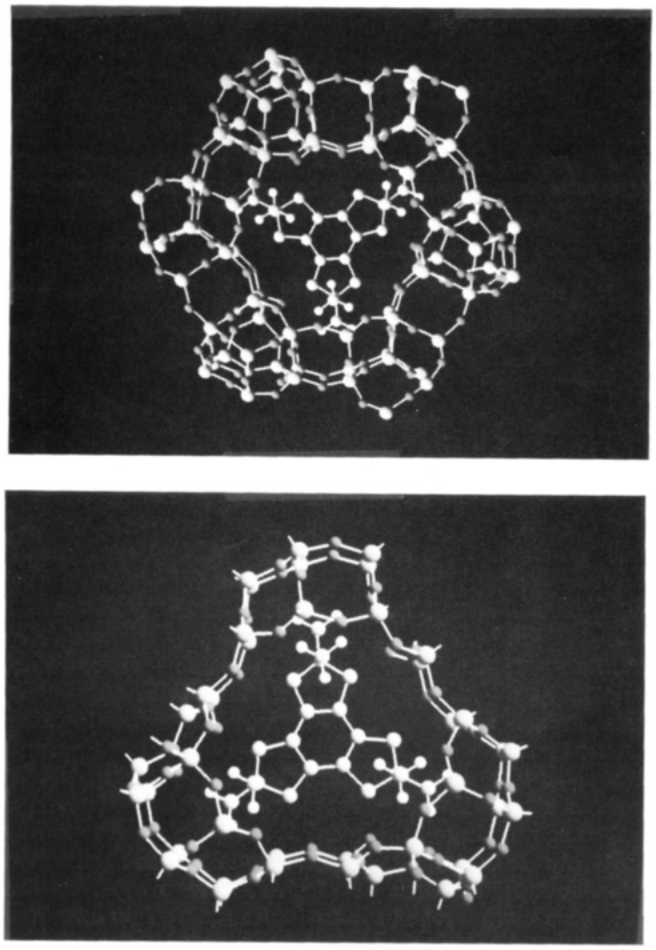

Figure 4. Schematic illustration of the tri-quat guest located in the cage of ZSM-18. The minimization was carried out using the program CERIUS from Cambridge Molecular Design. The optimum position of the tri-quat is (0,0,0.23) which is not exactly the special position (0,0,0.25). The discrepancy is attributed to the bending motion of the nitrogen-containing rings about the plane of the central aromatic ring.

for other organic molecules that reside in cages.[61] Rotations about axes of symmetry are commonly observed and imply that the guest molecules are not tightly accommodated. If the organic guest is free to at least rotate, then the host volume need conform not to the geometry of the guest but rather to the geometry of the volume generated by the rotations of the molecule. Thus, the absence of free rotation of the guest molecules suggests that true templating may have occurred. While structure-direction and templating both imply that a specific structure is synthesized from a given organic species, enhanced guest–host interactions distinguish templating from structure-direction.

Tetraalkylammonium salts are common structure-directing agents in the synthesis of high-silica zeolites. These cations are known to form hydrates.[62] Many quaternary ammonium ions are regarded as structure-forming ions in aqueous solutions ever since Frank and Evans[63a] proposed a theory of "iceberg" formation around the hydrocarbon groups of these ions, i.e., hydrophobic hydration. (For a more recent reference see ref 63b.) Small inorganic cations are regarded as structure-breaking in aqueous solution. However, since they are energetically hydrated they may contain small clusters of water as well. Shimizu and Taniguchi[64] have recently investigated the motion of D_2O in aqueous alkali-metal ion and quaternary ammonium ion solutions by NMR. Water molecules in the vicinity of TMA^+ are influenced mainly by the charge effect, which is less important for TEA^+ (tetraethylammonium) and negligible for TBA^+ (tetrabutylammonium). Additionally, TPA^+ (tetrapropylammonium) and TBA^+ form a hydrogen-bonded network of water, while TMA^+ does not and TEA^+ reveals behavior intermediate to TMA^+ and TPA^+. If it is envisioned that the water associated with these species is partially displaced by silicate and/or aluminosilicate species to form precursors for nucleation centers to allow for the structure-direction to occur, then these effects should be observable. Weibcke[65] very recently discussed structural links between zeolites and aluminosilicate hydrates. For example, TBA^+ forms a hydrate[62] in aqueous solution and a silicate hydrate[66] that is a close structural analog to zeolite A is crystallized from an aqueous TBA^+ silicate solution. Additionally, a hydrate of TMA^+ can be formed that has the sodalite structure[67] and a TMA^+ aluminosilicate hydrate[68] has been synthesized with the same topology as octadecasil[69] and $AlPO_4$-16.[70] Thus, the idea of ordering water and silica and/or aluminosilicate species by organic molecules is plausible. However, the step from an ordered microenvironment within a synthesis medium to the formation of a fully four-coordinate oxide framework has yet to be observed experimentally.

The concept of structure-direction is illustrated by the work of Gies and Marler.[71] Silica, water, and organic molecules were combined to crystallize a wide variety of porosils (general term to denote xM·SiO_2 where M is a guest molecule and x can vary widely). Porosils include clathrasils (cagelike voids occupied by guest species with openings too small to expel the guest species without decomposition[71]) and pure-silica zeolites, e.g., ZSM-48, ZSM-22, ZSM-5, ZSM-11, ferrierite (FER), and ZSM-12. Aqueous solutions containing silica and organic species were sealed in silica tubes and heated to 150–250 °C for up to 6 months. Methyl, ethyl, and trimethyl, and mono-, bi-, and tri-cyclic amines, e.g., piperidine, quinuclidine, and 1-aminoadamantine, respectively, were found to structure-direct the formation of clathrasils. In general, the size of the clathrating silica cage was found to correlate with the size of the guest amine. Also, the symmetry of the cages was higher than that of the guest species. This is probably due to the rotational freedom of the guest amines. When linear diamines were used, zeolites with one-dimensional channels were formed. For example, diaminopropane and 1,3-piperidylpropane yielded ZSM-48 and ZSM-12, respectively. Although these molecules still contain an axis of rotation, the elongated dimension gives them a shape appropriate for channel formation (as opposed to the formation of cages). The size of the piperidyl groups may force the formation of 12 T-atom ring pores while the diaminopropane is sufficiently small to be accommodated in pores consisting of 10 T-atoms. Finally, triethyl-, tripropyl-, and tributylamine were used to crystallize ZSM-5, while TBA^+ was used to synthesize

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ZSM-11. ZSM-5 and ZSM-11 have intersecting pores. In these cases, hydrophobic hydration is not sufficient to mask the three-dimensional geometry of the aqueous tri- and tetraalkylammonium species. Gies and Marler conclude that since there are no ionic interactions between the guest molecules and the silicate structures, the close guest–host geometrical fit most likely reflects an optimized configuration for van der Waals interactions.[71]

The work of Gies and Marler[71] in combination with the observations by Weibcke[65] led to a fairly convincing argument for structure-direction in the synthesis of high-silica zeolites. The questions that remain are (i) does structure-direction occur for all organic species and (ii) can true templating be accomplished? The results from Gies and Marler[71] show that in principle organic molecules that are water-soluble and stable to the synthesis conditions should structure-direct via hydrophobic interactions with the silica. However, this is not always the case. There are many examples where organics fail to produce zeolites from pure-silica reaction mixtures. One critical issue here is the kinetics of the systems investigated. Most studies may not have employed sufficiently long crystallization times; Gies and Marler reported crystallization times as long as 6 months. Organic molecules that appear to have no structure-directing effect may in fact exhibit one if the crystallization times are significantly increased. For example, Gies and Marler synthesized pure-silica ZSM-12. We have synthesized pure-silica ZSM-12 using alkali-metal ions in addition to silica and organic species.[72] When the ratio of $SiO_2/Na_2O = 5$, ZSM-12 is crystallized in 7 days at 150 °C. If sodium is not added, pure-silica ZSM-12 can be synthesized in 84 days.[73] Additionally, we have shown that increasing alkali-metal concentration at constant concentrations of organic species and hydroxide ion shortens the crystallization time necessary for obtaining pure-silica ZSM-12.[73] Thus, while several pure-silica zeolites like ZSM-5 and ZSM-11 can be synthesized in relatively short periods of time (less than a week) in the absence of alkali-metal ions, there may be new structures heretofore not observed because the crystallization times may be very long. The addition of alkali-metal ions to pure-silica synthesis mixtures may enhance the crystallization kinetics of illustrated by the ZSM-12 example. However, addition of large amounts of alkali-metal ions and aluminum may alter the gel chemistry sufficiently to override or modify the structure-directing effects of the organic species.

Gies and Marler conducted their crystallizations in silica tubes.[71] The silica tube may in some cases be important for the formation of the porosils. For example, Gies and Gunawardane[74] synthesized pure-silica ferrierite using ethylene diamine at 160–180 °C in 8 weeks. We repeated this synthesis in Teflon-lined autoclaves (very common in zeolite synthesis). We were unable to crystallize ferrierite in the autoclaves unless glass beads were added; the ferrierite grew off of the surface of the beads. These results suggest that an appropriate nucleation surface may aid the synthesis of some porosils.

When the concentration of aluminum and alkali-metal ions in the synthesis mixture are increased, the reaction chemistry changes from that of pure silica and the "structure-directing" effect of the alkali-metal ions can become important.[50] Thus, the interpretation of this situation is more complicated. Systematic variations of a single variable in the synthesis conditions are difficult to achieve. For example, many references show the effect of changing alkali-metal ion concentration. Unfortunately, the change in alkali-metal ion concentration is many times accompanied by a change in the hydroxyl ion concentration, and interpretation of the results obtained is not straightforward. In general, as the aluminum concentration (and accompanying alkali-metal ion concentration) is increased relative to the silica concentration, structures with lower Si/Al ratio are crystallized; as expected, these structures are hydrophilic. Additionally, high-silica zeolites have a large number density of five T-atom rings while aluminum-rich zeolites do not (mainly four and six T-atom rings). For example, when using TEA^+, high Si/Al ratios yield ZSM-12, intermediate Si/Al ratios give zeolite β, and low Si/Al ratios produce faujasite. Thus, a multitude of factors are changing as the Si/Al ratio (and associated Si/alkali-metal cation ratio) decreases.

Because of the hydrophobic interactions between silica and organic species and the ability to control the steric and electronic structure of the organic species, high-silica syntheses appear to be the most amenable to manipulation. As mentioned above, pure-silica synthesis mixtures appear to show structure-direction via the organic species, but the kinetics of the process are an issue of practical importance. Further work is necessary to elucidate the effect of inorganic ions in the kinetics of high-silica crystallizations. Additionally, one must answer the question of whether the inorganic cations perturb the structure-directing interactions between the silica and the organic. Most likely, the alkali-metal cations interfere with the organic structure-directing effect at high concentrations. Zones has shown that *N,N,N*-trimethyl-2-adamantylammonium iodide becomes less soluble in high ionic strength media.[75] Thus, one plausible mechanism for the reduction in structure-direction at high concentrations of alkali-metal ion is simply a reduction in organic concentration through precipitation.

Zeolite syntheses are performed at high pH conditions. Normally, OH^- is used to solubilize silicate and aluminate species. Several years ago, Flanigen and Patton introduced a new route for zeolite synthesis that involved the use of F^- as the mineralizing agent.[76] This method has been developed further by Guth and Kessler.[77,78] Replacement of OH^- by F^- allows the crystallization of zeolites at neutral or acidic conditions (we have used this method to synthesize pure-silica ZSM-5 at $pH \geq 5$). Structures such as MFI, FER, MTT, MTN, and TON (Table II) have been crystallized using the F^- synthesis method.[77,78] Of particular importance is the fact that heteroatom-substituted (B, Al, Fe, Ga, Ti) high-silica zeolites can be synthesized using F^-.[77,78] In general, aqueous transition-metal ions are not stable at high pH. For example, mononuclear iron species are stable at low pH, while at high pH they condense to higher nuclearity. The addition of F^- forms stable fluoride complexes with heteroatoms in the synthesis media and allows for significant levels of incorporation into the zeolite products. Finally, Kessler has extended the use of F^- into phosphate-based molecular sieves and has found that F^- has a strong propensity to form double four-membered silicate and aluminophosphate rings (F^- resides within the cube formed by the double four-membered rings).[79] The fluoride method has produced three new

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structures; pure-silica octadecasil (AST), triclinic chabazite-like AlPO$_4$ and the gallophosphate cloverite (CLO). Further studies on the fluoride method are warranted since its use is not restricted to any particular class of zeolite or molecular sieve synthesis.

Phosphate-Based Molecular Sieves. In addition to the aluminophosphate-based molecular sieves,[12,13,29] other phosphate-based molecular sieves exist,[18,19] e.g., gallium phosphates—most notably cloverite[80] (Figure 1). However, we will base our discussion of the synthesis of phosphate-based molecular sieves on AlPO$_4$'s[81–83] since synthetic studies of other phosphate-based molecular sieves are rare. Dense phase AlPO$_4$ structural analogues of SiO$_2$, e.g., quartz, cristobalite, and tridymite have been synthesized. In addition, aluminophosphate hydrates have been prepared at temperatures near 100 °C.[84] The synthesis of molecular sieve AlPO$_4$'s involves the use of organic agents.[12,13,29] As described with high-silica zeolites, the organic agents can act as space-fillers, structure-directing species, and maybe even templates. AlPO$_4$-5 (AFI) can be synthesized using over 20 different organic species. On the other hand AlPO$_4$-20 (SOD) can be crystallized only with TMAOH. The primary differences between high-silica and AlPO$_4$ syntheses are that the AlPO$_4$ syntheses are at low pH and aqueous AlPO$_4$ species have a decreasing solubility with increasing temperature, while the solubility of silica increases with increasing temperature.

Aluminophosphate molecular sieves can be crystallized via solution-mediated transport mechanisms[85] and solid–hydrogel reorganizations.[83] As in the case of zeolites, the crystallization mechanism is dependent upon the conditions of the synthesis. Pang et al. have synthesized element-substituted aluminophosphates from clear homogeneous solutions.[85] These results suggest that solution-mediated crystallizations can occur with phosphate-based syntheses. Davis et al. demonstrated that VPI-5 can be synthesized by a solid–hydrogel reorganization mechanism; the crystallization required the use of organic species.[83] However, unlike other AlPO$_4$'s, the organic species are not occluded into the micropores. Recently, a procedure has been developed to synthesize VPI-5 in the absence of organics.[86] To date, VPI-5 is the only AlPO$_4$ molecular sieve to show this property. Because the pores of VPI-5 are large, they can accommodate small molecules in packing arrangements significantly different from smaller pore materials. In fact, the water molecules in as-synthesized VPI-5 are speculated to be ordered in a triple helix.[87] Although it is clear that some of the water in VPI-5 is ordered, the precise structure is not clear at this time.[88] The water structure in VPI-5 may play some role in the stabilization of the framework. Thus, the synthesis of VPI-5 is unusual when compared to the synthesis of the other AlPO$_4$'s.

The AlPO$_4$ syntheses have provided more than 27 different structures and over 13 elements have been partially substituted for either Al or P.[82] This tremendous diversity is accomplished in spite of the fact that the number of T atoms in a particular ring must be an even number (strict alternation of Al and P). Since the AlPO$_4$ framework is neutral, only van der Waals interactions occur between the organic guest species and the host framework. Reaction mixtures for synthesizing AlPO$_4$'s generally are $R\cdot Al_2O_3\cdot P_2O_5\cdot xH_2O$ where $40 \le x \le 400$ and R denotes the organic species. Thus, AlPO$_4$ syntheses do not have as many synthesis variables as aluminosilicate syntheses.

There are several aluminophosphate structural analogues of pure-silica molecular sieves. For example, AlPO$_4$-20 (SOD), AlPO$_4$-5 (AFI), and AlPO$_4$-16 (AST) all have corresponding pure-silica frameworks. In theory, every AlPO$_4$ material has a pure-silica analogue. Unfortunately, this has not been observed. As the Si/Al ratio increases in zeolites, there is a tendency to form a large number density of five T-atom rings in the framework. For example, zeolite Y (Si/Al = 2.4), ZSM-5 (essentially pure SiO$_2$), and mordenite (Si/Al = 5) have 0%, 85%, and 95% five T-atom rings in their structures, respectively.[89] Therefore, pure-silica molecular sieves with no five T-atom rings are rare. If five T-atom rings could be eliminated, new pure-silica molecular sieves could be obtained. At present, such control is not possible. Further work on the crystallization mechanism of SSZ-24 (pure-silica analogue of AlPO$_4$-5) may prove useful in determining the underlying reason for the lack of five T-atom ring formation.

Stuckey and co-workers have recently synthesized a number of new zinco- and beryllophosphates.[18,90] In addition to the preparation of zeolite analogues, e.g., SOD, FAU, RHO,[18] several new structures[90] have also been obtained. These materials have been synthesized at temperatures less than 100 °C. Haseman et al. crystallized 150 aluminophosphate and iron phosphates (many at low temperature) over 40 years ago.[91] The work of Haseman et al. needs to be reinvestigated in light of the new phosphate-containing materials currently being reported from low-temperature syntheses.

Because there are fewer synthesis parameters in the crystallization of AlPO$_4$'s, the main route open for the synthesis of new AlPO$_4$'s appears to be that of using new organic species. Since phosphate-based molecular sieves are not stable in basic media (pH $\leq$9),[92] the synthesis conditions are limited to low pH. In addition, it is clear that for reasons unknown at this time, phosphate-based materials are capable of forming large pores (Figure 2). A particularly intriguing area is the synthesis of very-large-pore materials. For the known three very-large-pore materials VPI-5 (VFI), AlPO$_4$-8 (AEI), and cloverite (CLO), none is synthesized with large organic molecules. Thus, the structure-direction of a very-large-pore material by an appropriately sized organic species would be of interest, especially in attempting to understand further the mechanism of structure-direction.

Rational "Design" of a Zeolite Synthesis

On the basis of the knowledge accumulated thus far, one can attempt to control particular aspects of the synthesis

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Table III. Enantiomorphic Space Group Pairs from Ref 103

$P4_1$	$P4_3$	$P6_1$	$P6_5$
$P4_122$	$P4_322$	$P6_2$	$P6_4$
$P4_12_12$	$P4_32_12$	$P6_122$	$P6_522$
$P3_1$	$P3_2$	$P6_222$	$P6_422$
$P3_112$	$P3_212$	$P4_332$	$P4_132$
$P3_121$	$P3_221$		

to obtain a particular structure. However, in the true sense of the word design, the synthesis of zeolites and molecular sieves cannot be designed as yet. As previously mentioned, it is much easier to rationally "design" the shape of the organic structure-directing agent than it is to tailor the structure of the inorganic material. We conclude this review by illustrating the rational design of a zeolite synthesis using the example of the synthesis of a chiral structure.

Enantioselective separations and syntheses are clearly of importance. Unfortunately, the number and types of chiral solids that can perform enantioselective catalysis are very limited.[93] The use of organic solids to carry out chiral synthesis has been reported for quite some time,[94] and many chiral inorganic solids are known.[95-97] Quartz exists in the *d* and *l* forms. Because natural quartz can form in large crystals, crystals of *l* and *d* quartz can be separated and their enantioselective adsorption and catalytic behavior investigated. Kavasmaneck and Bonner studied the adsorption of isopropylester hydrochlorides of *R*- and *S*-alanine on *d*- and *l*-quartz.[98] *l*-Quartz preferentially adsorbed the *R*-alanine enantiomer, while *d*-quartz preferentially adsorbed the *S*-enantiomer. The enantiomeric excesses (ee) did not exceed 12%. Additionally, Pd and Pt deposited onto chiral quartz crystals performed enantioselective hydrogenation, although the ee's were less than 10%.[99] These studies indicate that chiral silica can perform enantioselective separations and syntheses.

Quartz is a dense material and has a very low surface area. The synthesis of a chiral zeolite would increase the interfacial area between the contacting fluid and the surface by at least 4 orders of magnitude. Thus, chiral zeolites would most likely yield larger ee's in adsorptive and catalytic processes and would also exhibit shape-selectivity.

Zeolite β is an intergrowth of two distinct but closely related structures, the so-called polymorphs A and B.[100] In polymorph A, the building unit stacks in either a right-handed 4_1 or a left-handed 4_3 manner. If the sheets stack in a pure 4_1 sequence (RRR...), one enantiomorph of polymorph A, in space group $P4_122$, is obtained and if the sheet stacking is in a pure 4_3 sequence (LLL...) the other enantiomorph of polymorph A is formed (space group $P4_322$). Polymorph B is obtained when a recurrent alternation of right and left stacking sequence is formed (RLRL...). Polymorph A has a helical pore along the *c* axis of the tetragonal unit cell: the pore is right- or left-handed. Figure 5 illustrates the simulated X-ray powder diffraction patterns from the theoretical polymorph A and B of zeolite β and the intergrowth structure that closely matches the experimental patterns from zeolite β.[101] It appears that each layer formed during the crystallization has a near 50% chance of being in a right or left stacking sequence. This means that the growing crystals of zeolite β have "no memory" in the sense of the "handedness" of the crystals from a few layers below.[101]

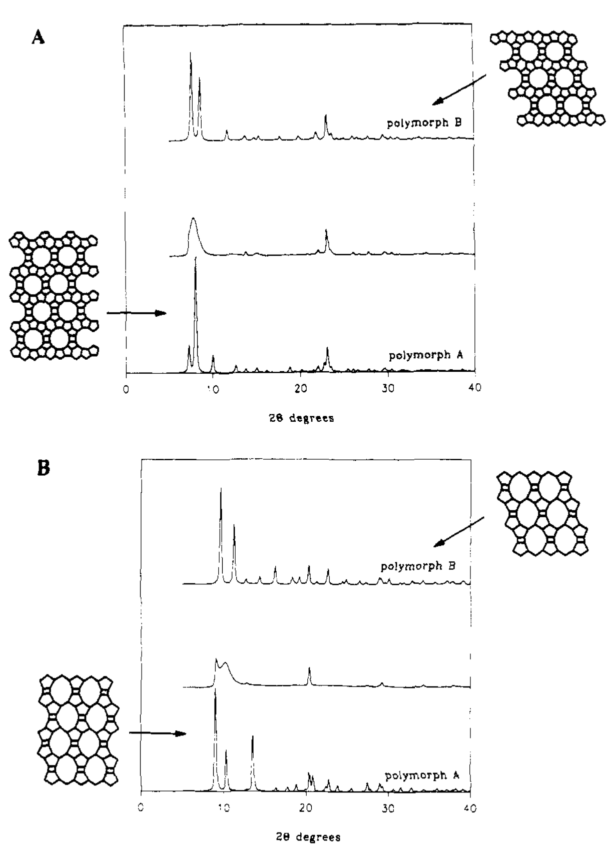

Figure 5. Simulated X-ray powder diffraction patterns of (A) polymorphs A and B and zeolite beta and (B) polymorphs A and B and the intergrowth of a new theoretical structure. Cu Kα radiation.

Zeolite β is not a unique example of how a chiral zeolite may exist. Table III shows the 11 enantiomorphic pairs of crystallographic space groups.[102,103] These space groups are devoid of symmetry elements that include reflections (mirror planes, inversion centers, improper rotation axes or glide planes) but do involve screw rotation operations (generates chirality). The mineral quartz crystallizes in a structure with space group $P3_121$ or $P3_221$ (as does the $AlPO_4$ analogue of quartz, berlinite). (Polymorph A of zeolite β forms an enantiomorphic pair with space group symmetries $P4_122$ and $P4_322$ that have helical pores: right- or left-handedness for $P4_122$ or $P4_322$, respectively.) Thus, numerous chiral structures are theoretically possible. Figures 5B and 6A illustrate a theoretical structure that we have generated. This structure is related to zeolite β in the sense that it is formed of sheets that are stacked in a left- or right-handed manner, one over the other. In analogy to zeolite β, a polymorph A (enantiomorphic pair), a polymorph B, and an intergrowth structure can be formed. Polymorph A of this hypothetical structure contains three intersecting pores that are each circumscribed by 10 T-atom rings. The pore along the *c* direction of the unit cell is helical as with polymorph A of zeolite β. Another hypothetical chiral crystal with space group $P4_122$

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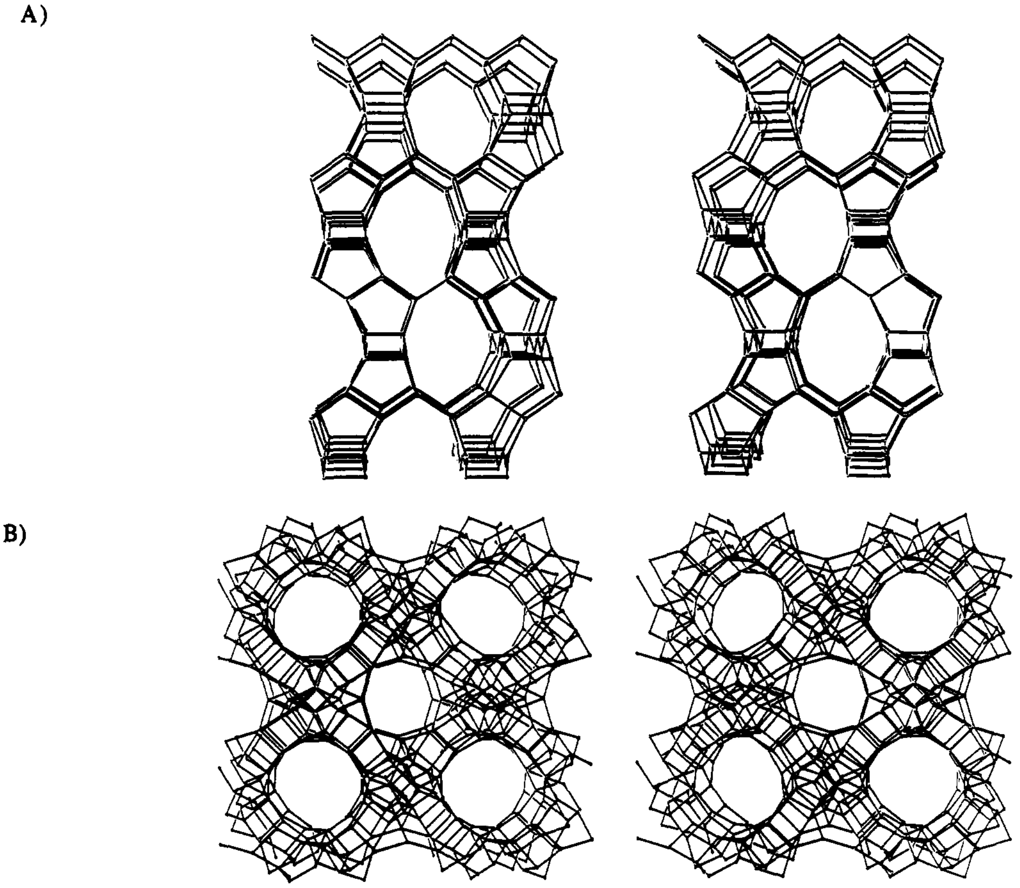

Figure 6. Stereoview of the framework structure given in Figure 5B (A) and the stereoview of the chiral framework structure generated from the building units of ZSM-5 (B).

(or $P4_322$) can be generated from the building units of ZSM-5 (Figure 6B). With this structure, it is not possible to form an intergrowth. Thus, like quartz, each crystal with this structure would be chiral.

Although several theoretical, chiral zeolite structures can be generated, the challenge is to actually synthesize a chiral zeolite. Tomlinson et al.[104] show that the lattice energies of polymorph A and B of zeolite β are essentially the same by using lattice energy minimization calculations. This partly explains why an almost random stacking sequence is found in zeolite β. The synthetic problem is to influence the stacking such that the left stacking is more probable than the right one (or vice versa). How can the symmetry of the system be broken? Recently[105,106] the spontaneous chiral resolution of sodium chlorate was reported, but because of the "short memory" of the stacking sequence of zeolite β, it is very unlikely that such a spontaneous resolution will happen in this case. Another option is the addition of a dissymmetric agent, as is often used in the resolution of racemic mixtures,[105] and to use a chiral "template" as suggested by Newsam and Treacy.[101] In this paper we have distinguished between structure-directing agents and true templates. To synthesize a chiral zeolite, we believe a chiral template must be found. That is, the energy of the appropriate enantiomorph of the template–chiral zeolite framework composite must be lower than all other guest–host energies, e.g., template–polymorph B for zeolite β. We find it difficult to envision the synthesis of a chiral zeolite without utilizing a chiral template.

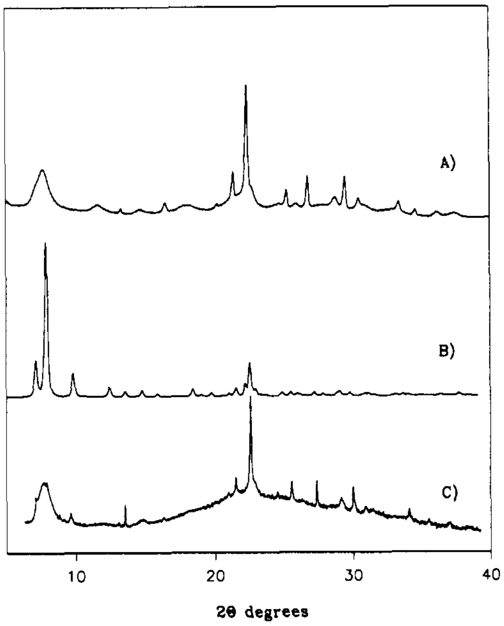

Figure 7. X-ray powder diffraction pattern of (A) as-synthesized zeolite β, (B) pure (no organic present) polymorph A (simulated), and (C) zeolite β synthesized in the presence of a chiral organic molecule. Cu Kα radiation.

We have approached the synthesis of a chiral zeolite as follows.[107] The idea is to synthesize one enantiomorph of polymorph A. The inorganic portion of the synthesis mixture should remain the same as a zeolite β synthesis

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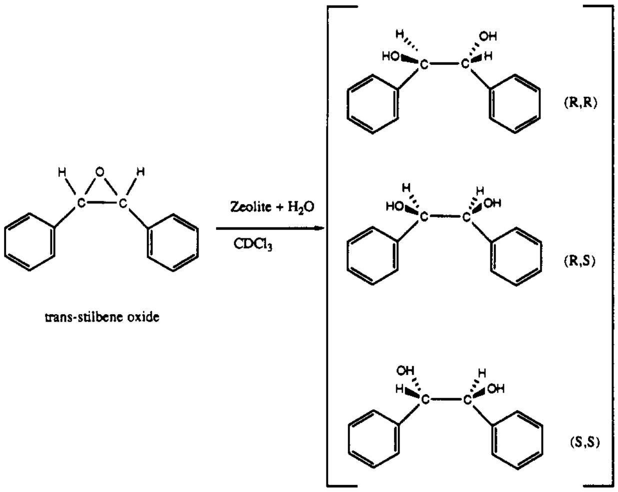

Figure 8. Reactions on zeolite β.

gel since we know that it produces polymorph A. Next, an appropriate template molecules must be developed according to at least three constraints. First, the molecule must be chiral. Second, the size of the molecule is important. Differences between polymorphs A and B of zeolite β arise from the stacking of layers that are a quarter of the *c* dimension of the unit cell apart. Thus, the organic molecule must be at least 10 Å in length (or half the *c* dimension of the unit cell of polymorph A). Third, the organic molecule must be stable at the synthesis conditions of high pH and temperatures less than 125 °C. Using this strategy, we have recently explored the possibility of synthesizing chiral zeolite β. Figure 7 illustrates the X-ray powder diffraction patterns of "normal" zeolite β, a zeolite β synthesized in the presence of a chiral molecule and the simulated pattern of polymorph A. Note that at high *d* spacings, the X-ray powder diffraction pattern of the sample synthesized in the presence of a chiral organic molecule has on average larger domains of polymorph A than "normal" zeolite β. X-ray powder diffraction cannot reveal whether these domains of polymorph A are "racemic" or enhanced in one enantiomorph. To ascertain the chirality of a particular sample, tests other than X-ray powder diffraction are necessary (vide infra). Nonetheless this sample has more polymorph A than the "normal" zeolite β and shows that in principle the synthesis of pure polymorph A should be possible. Additionally, since a chiral template is being used, one would expect that if pure polymorph A were synthesized, it would be enantiomerically pure as well.

To test whether this new sample of zeolite β can perform enantioselective adsorption and catalysis, the following experiments were conducted. The zeolite sample was placed in its acid form and contacted with *trans*-stilbene oxide and then water. The recovered reaction products were then tested for optical activity. The zeolite β sample enriched in polymorph A revealed an ee of ~5% (*R*,*R*-diol, Figure 8) while "normal" zeolite β gave an ee of zero. Also, a racemic mixture of the diols ((±)-hydrobenzoin) was slurried with the zeolite β samples. The zeolite β sample enriched in polymorph A preferentially adsorbed the *R*,*R* isomer (ee again <5%) while "normal" zeolite β did not. Although the ee's from these experiments are low, they are nonzero and are outside the error limits of the experiments. Thus, these results suggest that a chiral zeolite could perform enantiomeric separations and syntheses and that the rational "design" of zeolite syntheses is most likely possible.

Acknowledgment. Support of this work is provided by the NSF Alan T. Waterman Award to M.E.D. We thank Dr. Mike Treacy for providing us with the computer program DIFFaX which was used to generate the simulated X-ray patterns of the intergrowth structures illustrated in Figure 5, Dr. Peter Wijnen for a preprint of his work, Stacey Zones of the Chevron Research Co., and the reviewers for providing helpful suggestions concerning the contents of this paper.