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Structure-Direction in Zeolite Synthesis

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1. Introduction

Zeolites and molecular sieves are important industrial materials that have a broad range of applications. Many zeolites with different structures and compositions are commercially available and used in refining and chemical processing as catalysts, absorption materials, and drying agents, as well as in ion-exchange operations [1,2]. Zeolites and molecular sieves show a strikingly close relationship between their microscopic structure and macroscopic properties. This relationship is particularly clear in their ability to sieve organic and inorganic molecules based on size. Also, the rigorous steric control that zeolite frameworks offer over the chemical reactions occurring inside their pores is directly related to their microscopic structure.

The relationships between the microscopic structure and macroscopic properties have been large driving forces for the synthesis of new materials with novel pore architectures and crystal compositions. It is expected that molecular sieves with new pore structures will show catalytic properties not observed before. Although over 89 different structures are known [3], this is just a small fraction of all the hypothetical structures that have been proposed [4,5].

In this review, we will focus on the relationships between the geometrical and chemical properties of the organic molecules used to direct the crystallization of a particular zeolite structure, and the geometry and characteristics of the cages and pores of the zeolites in which the organic molecules have been occluded. Additionally, we will look at the effects of alkali-metal ions and trivalent and divalent tetrahedral atoms on the zeolite structures formed and how these effects are coupled to the actions of the organic structure-directing agent.

We will emphasize high-silica materials because these molecular sieves are the ones that offer the greatest possibility of control through the use of organic molecules in the synthesis gel. Many new microporous aluminophosphates ($AlPO_4$) and metal-substituted aluminophosphates (MAPO) have been and are continuing to be reported. However, the connection between synthesis conditions and the structures of these molecular sieves is very poorly understood. In these materials, the crystal structure of the final product often depends on the presence of a particular organic molecule in the synthesis gel. However, the relationship between the organic molecules and the pores or cages is very loose, and sometimes the organic molecule is not even present inside the pores of the molecular sieve as is the case for VPI-5 [6,7]. Also, aluminosilicates and borosilicates with low ratios of SiO_2/M_2O_3 will not be covered because the structure of these hydrophilic and highly anionic framework materials is mostly dependent on interactions with the inorganic cations of the synthesis gel.

In addition to an enhanced interaction with organic structure-directing agents, materials formed mostly from tetrahedral silicon atoms (T) have the advantage over $AlPO_4$'s and aluminosilicates in that the T—O—T angle with only Si as the T atoms is much more flexible than other T—O—T angles [8,9]. This is an indication that, in principle, more frameworks should be attainable. Also, high-silica materials can have, among their structural building units, rings with odd and even numbers of tetrahedral atoms, which are not found in $AlPO_4$'s because of the rigorous aluminum-phosphorus alternation.

We begin our discussions with an introduction to the concepts of structure-direction by illustrating the synthesis of clathrasils. Next, we describe recent findings on the relative energetic stability of different pure-silica framework structures and discuss different factors that may affect the crystallization kinetics of zeolites. In the following section, we return to explore more complex zeolite syntheses in which the structure-directing effects not only depend upon the organic structure-directing agent, but also are influenced by the presence of different alkali-metal cations and trivalent and divalent T atoms - such as aluminum and zinc - in the synthesis gel.

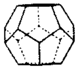
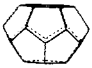
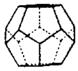
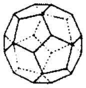
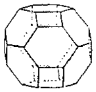
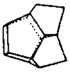
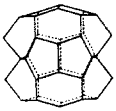
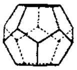
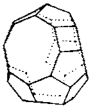
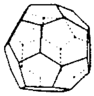
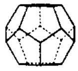
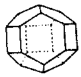
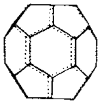
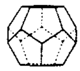
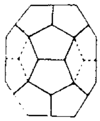
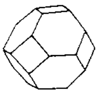
The three-letter code of the International Zeolite Association will be used throughout this review [3] and some familiarity with zeolites and zeolite synthesis will be assumed on the part of the reader. Previous reviews and articles related to the material covered here can be found in the references [10-14] as well as in the general discussion of zeolite structure and properties in Chapter 1 of this volume by Abrams and Corbin.

2. Clathrasils

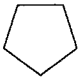
Clathrasils are a group of tectosilicates formed of polyhedra (cages) that enclose relatively small organic or inorganic molecules. The clathrasils can be considered as zeolites with pores of 0-dimension. The different cages found in the known clathrasils are illustrated in Table 1 and many of the structure-directing agents used for the synthesis of these tectosilicates can be found in [13].

Gies and Marler [15] have carried out the synthesis of clathrasils using the simple reaction system SiO_2/structure-directing agent/H_2O, by systematically changing the nature of the structure-directing agent. The advantage of this simple gel composition is that changes in the clathrate structure can be unambiguously attributed to the effect of the structure-directing agent. Gies and Marler found that sixty-one molecules varying from noble gases such as Kr and Xe to large amines such as 1-aminoadamantane can be used to control the structure of the clathrasil formed.

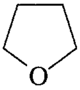
Table 1. Summary of the different cages found in the structures of clathrasils [15].

Clathrasil	Code	FD ($T\ nm^{-1}$)	V of Largest Cage (nm^3)	Clathrasil Cages		
Melanophlogites	MEP	18.9	0.160	 $[5^{12}]$	 $[5^{12}6^{2}]$	—
Dodecasils 3C	MTN	18.7	0.250	 $[5^{12}]$	 $[5^{12}6^{4}]$	—
Octa-decasil	AST	16.7	0.280	 $[4^{6}]$	—	 $[4^{6}6^{12}]$
Nonasil	NON	19.3	0.290	 $[4^{1}5^{8}]$	 $[5^{8}6^{12}]$	 $[5^{5}6^{4}]$
Deca-dodecasil 3R	DDR	17.6	0.350	 $[5^{12}]$	—	 $[4^{3}5^{12}6^{1}8^{3}]$
Sigma-2	SGT	17.8	0.390	 $[4^{3}5^{6}6^{1}]$	 $[5^{12}6^{8}]$	—
Dodecasil 1H	DOH	18.5	0.430	 $[5^{12}]$	 $[4^{3}5^{6}6^{3}]$	 $[5^{12}6^{8}]$
Deca-dodecasil 3H	—	—	0.540	 $[5^{12}]$	—	 $[5^{18}6^{2}8^{3}]$
Sodalite	SOD	17.2	0.230	—	 $[4^{6}6^{8}]$	—

Guest molecules of similar size and shape were found to direct the crystallization of the same product, regardless of differences in chemical properties. The following series of molecules formed the MTN structure in all cases:



I



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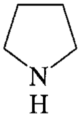
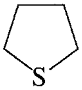
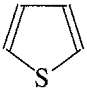


III



IV

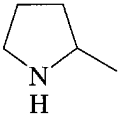


V

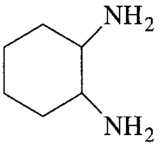
Although the structure is independent of the chemical properties, they found that the kinetics of crystallization are very dependent on the basicity of the organic molecule [16]. The most basic molecule (**III**) gave the highest rate of crystallization and the least basic (**I**) gave the slowest.

Several guest molecules formed different frameworks under different synthesis conditions, and a strong dependence of the structure type on synthesis temperature was observed. For example, 1-aminoadamantane was found to form DDR, SGT, DOH, and deca-dodecasil 3H as the temperature was increased from 140 to 200° C. In general, the smaller cage was found at the lower synthesis temperatures. Although large molecules form crystals with larger cages, some relatively small molecules - like 2-methyl-pyrrolidine - were found in the large $[5^{12}6^{8}]$ cage of DOH.

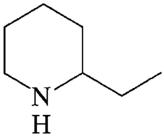
The relation between the geometry of the organic molecule and the geometry of the cage is limited for clathrasils. For example, the following molecules can be used to synthesize DOH:



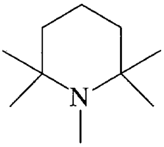
VI



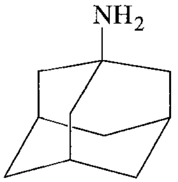
VII



VIII



IX



X

These results when viewed in combination with the effect of the temperature on the size of the cage suggest that the thermal motion of the molecule in the crystallization gel may inhibit the imprinting of the detailed geometry of the molecule, and that the silicate gel 'senses' only the geometry of the volume of revolution of the structure-directing molecule.

We carried out a set of experiments similar to the ones reported by Gies and Marler in which the only components of the gel were the structure-directing agent, the silica source (Cab-O-Sil, M5) and water. The results of these experiments (Table 2) are roughly in agreement with those reported by Gies and Marler. Large molecules form clathrasils with large cages and smaller molecules form crystals with smaller cages.

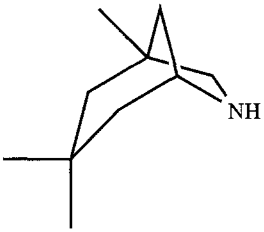
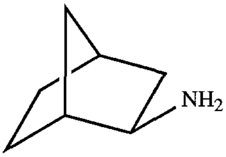
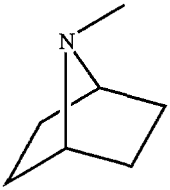
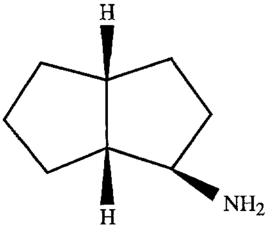
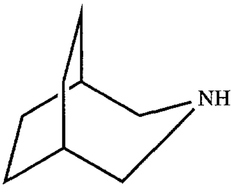
Clathrasils can be also prepared using non-hydrothermal synthesis conditions, e.g., using an organic solvent. The synthesis of SOD was first reported in this manner by Bibby and Dale [17] and ethylene glycol was used as solvent and as the structure-directing agent. Originally, this result was intriguing because the sodalite structure is the only pure-silica clathrasil - besides AST - that contains only even-membered rings in the structure. The remainder of the clathrasils contain a large fraction of 5-rings as is generally observed for high-silica zeolites. The molecules of ethylene glycol are found inside the sodalite cages and are necessary for the synthesis of the material. However, recently, Post and co-workers [18] and Chen [19] reported the synthesis of pure-silica SOD under hydrothermal conditions using trioxane and ethylenediamine as structure-directing agents, respectively.

Although, there have been proposals suggesting that there is a relationship between the symmetry of the organic molecule and the symmetry of the cage [20,21], the results reported by Gies and Marler and those presented in Table 2 suggest that the relationships found between the point group of the molecule and the point group of the cage are probably accidental. Molecules with no symmetry - except the identity operation - are capable of directing the formation of cages with very high symmetry (compare Tables 1 and 2). As suggested above, it seems that the thermal motion of the organic molecule may average out the geometrical differences between the molecules. Definitive proof of the rapid motion of guest molecules inside the cages of clathrasils was recently provided by Gies [14] using static ^{13}C solid-state NMR. Gies showed that organic molecules inside the cages of MTN, DOH, and NON are rotating on a time-scale that is smaller than the time-scale of the NMR experiment. The rapid rotation of organic molecules inside the pores and cages of zeolites has also been reported by Hong and co-workers [22,23].

Using solid-state NMR with and without magic-angle spinning (MAS), they show that adamantane and naphthalene undergo rapid motion inside the pores of zeolite Na-Y. Although these molecules were absorbed inside the zeolite pores after the zeolite synthesis, similar results have been obtained for 15-crown-5 and 18-crown-6 that were used as structure-directing agents in the synthesis of FAU and EMT [24]. These results indicate that rapid motion of the structure-directing agents in the clathrasil cages is likely to be the 'normal' state of the organic molecule at synthesis temperatures.

Clathrasils have several types of cages in each framework structure (Table 1). How are these voids stabilized? Are any of them empty? Crystallographic studies of clathrasils show that the organic structure-directing molecules are found inside the large cages and small molecules are usually located inside the small cages. N_2 and Kr are occluded inside the [5^{12}] and in the [$5^{12}6^{2}$] cages of MEP [25], N_2 and ammonia are found inside

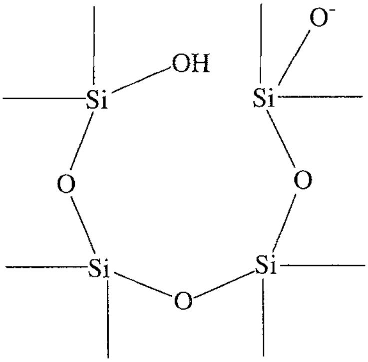
Table 2. Results from the synthesis of pure-silica clathrasils using different organic molecules as structure-directing agents.

Structure Directing Agent	Clathrasil
	DOH
	DOH
	STG, DOH
	NON
	NON

the $[5^{12}]$ and the $[4^3 5^4 6^3]$ cages of DOH [26,27] and N_2 is also located in the $[5^{12}]$ cages of MTN and DDR [28,29]. Note that the occluded N_2 was not purposely added to the synthesis, but was 'captured' from the small amount of atmospheric air trapped inside the silica-glass tubes used for the synthesis [26]. Cages smaller than the $[5^{12}]$ cage are probably not filled with any molecules because the available void is too small to be occupied by guest species. It is interesting to speculate whether these materials could be synthesized in the absence of any small guest molecules that could fill these small cages, especially in the light of what is observed for other aluminous zeolite polymorphs. The small cages of many aluminous zeolites such as CAN, GME, OFF, SOD, etc., are invariably occupied by alkali-metal cations which stabilizes the cage. Therefore, it seems that in general, with zeolites and clathrasils, small cages are only formed when small guest molecules are present as stabilizing agents.

These crystallographic studies have shown that frequently the point group of the organic structure-directing agent is a subgroup of the point group of the cage. However, the axis of symmetry of the molecules and the cages often do not coincide with each other. 1-Aminoadamantane in the $[5^{12}6^8]$ cage of SGT [30,31] is disordered and the axis of the molecule in the dominant conformation does not correspond to the axis of the cage. Also, the axis of 1-aminoadamantane in the $[5^{12}6^8]$ cage of DOH [24], where the cage belongs to the same point group as the organic molecule, is rotated about 20° with respect to the six-fold axis of symmetry of the cage. On the other hand, the axis of 1-aminoadamantane was found to coincide with the three-fold axis of symmetry of the $[4^3 5^{12} 6^1 8^3]$ cage of DDR [29]. These studies have been carried out at room temperature and as indicated above, it is likely that the organic molecule at synthesis temperatures (140° C – 200° C) is rapidly rotating. The results described above must be carefully interpreted when extrapolating to synthesis mechanisms.

Amines and quaternary ammonium ions are the organic molecules used most frequently in the synthesis of clathrasils and molecular sieves. The hydrophobicity of pure-silica frameworks suggests that the positive charge of the organic cation is balanced by a negative charge formed by a defect in the framework that could be illustrated as follows:



We investigated the possibility that defects such as these could balance the charge of the quaternary ammonium ions by obtaining ^{29}Si MAS-NMR on two pure-silica samples of nonasil (NON) synthesized with cyclohexylamine and a quaternary ammonium ion as structure-directing agents (Figure 1). The sample synthesized with a quaternary ammonium cation (Figure 1A) shows two peaks that can be assigned to the presence of both Q_3 and Q_4 silicon atoms (Q_i: $Si(OSi)_iO_{4-i}^-$). The presence of Q_3 and Q_4 suggests that the charge of the structure-directing agent is balanced by a defect (deprotonated silanol group) in the zeolite structure. Similar results have been reported for a sample of pure-silica AFI [32] and for high-silica MFI [33] synthesized with quaternary ammonium ions as structure-directing agents. The resolution of the MAS-NMR spectrum of the sample synthesized with the amine (Fig. 1B) is enhanced to the point of recognition of most of the different tetrahedral environments present in NON [3]. The increase in resolution of ^{29}Si MAS-NMR spectrum has been linked to the absence of defects in the framework [34,35] and suggests that the amine is not protonated inside the NON cages. These results are in agreement with the idea that the charge of quaternary ammonium cations in high-silica zeolites is often balanced by deprotonated silanol groups in the structure. The infrared spectra of these two samples, only show weak evidence to suggest

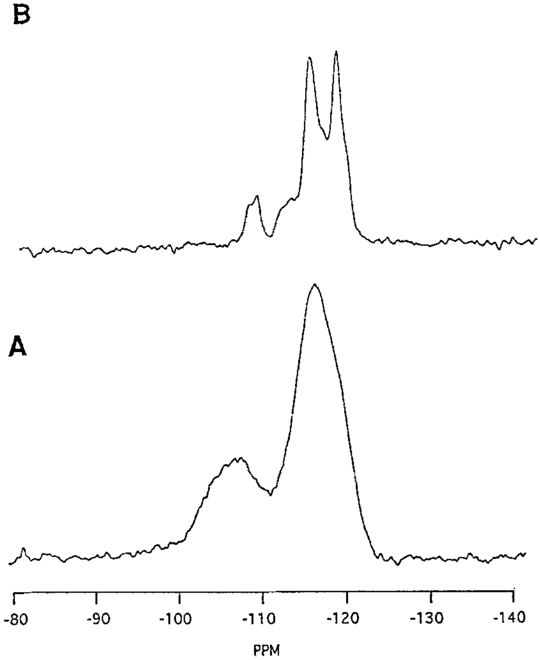
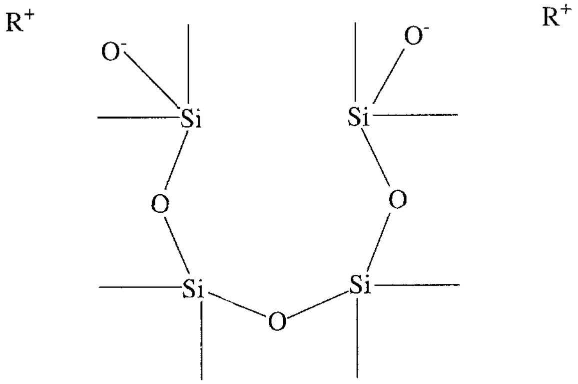


Figure 1. ^{29}Si CP/MAS-NMR spectra of samples of pure-silica nonasil (NON) synthesized using a quaternary ammonium cation (A) and an organic amine (B) as structure directing agent.

the presence of the O—H stretching band (expected at approximately 3300 cm^{-1}), indicating instead that the structure of the defects is closer to the following illustration:



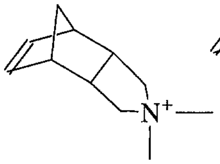
In this second alternative, two positive charges are balanced for each defect. If defects are energetically destabilizing, then it is expected that the structure will crystallize such that the least number of defects are formed to balance the positive charge of the organic guest molecule. This is accomplished by a mechanism best represented by the second illustration. However, this model does not necessarily exclude the formation of defects with protonated silanol groups. From the perspective of structure-direction, this is important because it suggests that molecules with large charge/volume ratio - tetramethylammonium, for example - are not good alternatives for the synthesis of clathrasils. It also indicates that materials with a large void fraction require organic guests with a very low charge/volume ratio, for the defects to have a small impact on the stability of the organic-inorganic composite.

The above discussions illustrate several important issues on the synthesis of clathrasils and pure-silica molecular sieves. The conditions at which an organic guest will best form a clathrasil have been summarized by Gerke, Gies and Liebau [cited in ref. 36] and are as follows:

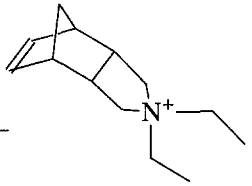
1. The molecule should have sufficient room within a particular cage or pore.
2. The molecule must be stable under the synthesis conditions.
3. The molecule should fit the inner surface of the cage with as many van der Waals contacts as possible, but with the least deformation.
4. The guest molecule should have only a weak tendency to form complexes with the solvent.
5. More rigid molecules will tend to form clathrasils more easily than flexible molecules.
6. The tendency to form a clathrasil will increase with the basicity or polarizability of the guest molecule.

From the molecular point of view, the first condition indicates that if the organic molecule is bigger than the polyhedral cage, steric forces inhibit the formation of the clathrasil. The second point suggests that molecules that can react under basic, hydrothermal synthesis conditions will of course change during the synthesis and their decomposition products will affect the structure of the product. The third and fourth conditions are energetic considerations that indicate that during the formation of the clathrasil, the optimum of the van der Waals interactions between the organic molecule and the cage or zeolite pore depends on the organic guest, and that the energy employed in changing the conformation of the organic guest to fit the geometry of the pore or the cage destabilize the organic-inorganic composite. Finally, the basicity of the molecule is related to a) the effect that a higher pH has on the kinetics of silicate hydrolysis, and b) to the stabilizing effect that a higher polarizability of a molecule within the electric field created by the partial ionic character of the Si—O bond, has over the total energy of formation of the composite.

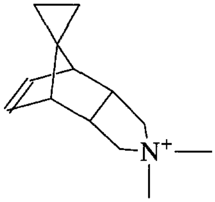
What is observed if we continue to increase the size of the structure-directing agent? This question was recently addressed by Nakagawa and Zones [37]. The following series of organic molecules were synthesized and used as structure-directing agents:



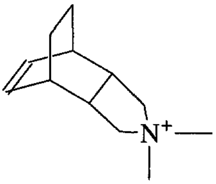
XI



XII



XIII



XIV

In the absence of any structure-directing agent, the product of the synthesis mixture was quartz. Using molecules **XI**, **XII**, **XIII** and **XIV**, the clathrasil nonasil and the one dimensional large-pore zeolites MTW, SSZ-31 and SSZ-31, were formed, respectively. Thus, Nakagawa and Zones found that when the size of the structure-directing agent is increased to a certain dimension, the product formed changes from a clathrasil to a microporous, large-pore molecular sieve.

If instead of the size, the geometry is changed from cyclic molecules to linear molecules, there is also a transition from clathrasils to microporous molecular sieves but now to microporous silicates with 10-ring pores [15]. For example, piperidine forms the NON clathrate, but 1-aminobutane forms TON and ZSM-48 at 160 °C and 180 °C, respectively. The size of the linear organic molecule is of relatively little importance compared to the effect of temperature on the structure of the zeolite formed and small molecules such as ethylenediamine (Table 2) and 1,5,9,13-tetraazatridecane [15] form ZSM-48 under approximately the same conditions.

There is another transition from 1-dimensional, 10-ring materials to 3-dimensional, 10-ring materials as the organic molecule geometry is changed from linear to branched. Diethylamine and dipropylamine form ZSM-48 (a linear 10-ring) but triethylamine and tripropylamine form the MFI structure. Note that in these organic-inorganic composites, the good geometrical fit reflects an optimization of the van der Waals contacts between guest and host [15].

3. Thermochemical Stability of High-Silica Zeolites

Zeolites are thermodynamically metastable phases accessible by kinetically favored pathways under hydrothermal synthesis conditions [39]. Recently, Petrovic and co-workers [40] shed some new light on the thermodynamics of high-silica zeolites. The enthalpy of formation of a series of high-silica zeolites (MFI, MEL, MTW, AFI, FAU and EMT) was determined using a high-temperature solution calorimetry method. The results were compared to the enthalpy of formation of dense polymorphs of silica. All the microporous frameworks are only 7-14 kJ mol^{-1} less stable than quartz. Additionally, no clear correlation between the enthalpy of formation of the zeolites and the framework density - or degree of *openness* - secondary building units such as large or small rings in the structure, or the mean Si–O–Si angle was found (however, see [41] for a different interpretation of the data).

In pure-silica zeolite structures, every silicon atom is bonded to four oxygen atoms in a relatively undistorted tetrahedral coordination and the oxygen atoms are connected to two silicon atoms with an average Si–O–Si angle close to 145°. Ab initio molecular orbital calculations have shown that there is a small barrier to variations in the Si–O–Si angle between 140° and 180°, but that there is a sharp increase in the energy for angles less than about 135°. Therefore, based on the above evidence and to a first degree of approximation, it seems now understandable that the energy of all these pure-silica frameworks should be very similar.

Petrovic et al. showed that there is a correlation between the fraction of Si–O–Si angles $\leq 140°$ and the enthalpy of formation of these pure-silica molecular sieves. This correlation is consistent with the shape of the potential energy curve of the Si–O–Si angle that suggests that small angles are much more destabilizing than large ones. The authors, however, note that these angles have been obtained mostly from analyses of X-ray powder diffraction data. These XRD data contain very short Si–O bond lengths (1.49 and 1.53 Å), very long Si–O bond lengths (1.67 to 1.70 Å), and a large range of O–Si–O angles (92° to 133°). By comparison, the bond lengths and O–Si–O angles of the single crystal structure determination of MFI are in very good agreement with the single crystal data from quartz. Therefore, these unexpected bond lengths and angles may be the result of the difficulty in obtaining a stable and acceptable solution with the Rietveld refinement methodology. Also, based on their work with the relatively simple structure of sodalite, Hu and Depmeir [42] have suggested that the symmetries of zeolites may have been overstated and that some zeolite structure solutions may need to be revised. In summary, to draw further conclusions, it may be necessary to wait until new single crystal X-ray data or other technique improvements confirm the anomalous bond lengths and angles.

The numerical similarity of the enthalpies of formation of the different pure-silica zeolites imply that the role of the organic molecule may be to select a particular structure among many possible of similar energy - i.e., a more kinetic rather than thermodynamic role. However, the incorporation of the structure-directing agent inside the zeolite pores reduces the total free energy of formation of the composite in the same way that a solution of ethanol and water has lower total free energy of formation than pure ethanol and water separately. Interactions that stabilize the organic-inorganic composite are the optimization of van der Waals contacts between the organic molecule and the surface of the pores or cages.

Is it energetically favorable for the structure-directing agent to be occluded inside the zeolite pores? Although most structure-directing agents are soluble in water, studies on the interactions between tetramethylammonium (TMA), tetraethylammonium (TEA), and tetrapropylammonium (TPA) [43,44] and water indicate that the interactions between TMA and water are mainly hydrophilic in character, but TPA, in spite of its positive charge, shows mostly a hydrophobic character due to its longer hydrocarbon chains. TPA orders water around itself with a concomitant entropic cost that balances the energetic gains obtained from the solvation of the positive charge. In an attempt to investigate these interactions with a greater variety of structure-directing agents, Zones has studied the transfer of different charged organic-structure directing agents from an aqueous solution to a chloroform phase as a function of the C/N^+ ratio. He found that the percentage of transfer is low (less than 10%) for molecules with a $C/N^+<11$ and that it is very large (more than 70%) for $C/N^+>15$ (see Figure 2). Interestingly, it is observed that organic molecules with C/N^+ between 11 and 15 work well as structure-directing agents yielding a great variety of new high-silica molecular sieves. This trend suggests that molecules that are moderately hydrophobic are the best candidates for structure-direction. This result is also in agreement with the ideas of Gerke, Gies, and Liebau [36] who indicated that the guest molecule should only have weak tendency to form complexes with the solvent. The percentage of transfer, however, does not correlate with the kinetics of zeolite crystallization, suggesting that geometrical properties also play an important role in the formation of crystal nuclei.

The size of the molecule (carbon+nitrogen atoms) correlates strongly with the selectivity of different structure-directing agents. As indicated previously, often one organic guest molecule can direct the crystallization of more than one zeolite structure. Zones has observed that as the number of carbon plus nitrogen atoms in the structure-directing molecule is increased, this tendency is reduced until finally for large molecules, only one structure is observed. Figure 3 illustrates this trend for a variety of molecules. The conclusion is that, in order to form new structures, larger molecules should be explored more carefully as structure-directing agents. This trend has to be balanced against the effect of the C/N^+ ratio as indicated above. If only one quaternary nitrogen is

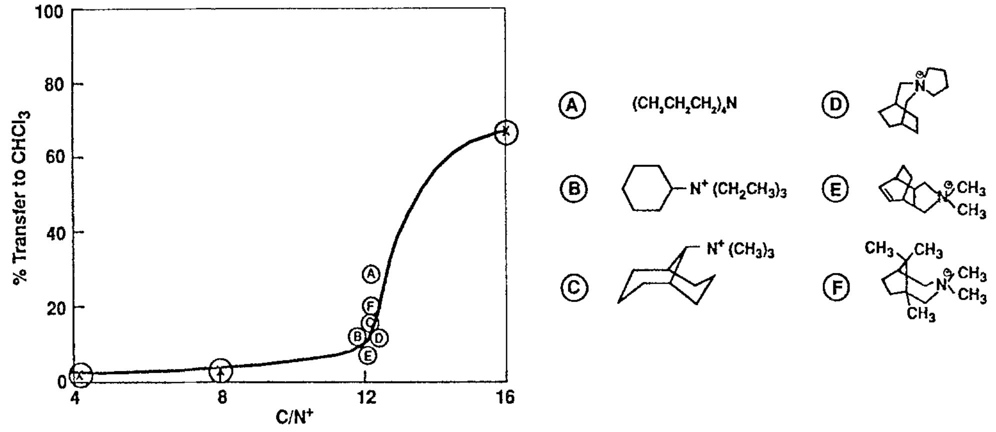


Figure 2. Partition of quaternary ammonium compounds between water and $CHCl_3$.

included in the molecule, eventually the hydrophobicity of the molecule will overcome the solvation possibilities of water and the organic molecules may aggregate to form a separate phase.

4. Kinetics of Zeolite Crystallization

The kinetic nature of the crystallization of silicate frameworks is clearly observed if a structure, less stable than quartz, is formed without the occlusion of organic molecules. This is a common experimental observation when the product of a zeolite synthesis is tridymite or cristobalite, as often occurs during the preparation of high-silica zeolites. Thermodynamic data show that these dense phases are less stable than quartz at synthesis temperature and pressure [45]. However, tridymite and cristobalite are often the product of a zeolite synthesis, indicating that the kinetics of crystal nucleation and growth are the controlling factors determining the structure of the crystallization product.

In the following section we discuss issues involving the effects of alkali-metal cations on the rate of nucleation and crystal growth of high-silica zeolites. We also briefly illustrate how one structure-directing agent can direct the crystallization of different zeolites through seeding of the synthesis gel.

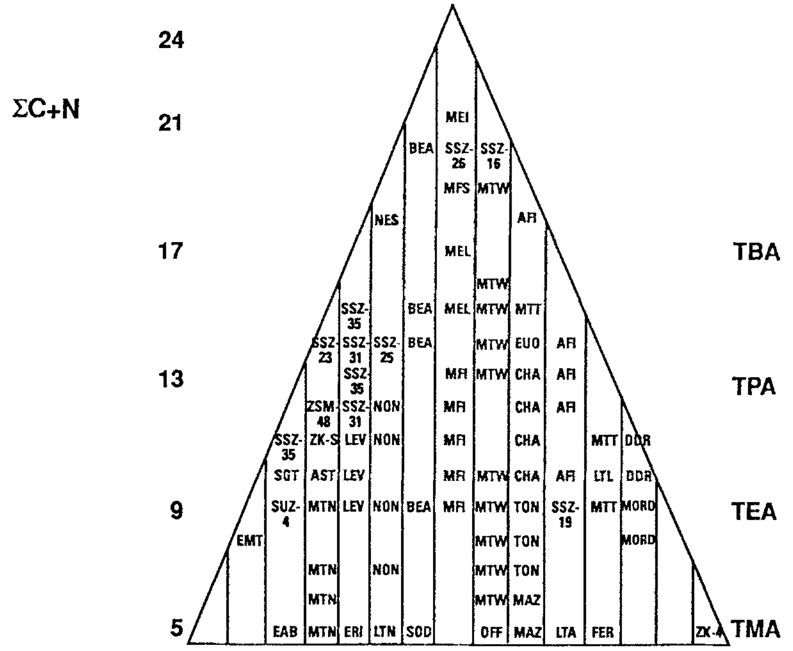


Figure 3. Illustration of the increased selectivity of different structure-directing agents as the size of the molecule (C+N) is increased.

4.1 EFFECT OF ALKALI-METAL CATIONS

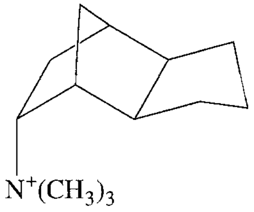
The synthesis of most zeolites is carried out under basic conditions using sodium or potassium cations as one of the main components of the reaction mixture. Other mineralizing agents, fluoride in particular, are also often used (this method is not covered in this review) [see ref. 12]. The effect of alkali-metal ions on the synthesis of pure-silica zeolites was not systematically studied until it was found that the incorporation of titanium into zeolite frameworks was negatively affected by the presence of alkali-metal cations. Titanium-containing zeolites (TS-1 and TS-2) are very active catalysts for the selective oxidation of alkanes and alkenes using hydrogen peroxide as the oxidant [46]. The search for titanium-containing zeolites with new structures prompted the study of zeolite syntheses in the absence of alkali-metal cations.

It was found that most zeolite syntheses are sensitive to the presence of alkali-metal cations in the synthesis gel. Except for the MFI and the MEL structures using TPA or tetrabutylammonium (TBA) as structure-directing agents, other zeolites are very difficult to synthesize in the absence of alkali-metal cations. For example, Goepper et al. [47]

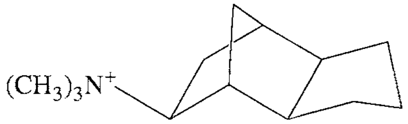
studied the synthesis of pure-silica MTW in the presence and absence of alkali-metal cations at constant hydroxide concentration. They found that the addition of sodium and potassium decreased the crystallization time from 84 days to 7 days and suggested that alkali-metal ions participate in both the nucleation and crystal growth processes.

The study of the dissolution of quartz into aqueous solutions of alkali-metal cations aids the understanding of the role of sodium and potassium in the synthesis of zeolites. Brady and Walters [48] and Dove and Crerar [49] investigated the rate of dissolution of quartz in aqueous solutions of NaCl, KCl, LiCl, and $MgCl_2$. They found that small concentrations of electrolytes increase the rate of dissolution by as much as 15 times, compared to the rates measured for deionized water. The effect is greatest for NaCl and KCl and increases for concentrations up to 0.05 M. The faster dissolution rates observed for sodium and potassium relative to magnesium and lithium are probably related to their potential for adsorption onto the quartz surface. Mg^{2+} and Li^+ have a low potential for adsorption because they are strongly coordinated to water molecules in the solution as the result of their large charge to size ratio. Extrapolation of these results to zeolite synthesis suggests that sodium and potassium are involved in the polymerization and depolymerization of the silicate species in the gel and that this is at least one of the processes through which they increase the nucleation and crystal growth rates of high-silica zeolites.

The effect of high concentrations of sodium on the crystallization of zeolites has recently been reported by Zones [50,51]. Zones studied the effects of the concentration of the inorganic species in the synthesis of large-pore borosilicates using the tricyclo[5.2.1.0]decanes as structure-directing agents:



endo
XV



exo
XVI

The endo derivative produced zeolites SSZ-33 and SSZ-31 at high and low boron substitution, respectively. Similarly, the exo isomer yields boron zeolite beta or MTW in going from high to low boron substitution. Zones investigated the effect of increasing the sodium concentration in the synthesis gel and found that at Na/Si ratios of 0.1, microporous molecular sieves were formed. However, as the sodium concentration was increased to Na/Si ratios of 0.18-0.26, Kenyaite (a layered silicate) is obtained as the final product. It seems that at high concentrations, alkali-metal cations begin to compete with the organic molecules in a structure-directing role.

These examples illustrate the compromise that is needed in zeolite synthesis to obtain an optimum balance among the different effects that the components of the synthesis gel may have on the final product. Alkali-metal cations are needed to increase the rate of crystallization of high-silica zeolites, but excessive amounts of these components in the synthesis mixture will override the structure-directing effects of the organic molecules, and favor the formation of layered compounds.

4.2 SELECTIVITY OF A STRUCTURE-DIRECTING AGENT TOWARDS ZEOLITE FORMATION

As was illustrated in the section on clathrasils, one structure-directing agent can be used to synthesize several clathrate structures depending on the synthesis conditions. Zones et al. [52] studied how perturbations on the synthesis procedure of SSZ-33 (using molecule **XV**) dramatically affect the product formed. Table 3 shows the effect of mixing molecules **XV** and **XVI** in the synthesis gel. The synthesis of SSZ-33 is sensitive to the presence of molecule **XVI**. When the ratio of **XV/XVI**~5, zeolite beta starts to be detected in the product. The yield of crystalline product and ^{13}C MAS-NMR of these samples indicate that both molecules are occluded inside the pores of zeolite beta for **XV/XVI**<3. These data indicate that molecule **XV** can stabilize SSZ-33 and zeolite beta. The data also indicate that the nucleation of crystals of SSZ-33 is very sensitive to the geometry of the structure-directing agent, but that the crystal growth process is more flexible and can be accomplished simultaneously by several structure-directing agents. If

Table 3. Products from syntheses using mixtures of structure-directing agents **XV** and **XVI**.

Ratio XV to XVI	SSZ-33	B-Zeolite Beta
19	100%	0%
9	100%	0%
5.7	Major	Minor
4	Minor	Major
3	0%	100%

seeds of SSZ-33 are added to the same set of experiments, zeolite beta is not observed any more in the final product. The effect of seeding is to bypass the need for the spontaneous formation of SSZ-33 nuclei and effectively stops the formation of zeolite beta [52]. Harris and Zones [53] who investigated the synthesis of pure-silica nonasil, have reported a correlation between the tightness of the fit of the organic molecule in the cage and the rates of nucleation. The faster nucleation rates were observed for syntheses in which the agreement between the size of the molecule and the size of the cage was especially good, indicating that a tighter fit of the organic molecule in the clathrasil cage promotes faster nucleation rates.

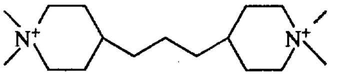
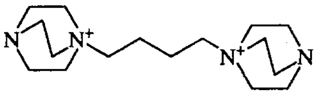
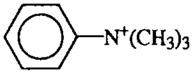
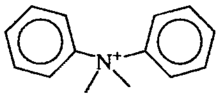
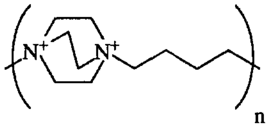
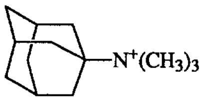
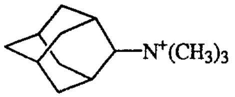
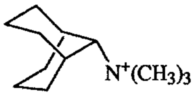
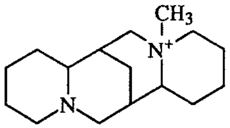
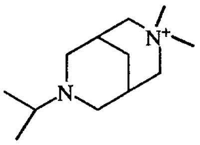
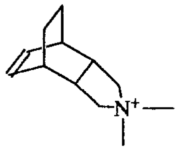
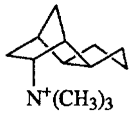
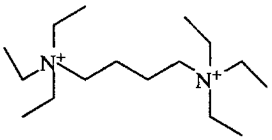
5. Pure-Silica Large-Pore Materials

There are three known pure-silica, large-pore zeolites: ZSM-12 (MTW), SSZ-24 (AFI) and SSZ-31. All these zeolites can be synthesized under the same synthesis conditions except for the use of different structure-directing agents. MTW has relatively small elongated pores (5.5 x 5.9 Å) [3] and can be synthesized using several structure-directing agents (Table 4). The MTW structure is typical of high-silica zeolites and contains 4-, 5- and 6-rings. In contrast, the pure-silica polymorph of $AlPO_4$-5, SSZ-24, contains only 4- and 6-rings and a large 12-ring pore of 7.3 Å in diameter. In spite of these differences in shape and size, the structures of MTW and AFI appear very similar when they are viewed as an assemblage of tubular building units. From this perspective, the differences in the structures of MTW and AFI arise from assembling tubes, in two different forms, with walls formed only of 6-rings. According to the description of Kirchner and McGuire [54], both zeolites have the type 1 pores in which the pore axis is parallel to the edge of a 6-ring.

Comparison of the structure-directing agents for MTW and the structure-directing agents for AFI indicates two main differences: firstly, in general the structure-directing agents for MTW are formed from smaller organic molecules than the structure-directing agents for AFI (cyclohexane and benzene rings vs. adamantane) and secondly, the structure-directing agents for MTW are very flexible compared to the ones for AFI. The combination of these two factors suggests that the structure-directing agents used for the synthesis of AFI are large enough to prevent (by steric forces) the small elongated 12-ring pores of MTW from forming and seem to shift the kinetics of crystal nucleation from MTW to AFI.

SSZ-31 is a pure-silica zeolite synthesized using the structure-directing agents shown in Table 4. Sorption experiments suggest that SSZ-31 is a one-dimensional 12-ring pore system [55]. NCL-1 is also a pure-silica large-pore zeolite [56] synthesized with bis-(triethylammonium)butane. The X-ray diffraction patterns of NCL-1 are very similar to the pattern of SSZ-31. The structure-directing agents for SSZ-31 are also rigid and can be loosely described as containing a large polycyclic body with a protuberance formed by the N-methyl groups. These 'bumps' suggest that the structure-directing agents

Table 4. Structure-directing agents used for the synthesis of MTW, AFI (SSZ-24), and SSZ-31.

MTW[a]	AFI[b]	SSZ-31[c]
     	    	  

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a. See ref. 13, 47.

b. See ref. 32, 56, and refs therein and Y. Nakagawa, *U. S. Patent 5,271,921* (1993).

c. See ref. 37, 57.

destabilize the formation of both MTW and AFI. In short, based on the size and shape of the structure-directing agent, the pores of SSZ-31 should have 'grooves' or 'pockets' to accommodate the shape of the organic guest molecules along the 1-dimensional pores.

It is noteworthy that, except for only one report (vide infra), large structure-directing agents have not given pure-silica materials with new, large, multidimensional pore systems. The reasons behind this observation are not understood, especially if contrasted with the easily synthesized multidimensional medium-pore silicalite-1 and silicalite-2. It can be speculated that T—O—T angles needed for the formation of a multidimensional pore system are not favored in pure-silica materials. Histograms of experimentally measured T—O—T angles (adapted from ref. 8) in Si—O—Si, Si—O—Al and the Si—O—B are shown in Figure 4. It can be observed that the variation in the Si—O—Si angle is larger than the variation in the Si—O—Al and Si—O—B. These histograms indicate that the substitution of Al or B for Si in the framework stiffens the T—O—T angle and shifts the optimum T—O—T angle to a value lower than expected in silicates.

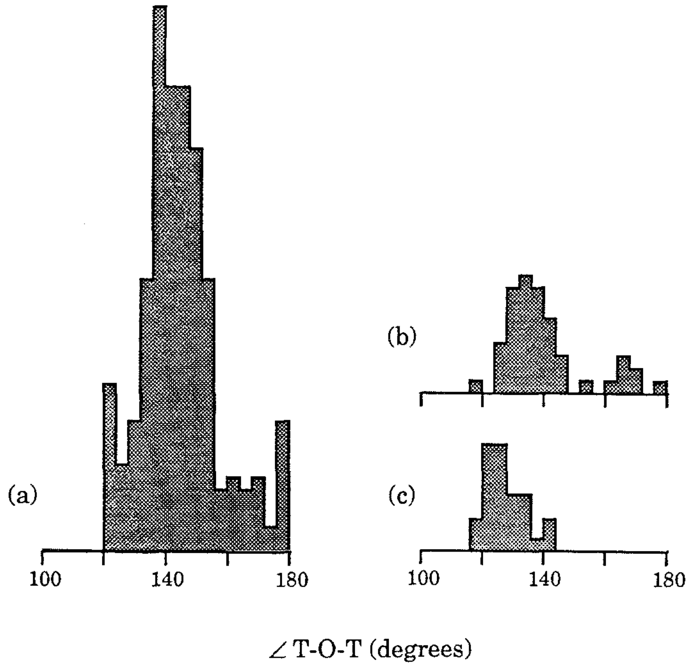


Figure 4. Histogram of experimentally observed T—O—T angles in a) Si—O—Si, b) Si—O—Al, c) Si—O—B, (adapted from ref. 9).

A second reason for the absence of pure-silica materials with intersecting large pores may be the effect of defects on the stability of the silicate framework. As suggested before, in pure-silica materials, the charge of the structure-directing agent is balanced by a deprotonated silanol group in the zeolite framework. For TPA in the MFI structure, this is equivalent to a defect for each 24 Si atoms. As the void volume of the zeolite framework is increased, the ratio Si/N^+ is drastically reduced, for example, for SSZ-33 synthesized using **XV**, $Si/N^+{\sim}15$ and for zeolite beta synthesized using TEA the $Si/N^+{\sim}7$. The charge of the structure-directing agent is largely balanced by B or Al in these two examples, but these numbers suggest that for certain Si/N^+, the density of defects necessary to balance the organic charge in the pure-silica material creates a large destabilization of the structure, thus inhibiting its formation. The exception to this rule was recently reported by van der Waal et al. [72], who synthesized the pure-silica polymorph of zeolite beta using dibenzyldimethylammonium hydroxide as structure-directing agent. The organic molecule contains a C/N=16, instead of C/N=8 in TEA, which therefore gives a $Si/N^+{\sim}14$. The number of defects in this preparation of zeolite beta would be about one half of the number of defects expected in a pure-silica sample of TEA. The smaller number of defects increases the stability of the final product and in this way allows the formation of the pure-silica polymorph of zeolite beta.

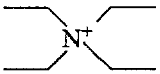
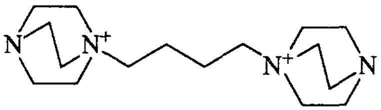
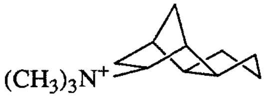
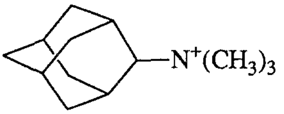
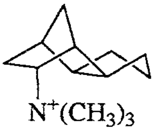
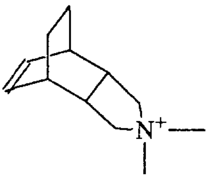
6. Heteroatoms and the Structure-Directing Effect of Organic Molecules

The addition of small amounts of tetrahedral atoms other than silicon (B, Al, Zn, etc.) has a striking effect on the structures of the zeolites formed using the *same* structure-directing agents. In this section, we will look at the changes observed in the structures of zeolites when Al, B, or Zn are added to an otherwise pure-silica synthesis gel. In addition to Al, B, or Zn, many other heteroatoms [2,13] have been incorporated in high-silica zeolite frameworks. In general, the effects of Ga and Fe are similar to the effect of Al. Ti has been found to have small structural effects, and Ge can substitute for Si. The reader may examine the references for more details [2,13].

An example of the effect of added Al on the structure of the zeolites formed when other variables are kept constant is illustrated with the syntheses of MTW and BEA using tetraethylammonium ions as structure-directing agent (Table 5). When the $SiO_2/Al_2O_3 > 50$, MTW is formed. As the amount of Al is increased beyond $SiO_2/Al_2O_3 = 50$, the product observed is BEA, and if the fraction of Al is increased even further ($SiO_2/Al_2O_3{\sim}15$), ZSM-20, an intergrowth of EMT and FAU, is obtained. Analogous results are observed when boron is used instead of aluminum. For low boron concentrations, MTW is the final product and, as the amount of boron is increased, zeolite beta is then crystallized. This effect is not restricted to TEA, but is also observed for other structure-directing agents (see Table 5).

The structure-directing effect of other organic guest molecules that form large-pore pure-silica molecular sieves is also strongly coupled to the presence of heteroatoms in the synthesis gel. Trimethyl-2-adamantylammonium forms the one-dimensional AFI structure with pure-silica synthesis gels but forms SSZ-33 [57] when boron is added.

Table 5. Effect of aluminum, boron, and zinc on the structure of zeolites obtained using organic structure-directing agents.[a]

	SiO_2	SiO_2/Al_2O_3 <50	SiO_2/B_2O_3 <30	SiO_2/ZnO 20
	MTW	BEA	BEA	VPI-8
	MTW	BEA	BEA	VPI-8
	MTW	MOR	BEA	Layered
	AFI	SSZ-25	SSZ-33	VPI-8
	SSZ-31	MOR	SSZ-33	__[b]
	SSZ-31	SSZ-37	SSZ-33	__[b]

a. From references 37, 51, 56, 61, 62, 63. Some of these results are from experiments carried out in our laboratories and not yet published.

b. No product formed after several weeks.

SSZ-33 is a new zeolite with intersecting 10- and 12-ring pores that can be synthesized using several structure-directing agents [58] when boron is in the synthesis gel. Other organic molecules that form SSZ-31 with a pure-silica gel, also form SSZ-33 when boron is added to the reaction mixture (Table 5). For these cases, molecules that form different structures with pure-silica, form a material with the same framework structure when boron is included in the synthesis gel. On the other hand, the molecules that form MTW, only crystallize BEA when boron is added to the synthesis gel.

A different result is observed when aluminum is added to the synthesis gel if molecule **XIV** is used as the structure-directing agent. Neither BEA nor SSZ-33 are observed as the final product but rather a new material, SSZ-37, is the crystalline solid formed [59]. The structure of SSZ-37 seems to be similar to the structure of NU-87 [60]. Slightly bigger or slightly smaller organic molecules do not yield the SSZ-37 zeolite. Note that the effect of Al and B are not the same. Although the addition of Al or B when using TEA as the structure-directing agent gives BEA in both cases, the structures of the products formed when using the heterocyclic molecule **XIV** are very different. Also, note that the molecules that form SSZ-31 and SSZ-33 have not been reported to form any crystalline material when Al is substituted for B.

As is observed with aluminum and boron, the addition of zinc to a synthesis gel also radically changes the structure of the zeolite product. In all cases, however, the molecular sieve VPI-8 is observed, regardless of the organic structure-directing agent used for its synthesis. VPI-8 was first synthesized by Annen [61,62] using zinc acetate as the source of framework zinc and TEA as the structure-directing agent. Sorption data indicate that VPI-8 is a 12-ring, large-pore, 1-dimensional molecular sieve. The formation of VPI-8 in the presence of a variety of organic guest molecules suggests that in these syntheses, the structure of the final product is controlled by the divalent zinc cation and that the principal role of the organic molecule is the stabilization of the voids forming the pores [63]. The Zn atoms appear to inhibit the nucleation of zeolite structures, other than VPI-8.

Trivalent and divalent T atoms in the synthesis gel are bound to have strong influence on the syntheses of high-silica zeolites for several reasons. Firstly, the substitution of Al, B, or Zn for Si in the zeolite produce a negatively charged framework that will tend to coordinate much more strongly to the inorganic cations (Na, K, and so on) found in the synthesis gel. Secondly, the T—O bond lengths and, in particular, the T—O—T angles are expected to influence the formation of certain secondary building units such as 4-rings. Finally, instead of the formation of a charged, deprotonated silanol group in the zeolite structure to balance the charge of the organic structure-directing agent, the charge can be balanced by the anionic framework of the zeolite.

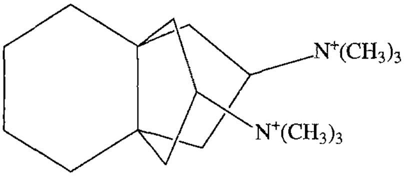
It is enlightening to compare the structures of MTW and BEA. The projection along the 12-ring pores of MTW is the same as the projection along the *a* and *b* axes of zeolite beta. Both structures are the result of the disorder stacking of silicate layers [35,64] and there are more 4-rings in the structure of BEA than in the structure of MTW. The presence of additional 4-rings in the structure of BEA may be regarded as the consequence of smaller T—O—Si angles promoted by the presence of Al or B. As was found in MTW and BEA, the projection along the 12-ring pores of AFI is the same as the projection along the 12-ring pores of SSZ-33. Also, the structures of SSZ-33 and BEA are related by the presence of similar secondary building units and both are highly faulted structures with open 3-dimensional pore systems.

The trends that have been outlined here have to be regarded as tentative. They are the result of a limited number of experiments using a small number of organic molecules and relatively narrow ranges of all the synthesis parameters. Further work, in particular, the structure solution of SSZ-31 and VPI-8 are needed in order to be able to understand further the observed experimental results.

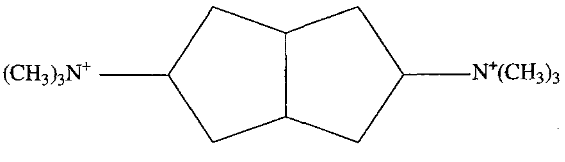
7. Examples of Structure-Direction

The concepts of structure-direction enumerated above are now discussed in terms of recent examples. These examples show a complementary relationship between the geometry of the structure-directing agent and the geometry of the void space in the zeolite.

Zeolite SSZ-26 is an aluminosilicate molecular sieve with intersecting 10- and 12-ring pores [65]. It is synthesized using the propellane molecule **XVII** [66].



XVII



XVIII

Zones and Santilli [66] found that molecule **XVIII** formed MTW and argued that the inclusion of an additional ring as in **XVII** would force the formation of an intersecting pore system as illustrated in Figure 5. Thermogravimetric and chemical analyses indicate (based on the solution of the structure [59]) that there is one guest molecule per channel intersection. Lobo et al. [67] carried out molecular force-field calculations on the propellane molecule **XVII** inside the pores of SSZ-26 and found a very good agreement between the geometry of the pore intersection and the geometry of the organic molecule. The minimum-energy conformation of the molecule inside the pore intersections (Fig. 6) closely resembles the conformation suggested by Zones and Santilli [66] (Fig. 5). Therefore, the synthesis of SSZ-26 appears to be the first case known to the authors where the geometry of a pore-architecture has been designed *a priori* and exemplifies the usefulness of the concepts of structure-direction as an aid in the synthesis of new molecular sieves. This example, however, is not the only one where there is a very good fit between geometry of the guest molecule and the geometry of the pore.

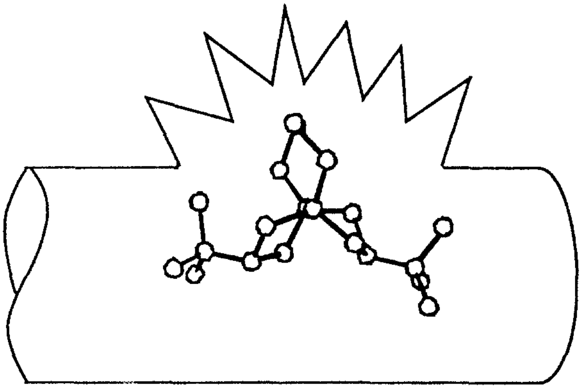


Figure 5. Proposed model for the formation of pore intersections using the propellane molecule **XVII**.

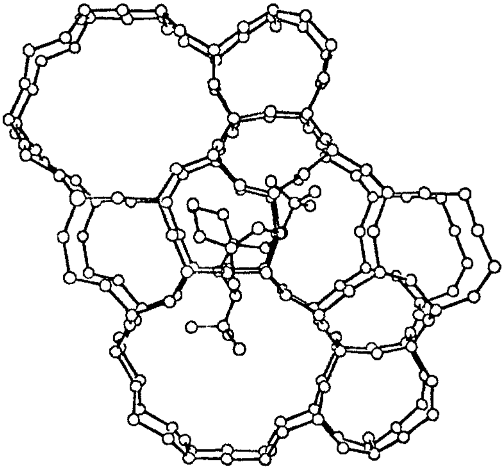


Figure 6. Minimum-energy conformation for the propellane molecule (**XVII**) in the pores of SSZ-26 as obtained from force-field calculations.

The structure of ZSM-18 (MEI) [68] is unique since it is the only aluminosilicate to contain 3-rings in the framework. With ZSM-18, a very good fit between the organic guest molecule and the zeolite cage is observed. Figure 7 shows an ORTEP drawing of the triquaternary ammonium molecule used as structure-directing agent inside the large cage of MEI. The rigidity, the size, and in particular, the three-fold axis of rotation of the organic molecule are the characteristics that favor the formation of the cage of ZSM-18. Hong et al. [19] have carried out CP/MAS ^{13}C and static NMR on this material and found that the triquaternary ammonium ion is tightly held inside the MEI cage. Recently, Schmith and Kennedy [73] reported the synthesis of ZSM-18 using molecules **XIX** and **XX**.

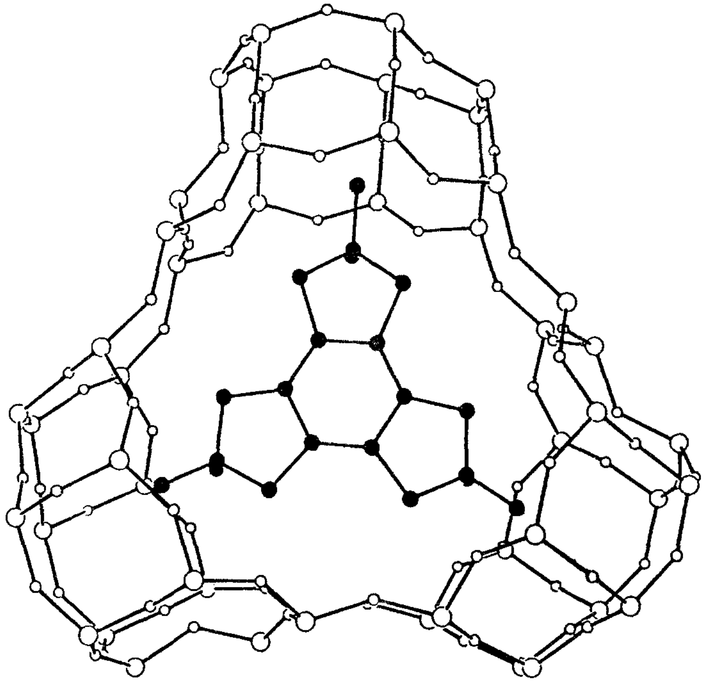
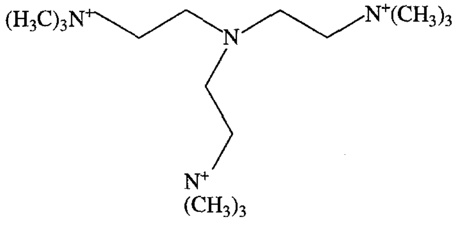
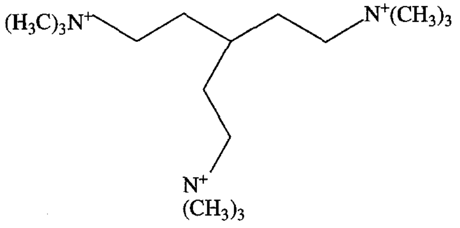


Figure 7. Position of the triquaternary ammonium molecule used as structure-directing agent in ZSM-18.

Their rationale was based on keeping the same total charge and symmetry, ease of synthesis and retaining only acyclics. The various possibilities were screened using molecular dynamics, which reduced the list to cations XIX and XX. This paper is the first example of the use of molecular dynamics to 'design' a structure-directing molecule.



XIX

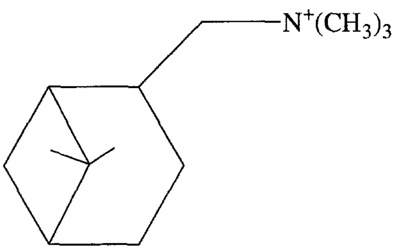


XX

Another good example of the relationship between the geometry of the structure-directing agent and the geometry of the cage is 18-crown-6 in the cages of EMT, the hexagonal polymorph of FAU. As with the triquaternary ammonium molecule in MEI, only the 18-crown-6 has been found to direct the formation of EMT. Recent crystallographic work [71] indicates that 18-crown-6 is found in the small cages of EMT and approximately conforms to the geometry of the cage.

The first example of the purposeful control of long-range order in the synthesis of zeolites through the use of structure-directing agents was shown by Arhancet and Davis [70]. By specifying the concentrations of 18-crown-6 and 15-crown-5 in the synthesis gel, Arhancet and Davis have been able to control the relative fractions of the hexagonal (EMT) and cubic (FAU) polymorphs of faujasite that are present in the zeolite product.

A second example of the control of long-range order using organic structure-directing agents has been recently reported [58]. In this case, Lobo et al. report the synthesis of two related materials CIT-1 and SSZ-33. These two zeolites are members of a family of intergrowths of two closely related structures, polymorph A and polymorph B [57]. CIT-1 is the pure polymorph B of this family of materials and SSZ-33 is an intergrowth of polymorph B and polymorph A with a 70% fraction of polymorph B. By synthesizing the materials in the presence of the structure-directing agent for CIT-1 (**XXI**) and the



XXI

structure-directing agent for SSZ-33 (**XV**), the fraction of polymorph B in the final material can be carefully controlled from materials which are 70% of polymorph B and 30% polymorph A (SSZ-33) to materials which are 100% polymorph B (CIT-1) [57]. Figure 8 shows the experimental XRD patterns of materials with different fractions of polymorph B. These two examples also illustrate how the long-range order in zeolites can be controlled using organic guest molecules.

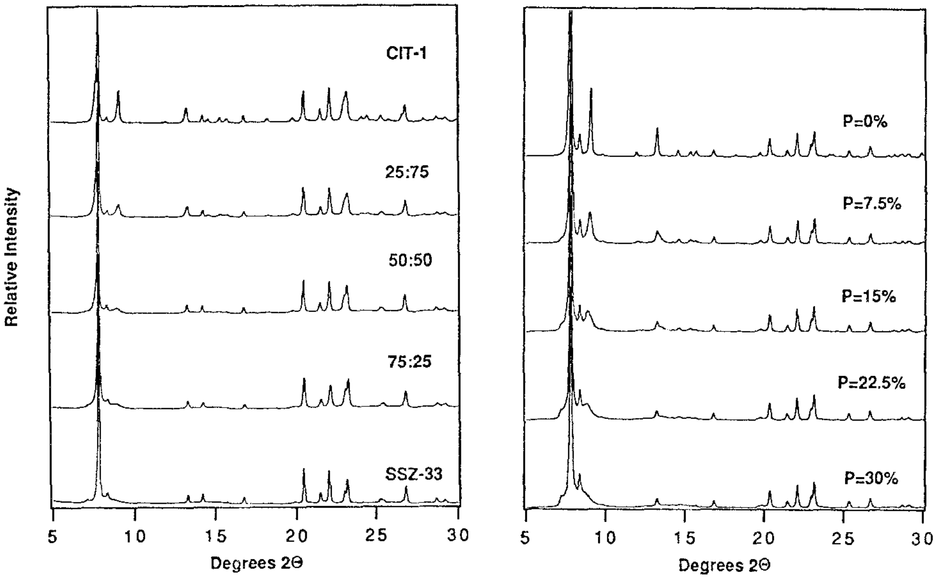


Figure 8. Experimental (A) and calculated (B) XRD patterns for intergrowths of polymorph A and polymorph B of SSZ-33.

8. Summary

We have discussed the myriad of factors that influence, in one way or another, the synthesis of zeolites. In Figure 9, we attempt to illustrate the effects that these factors have on the structures formed.

In the absence of structure-directing agents, silicate syntheses form dense (quartz, tridymite, cristobalite) or layered materials. Using only silica as the source of tetrahedral atoms, small molecules - amines in particular - direct the formation of clathrasils. The structure of the clathrasil obtained depends on the size of the molecule, on the synthesis temperature and to a minor extent on the specific geometry of the molecule. Linear molecules form in general 1-D, 10-ring pore molecular sieves. The most important factor that defines one structure from the several that can be synthesized with pure-silica, appears to be the temperature.

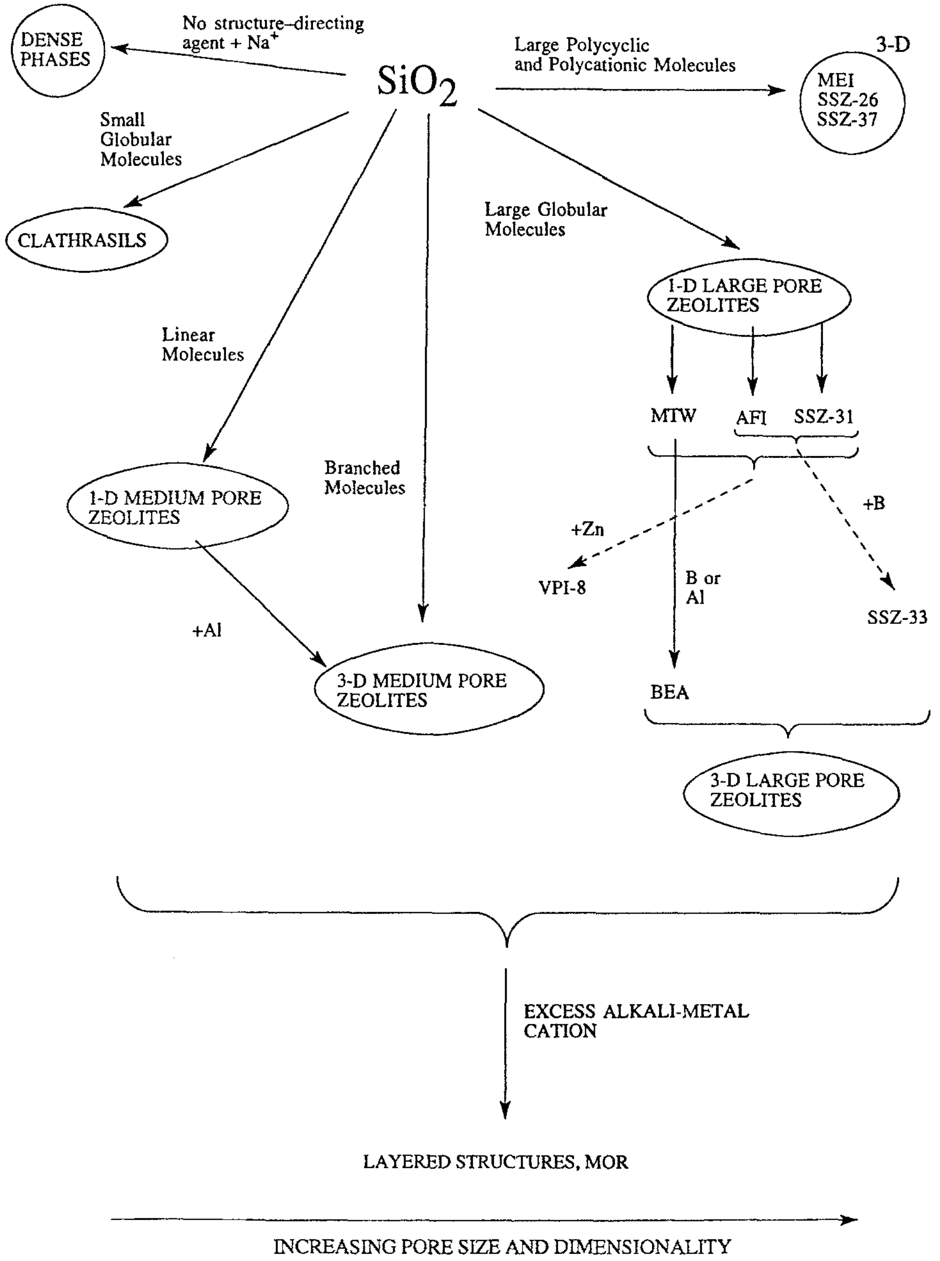


Figure 9. Summary of the trends between structure-directing agents and zeolite structures.

Branched molecules (TPA and TBA) form multidimensional medium-pore zeolites while large polycyclic molecules produce MTW, AFI, or SSZ-31 depending on their size and shape. No multidimensional, pure-silica, large-pore zeolites have been synthesized. Nakagawa, however, has indicated that, based on adsorption experiments [71], the pure-silica zeolite SSZ-35 is a multidimensional large-pore material. The structure of SSZ-35 must be solved to answer this question.

The selectivity of the structure-directing agents towards a specific zeolite structure is increased as the size of the molecule is increased. The most selective molecules are large, i.e., are formed of more than 16 carbon and nitrogen atoms, and contain two or three charges per molecule.

Small amounts of trivalent (Al, B, Ga, Fe) or divalent (Zn, Be) tetrahedral atoms have striking effects on the structures of zeolites. In general, the structures formed have multidimensional pore systems, except for Zn that (thus far) direct the crystallization of VPI-8, regardless of the structure-directing agent. Often, the projection along the 12-ring pore of 1-D pure-silica zeolites is the same as the projection along the 12-ring pores of multidimensional materials obtained after the addition of Al or B.

The thermodynamic stability of all pure-silica molecular sieves is relatively constant. This is an encouraging fact that suggests that the synthesis of many other zeolites with novel pore architectures is feasible.

The concepts of structure-direction have shown to be of tremendous power as guiding principles for the synthesis of new molecular sieves. The results presented in this review indicate that no limits are apparent to the number of structures that can be synthesized. The results also suggest that new zeolite structures will require the synthesis of larger structure-directing agents than the ones that have been prepared so far.

Acknowledgments

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Abstract. The concepts of structure-direction in the synthesis of clathrasils and high-silica molecular sieves are reviewed. The effects of size, geometry, and chemical nature of the organic structure-directing agent on the crystalline structures that are formed are discussed beginning with clathrasils (0-dimensional pore systems) and ending with 12-ring zeolites with 3-dimensional pore systems. Emphasis is focused on the energetic interactions between the organic guest and the inorganic framework. The energetic stability of porous frameworks is compared to the stability of dense pure-silica phases and the effects of trivalent (Al, B) and divalent (Zn) tetrahedral heteroatoms on the structure of zeolites formed is reviewed. The application of structure-directing concepts are described using the syntheses of ZSM-18 and SSZ-26 as examples, and the control over long-range order in zeolites by structure-directing effects is illustrated by the purposeful variation of the stacking probability of SSZ-33–CIT-1 and FAU–EMT intergrowths.