Guest/Host Interactions in High Silica Zeolite Synthesis: [5.2.1.$0^{2.6}$]Tricyclodecanes as Template Molecule

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Received December 19, 1995. Revised Manuscript Received May 21, 1996[⊗]

Abstract: Zeolite synthesis results for the use of a family of related quaternary ammonium derivatives of tricyclodecane hydrocarbons as structure-directing agents are described. The work continues our interest in how rigid polycyclic hydrocarbons, as charged derivatives, occupy space in developing guest/host zeolite lattices. The zeolite product chemistry was probed as to the three-dimensional structures formed, particularly in relation to synthesis variables like boron substitution for silicon in the lattice, OH^-/SiO_2 reactant concentration, and the stereochemistry of the polar substituents off the tricyclo[5.2.1.$0^{2.6}$]decane hydrocarbon frame; all three factors were found to have an impact on the zeolites which crystallized. Some correlations were also studied for how these factors influenced the size and architecture of the resulting pore systems. Monte Carlo methods were also applied to calculate favorable docking energies for geometry-optimized organo-cations placed in the host lattices.

Introduction

Molecular sieve host lattices are gaining increasing importance in a wide array of applied chemistry and engineering disciplines. Uses range from traditional catalyst and adsorbant technology to more novel electro-optical nanoscale devices and synthetic membranes. An expanding list of newly discovered three-dimensional structures and varying chemical compositions further adds to the choices of materials that can be studied.

Organic molecules, as guest components during synthesis, have a pronounced effect on the structure and composition of the resultant crystalline host lattices, especially in the silicate-based chemistry. Some novel approaches in the construction of such guest molecules, including micellular arrays or rigid, polycyclic hydrocarbons, have recently led to new host lattice types.[1] Much of our research emphasis has focused on understanding the details of the role that organo-cations play in the selective crystallization of molecular sieves.[2]

We have examined the spatial and stereochemical aspects of relatively rigid organo-cations as a means of influencing the pore characteristics of the crystallizing, zeolite structures. As an example, the use of a propellane-derived diquaternary ammonium compound produced zeolite SSZ-26.[3] The structure solution of the lattice framework confirmed that the propellane guest molecule had been effective in generating the first synthetic example of a zeolitic framework containing 10- and 12-ring interpenetrating channels.[4] Zeolite scientists often describe pore systems in terms of the number of tetrahedral atoms (bridged by oxygens) which define the opening; larger numbers or ring size indicate a larger pore. A typical aperture of a 10-ring pore would be 5.5 Å, whereas a 12-ring pore will have a diameter on the order of 7.5 Å.

Another approach to synthesizing novel guest molecules was recently reported from our laboratories and utilized Diels−Alder synthesis methodology to prepare conformationally constrained azapolycyclic organo-cations.[5] This approach allowed us to fine tune structural changes in the guest templates, which resulted in altering the zeolite phase selectivity during crystallization.

However, in a “templated” zeolite synthesis reaction, the product molecular sieve is not determined solely upon the basis of its fit with the organic component. Product phase selectivity can also be a function of available lattice substitution as well as other factors which influence nucleation selectivity. We have shown that both of these factors are responsible for *N*,*N*,*N*-trimethyl adamantammonium cations giving rise to three different zeolitic products under different inorganic reaction conditions: SSZ-24 (very high Si), SSZ-23 (Al-substituted), and SSZ-13 (high Al, high alkali hydroxide).[6] The influence of a given organo-cation within a range of nucleation/crystallization factors can be represented as a three-coordinate axis as shown in Figure 1. It is clear from this diagram that in some cases, nucleation factors and lattice substitution are not independent variables, and it was our desire to determine where regions of phase selectivity for a given organo-cationic templating agent existed on this “surface”.

In this investigation, we have probed the spatial features of the tricyclo[5.2.1.$0^{2.6}$]decane system by varying the substituents on the hydrocarbon framework. These derivatives can be visualized as functional group analogs of a relatively ubiquitous parent dicyclopentadiene. Nine organo-cations were studied. We have attempted to evaluate the effect of each structural change on the zeolite crystallization product obtained in the synthesis reactions using these organo-cations. The similarity in structure between these tricyclodecanes bearing external

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1996.

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S0002-7863(95)04246-6 CCC: $12.00

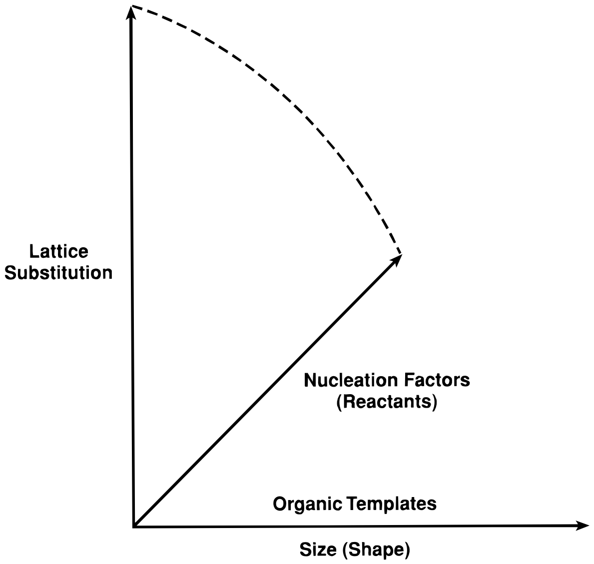


Figure 1. A representation of a three-coordinate axis system for the interplay of organo-cations and other factors which influence zeolite synthesis. Some new structures might only arise from very small microdomains found within this topological mapping.

substituents and the azapolycyclic templates described in one of our earlier studies will also be discussed.[5]

Experimental Section

The preparation of the tricyclo[5.2.1.$0^{2.6}$]decanes in this study was performed using organic synthesis methods we have previously described.[5,7] Organo-cations bearing trimethylammonium substituents were typically synthesized via reductive amination of the corresponding carbonyl derivatives.[8] The conformation of the tricyclo[5.2.1.$0^{2.6}$]-decane parent was determined to be *exo* based upon NMR literature.[9]

Zeolite syntheses were carried out in Teflon-lined stainless steel reactors (Parr Chemical Company, Catalog no. 4745). After mixing the organo-cation as its OH-salt with NaOH, water and aluminum or boron source, and finally a silica source, the closed reactors were loaded onto a rotating spit, built into a Blue M convection heating oven, and heated for specific period of time until a crystalline product was obtained. The reactors were rotated at 43 rpm. The recovered products (following filtration, washing, and air-drying) were analyzed on a Siemans D500 diffractometer.

Detailed synthetic conditions for SSZ-33 are given here. A solution of template **1**, as the salt was hydroxide-exchanged with BioRad AG1-X8 resin, was titrated with standard HCl solution and found to be 0.75 M in hydroxide. The solution of template **1** hydroxide (3.0 g) was mixed with 1.25 g of 1 N NaOH and 5.65 g of distilled, deionized water. $Na_2B_4O_7 \cdot 10H_2O$ (0.05 g) was dissolved into this basic solution. Finally, 0.75 g of Cabosil M5 silica were blended in and the Teflon cup closed. The reaction mixture was heated for 7 days at 160 °C and 43 rpm.

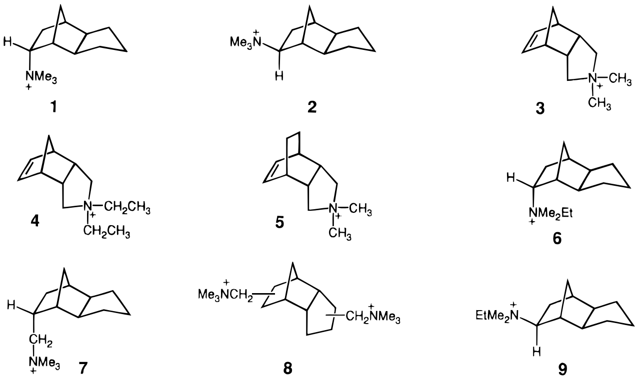
Further product characterization was performed by scanning electron microscopy (Hitachi 570A), elemental analysis (Galbraith Laboratories, Inc.), and adsorption techniques as previously described.[3] ^{13}C CP-MASNMR was performed on a Bruker 500 MHz instrument using TOSS (total suppression of spinning sidebands) sideband suppression and adamantane as an internal standard.[5]

Molecular modeling calculations were performed using software distributed by the Catalysis and Sorption Consortium of Biosym Technologies, Inc., San Diego, CA. In studying the interaction of templates with the beta and SSZ-33 structures, four template molecules per unit cell of zeolite were used. The four templates were expected to occupy zeolite channel intersections. Calculations were done with a two-step procedure.[10a,b] In the first step, a library of 20 zeolite/template conformations, each containing a unit cell of zeolite and four template molecules, was assembled. This was done by stepwise insertion of four templates with randomly selected positions and rotational orientations into the unit cell. To avoid inserting a molecule into the dense part of the framework, the insertion was repeated until an energy value below a cut-off was achieved. In the second step, each of the 20 zeolite/template conformations was energy minimized, using Ewald summation of nonbonded interactions to avoid errors due to finite atom-based cut-offs. The zeolite framework atoms positions were fixed. Biosym's CVFF forcefield was used for the calculations and coulomb terms were ignored. The final stabilization energy represents the difference of the energies of the zeolite/template conformation minus energies of the zeolite and templates at infinite separation.

$$\Delta E_{\text{stabilization}} = E_{\text{zeolite/template}} - (4E_{\text{template}}) - E_{\text{zeolite}}$$

As the zeolite atom positions were fixed, the energy of the zeolite framework does not change and the initial E_{zeolite} need not be calculated. The lowest energy conformation of the 20 was assumed to be representative of the global minimum energy configuration.

Table 1



Results

1. Inorganic Variables. Table 1 depicts the structures of the nine organo-cations used in this study. Aluminosilicate zeolite syntheses have historically been performed at high OH^- and Al^{3+} concentrations. Under these conditions, with high sodium silicate levels, templates **1**−**9** have given (as shown in Table 2), for the most part, only two zeolitic products: mordenite (MOR: 12-ring, large-pore) and SSZ-13 (CHA-type product with large cages but small, eight-ring pores). Both product types were shown by microanalysis to contain significant (>15 wt %) quantities of organic material. If the OH^-/Si ratio is increased even further (to greater than 0.80), frameworks comprised of five-rings, such as mordenite, are no longer observed as crystallization products. Zeolites such as SSZ-13, which are comprised solely of four- and six-ring, building units, become favored. The lack of diversity in the zeolitic products observed for this group of templates may in large part be attributed to the limitation in building unit structures which are favored under these reaction conditions. The inorganic chemistry dominates over the influence of the organic templating agent.

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Table 2. Use of Tricyclodecane Derivatives in a Relatively High OH^-/SiO_2 Reaction[a]

guest structure	zeolite product
1	mordenite
2	mordenite
3	SSZ-13[b]
4	SSZ-13
5	SSZ-13
6	mordenite
7	mordenite
8	SSZ-16[c]
9	mordenite

[a] $OH^-/SiO_2 = 0.65$, $SiO_2/Al_2O_3 = 35$, $H_2O/SiO_2 = 32$, 135 °C 43 rpm, organic/SiO_2 ~0.10, $Na/SiO_2 = 0.70$, Y zeolite = source of Al_2O_3. [b] Chabazite structure (see U.S. Patentt 4,544,538). [c] U.S. Patent 4,508,837.

Table 3. Reactant Parameters for Screening Tricyclodecane Derivatives

parameter	all silica	aluminosilicate	borosilicate
organic/SiO_2	0.15	0.15	0.15
$NaOH/SiO_2$	0.10	0.15	0.15
OH^-/SiO_2	0.25	0.30	0.30
Al/SiO_2	0.00	0.06	0.00
B/SiO_2	0.00	0.00	0.05
H_2O/SiO_2	44	27	44
time, days	6−10	6	6
temp, °C	150	160	160
rpm	0	43	43

2. Lowering the Alkali Content. If synthesis conditions are selected so that the alkali and hydroxide content are reduced such that OH^-/Si and $M^+/Si < 0.5$, a more diverse range of zeolite products can be obtained; presumably now the structure of the organo-cations plays a more important role in the crystallization process. These conditions can be achieved by using the organo-cations as the hydroxide salt (rather than the corresponding halide) and having it perform the dual function of template and hydroxide base.

The inorganic parameters given in Table 3 describe an all-silica reaction (SSZ-24),[11] an aluminosilicate reaction (SSZ-26),[12] and a borosilicate reaction (SSZ-33).[13] The zeolite denoted within the parentheses describes the novel material discovered in our labs using the given reaction conditions. It should be noted that the absence of an alkali cation can greatly retard or completely inhibit crystallization. Work by Davis and co-workers show the dramatic effects of lowering the alkali concentration on crystallization rates for ZSM-12, another high silica zeolite requiring similar reactant ratios during synthesis.[14] Their work supports a view that an alkali cation can have an important influence on exchange between silicate species in solution, leading to more rapid nucleation. The smaller alkali cation itself may serve in the capacity of a template in which the coordination sphere influences these silicate interchanges. However, once above an optimum concentration, these cations can help to stabilize undesirable layered phases such as Magadiite or Kenyaite.[15]

Table 4 lists the results of screening the nine templates (**1**−**9**) in the three reaction types described above. In contrast to the limited number of products obtained when using more typical reaction conditions [Table 2: high (Al), high alkali hydroxide (MOH)], one observes that with these modified conditions, a variety of 12-ring zeolitic structures are obtained as products using these guest molecules. Representation of the lattice framework for a number of zeolites discussed in this paper appear in Figure 2. The identity of the 12-ring structure produced appears to be strongly influenced by the available lattice substitution, and this will be discussed further, shortly. Only in the case of the smallest derivative (**3**) is a clathrasil product (Nonasil) formed. Although Nonasil has a cavity, it has no useful porosity.[16] Chang and Bell have described a model for zeolite crystallization where clathrate formation is the favored nucleation event which may or may not lead to open pore systems.[17] We believe that clathrate formation is favored (due to favorable van der Waals stabilization of the cavity by the template) until the guest molecule becomes too large to be accommodated within the clathrate cage.[10c] Nakagawa has recently reported an interesting series of templates and their resultant zeolite products which exemplify this view.[18] The schematic in Figure 3 depicts how the zeolite structures changes as the size of the organic guest molecule increases. This picture is best considered under high silica reaction conditions where the gel $SiO_2/Al_2O_3 = 50$. In this region, many reactions will produce products composed of pentasil (five-ring) subunits, and formation of almost all cavity and channel types are possible.[19] Once the guest molecules become too large to form clathrasils, intermediate or large pore molecular sieves having one-dimensional, parallel pore systems appear to become the next favored products. The pore size in these cases is dependent on the spatial requirements of the organo-cationic template. Use of template molecules whose shape and dimensions (possibly affected by hydration) make it difficult to form any of the previous structure types then increases the likelihood of crystallizing multidimensional products. Nakagawa also recently emphasized the importance of considering the packing of multiple organo-cations in stabilizing various channel systems.[18] It was demonstrated that two organo-cations were necessary to achieve maximum space-filling and, therefore, maximum van der Waals stabilization of the 12-ring regions of SSZ-37.[18]

3. Guest Stereochemistry and Zeolite Host Determination. Of particular interest is the change in product selectivity observed for isomers **1** and **2** under various reaction conditions. These isomers differ only in the stereochemistry of the trimethylammonium substituent at C-8 (*endo* in **1**, *exo* in **2**). Both isomers produce mordenite under high alkali/OH^- conditions (see Table 2), illustrating the minimal influence of the template structure on the final product under these conditions. However, each isomer gives rise to different products in the modified borosilicate reactions described in Table 4. In addition, as the amount of boron in the reaction is decreased such that the $SiO_2/B_2O_3 \rightarrow \infty$, two other different products are obtained. In the boron-rich cases ($SiO_2/B_2O_3 < 35$), the two products possess multidimensional, large-pore channel systems: zeolites SSZ-33 (from **1**)[4] and Beta (from **2**).[20] As we approach an all-silica system, the products become one-dimensional: SSZ-31 (from **1**)[7] and ZSM-12 (from **2**).[21] This type of transitional behavior, reduction in the dimensionality of channel systems with decreasing lattice substitution, has also been reported in aluminosilicate studies reported by Casci and co-workers, where

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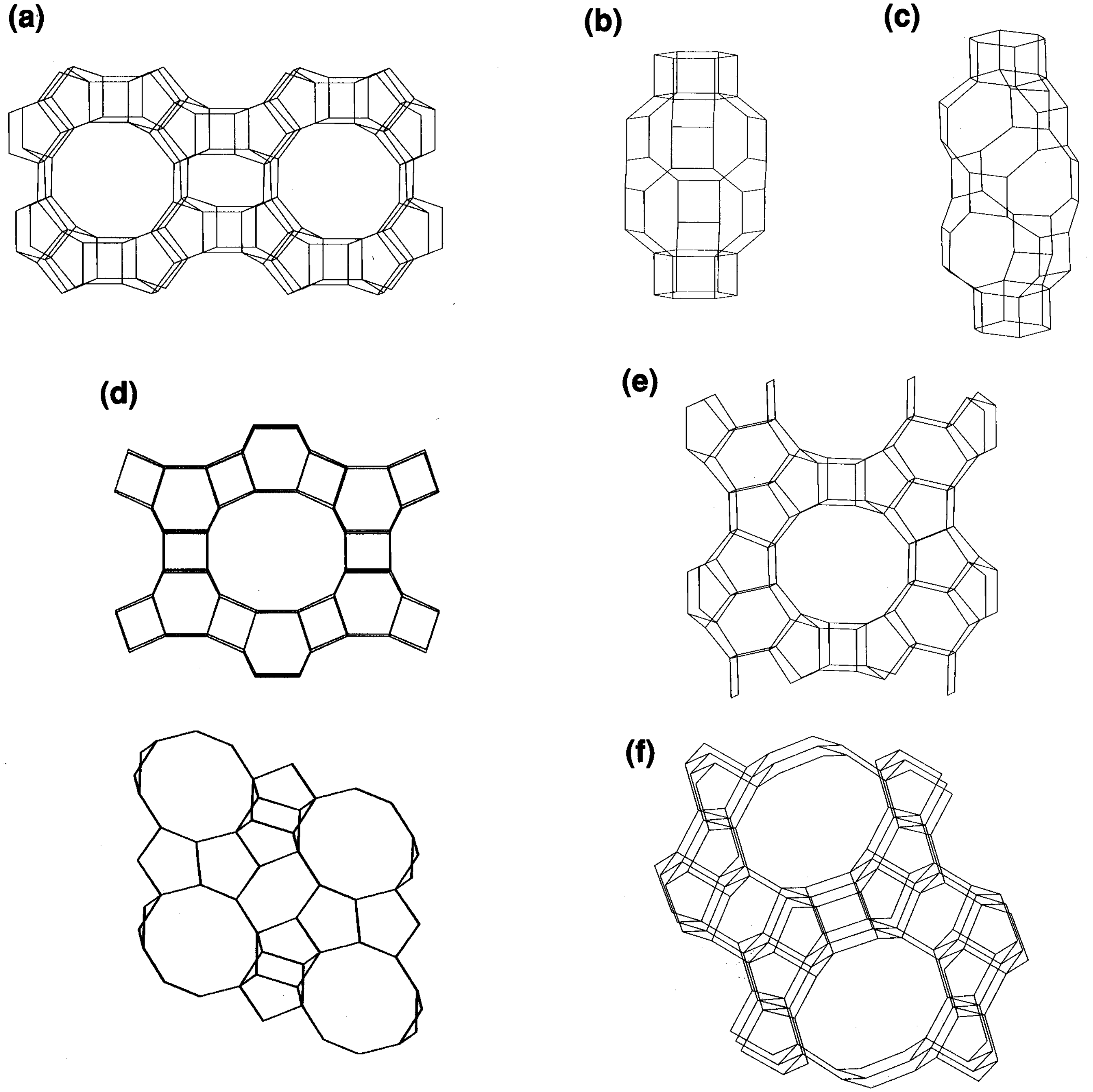

Figure 2. Representations of lattice frameworks of various zeolites: (a) mordenite, (b) chabazite, (c) SSZ-16, (d) SSZ-33 (two different projections), (e) beta, and (f) ZSM-12.

Table 4. Initial Screening of Tricyclodecane Derivatives[a]

reaction type: organic structure	all SiO_2	$SiO_2/Al_2O_3 = 35$	$SiO_2/B_2O_3 = 50$
1	SSZ-31	mordenite	SSZ-33
2	ZSM-12	ZSM-12	ZSM-12
3	nonasil	nonasil	nonasil
4	ZSM-12	ZSM-12	ZSM-12
5	SSZ-31	SSZ-37	SSZ-33
6	amorphous	amorphous	quartz[b]
7	amorphous	amorphous	amorphous
8	quartz[b]	amorphous	amorphous
9	ZSM-12	amorphous	ZSM-12

[a] The respective conditions for reactions are given in Table 3. [b] Formed after several weeks of reaction over which no zeolite phase had formed.

they observed the transition from EU-1 which contains large side pockets on either side of the medium-pore channels, to the one-dimensional medium-pore ZSM-48 product.[22]

Thus, the seemingly minor stereochemical change in **1** and **2** was sufficient to direct toward several different zeolitic products under the boron-containing conditions. Figure 4 shows the product selectivities for the two isomers as the boron concentration was varied. It can be seen that the transition from crystallization of zeolite Beta to ZSM-12 using template **2** (with decreasing boron concentration) occurs sooner than the corresponding transition of crystallization of SSZ-33 to SSZ-31 using template **1**. In the latter case, there may be intermediate boron concentrations which are not conducive to crystallization of either phase. Figure 5 shows the powder X-ray diffraction patterns for the four zeolites just described. Structural solutions have been proposed for all but SSZ-31. Representations of the large pore connectivities are shown in Figure 6.[4,21,22] One of the orientations for zeolite Beta (100) is similar to the large

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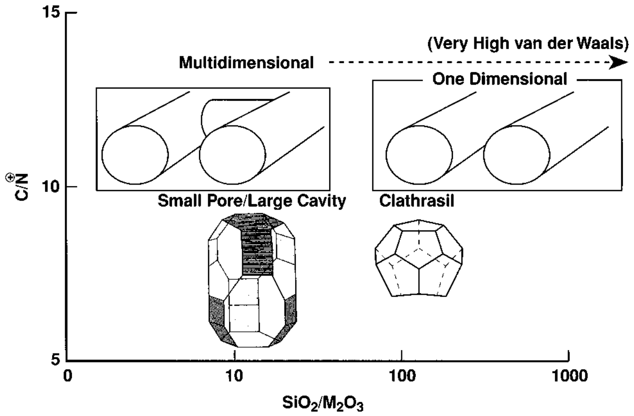

Figure 3. A graph of the typically observed zeolite product types over the regions of increasing C/N^+ in the organo-cation mapped out over lattice substitution for Si. Very favorable van der Waals interactions for guest/host interactions allow multidimensional channel systems to be stable well out into the diminished lattice substitution region.

Table 5. Zeolite Product Results from Mixing the Contribution of Templates 1 and 2

ratio 1/2	SSZ-33	B-beta
95/5	100%	0
90/10	100%	0
85/15	major	minor
80/20	minor	major
75/25	0	100%

[a] Reactions run as in Table 3 boron entry, except B/Si = 0.06.

Table 6. Product Analyses for Reactions Mixing 1 and 2[a]

1/2	wt % C	N	product	SiO_2/B_2O_3
95/5	14.50	1.18	SSZ-33	65
90/10	14.34	1.12	SSZ-33	56.8
85/15	14.07	1.13	SSZ-33/Beta	48.7
80/20	14.84	1.23	Beta/SSZ-33	44.10
75/25	13.64	1.07	Beta	45.08
5/95	13.93	1.19	Beta	43.90

[a] Starting gel SiO_2/B_2O_3 = 33.

pore system in ZSM-12, the default structure for template **2** as lattice substitution is decreased. A one-dimensional large pore channel system is speculated for SSZ-31 based on adsorption and catalytic data. Analogous to the Beta/ZSM-12 relationship, is the large pore of SSZ-31 similar to one of the projections shown for SSZ-33? To date, we have not been able to use the net topology of Akporiaye, an example of a very successful approach to determining zeolite structures via the relationship of parameters like unit cell dimensions to known symmetry operators for silicate chains,[23] to develop a structural model for SSZ-31 using the same two-dimensional AFI net found for SSZ-33.

4. Guest Stability. One of the principal ways to track the integrity of the guest organo-cation is to use ^{13}C MAS NMR on the zeolite product obtained. This has been demonstrated for a series of high silica molecular sieves made from an adamantyl derivative.[6] In this study, it was especially important to confirm that the stereochemical integrity of the guest molecules (*endo*-trimethylammonium group in **1**, *exo*-trimethylammonium group in **2**) had been retained during the crystallization process, since it appeared that each isomer was responsible for the distinct product which had been obtained. Figure 7 shows ^{13}C MAS NMR spectra for the halide salts of the tricyclodecane derivatives **1** and **2** compared with corresponding, MAS NMR spectra for the organic components contained within the channels of the as-made high silica molecular sieve products. The principal side reactions to be expected for these organo-cations under the zeolite synthesis conditions were base-promoted elimination reactions. Inversion of stereochemistry at C_8 was not anticipated, and the NMR spectra confirm that isomers **1** and **2** remain unchanged within the channels of their respective molecular sieve hosts.

5. Competitive Crystallization. Linear molecules such as *exo* isomer **2** appear to favor the formation of Beta zeolite at high boron concentrations. This might occur if there is a lower activation energy of formation for beta as compared to SSZ-33. Data in Table 5 show the effect of using various proportions of **1** *(endo)* and **2** *(exo)* as the templating agent on the product obtained. It is apparent that **2** favors the crystallization of beta zeolite, even when it is only a minor component (20%) of the template mixture. In both the pure products and in the mixtures, a relatively high degree of boron substitution is observed, consistent with the formation of beta zeolite and SSZ-33 (and the absence of ZSM-12, which is a high-silica material). The boron content of the products is presented in Table 6. Also included in Table 6 is the C and N content found in the organo-zeolites: this can be used to estimate the extent of pore filling by the organic component. One will notice that these values are quite similar, regardless of the starting isomer distribution or the product identity (Beta versus SSZ-33). This provides further evidence that SSZ-33 is indeed a multidimensional material, similar to beta.

The ^{13}C MAS-NMR data on the organo-zeolite from 75/25 **1/2** shows that both organo-cations are in the pores of beta. In addition at a fixed organo-cation/SiO_2 reactant ratio of 0.15, a 75/25 means that isomer **2** is only 0.0375 relative to SiO_2 in the starting synthesis mixture. In this experiment, **2** (the more favored template for Beta formation) is not present in sufficient quantity to fill the beta pore system. Therefore, once beta begins to nucleate, it must continue to grow by incorporating **1** as well. A pivotal part of this argument is the comparison of the amount of organo-cation found in the pores (>0.0375) and the overall yield of organo-silicate ($>90\%$ from reactants). The high degree of pore-filling can be seen from the percent C and N data in Table 6. The mixed template experiments suggest that there is not a large difference in stabilization energy for the templates fitting in beta or SSZ-33. (This result is supported by a similar recent study related to the polymorph phases of SSZ-33.)[24]

Table 7 shows calculated template/zeolite stabilization energies for isomers **1** and **2** in polymorphs A and B of both SSZ-33 and beta zeolites as well as for ZSM-12. The stabilization energies for ZSM-12 have been normalized for four template molecules. We have some question about how to compare the magnitudes of the calculated numbers of ZSM-12 to the results for SSZ-33 or beta, which were calculated on the basis of four template molecules per unit cell and which explicitly include template-template interactions. We see that there is less stabilization of the MTW structure by *endo*-isomer **1** than by *exo*-isomer **2**. Beta zeolite polymorph B is stabilized by both template isomers more than polymorph A. When normalized for the 50% faulting probability for polymorphs A and B in beta zeolite, the stabilization energies show that isomer **2** is more stabilizing. For SSZ-33, a similar situation exists. Polymorph A is clearly more stabilized by both template isomers than polymorph B. When normalized for the 70% fault probability of polymorph B, isomer **1** clearly stabilizes SSZ-33

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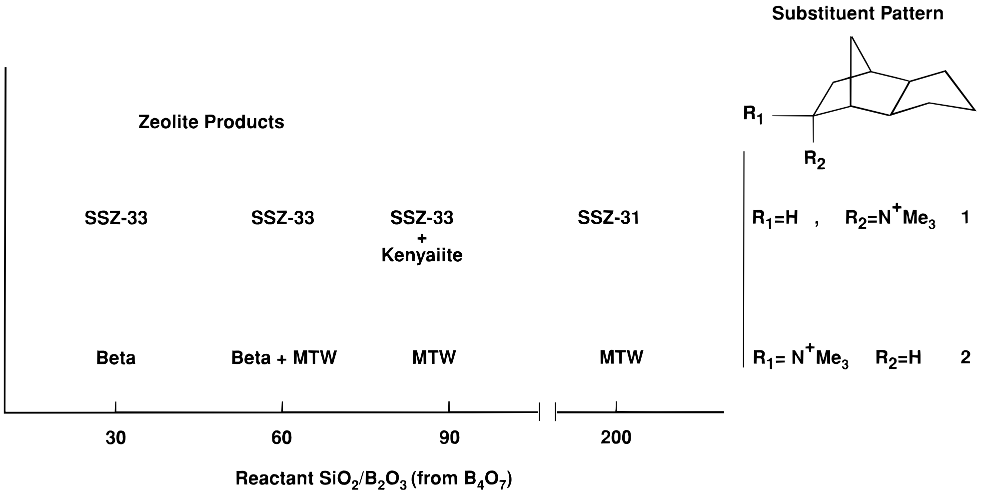

Figure 4. Transitions in the zeolite products formed for organo-cation isomers **1** and **2** as the degree of lattice boron substitution changes.

Table 7. Calculated Energies for Organocations and in Zeolite Hosts[a]

zeolite structure	1	2
MTW	−36.278	−45.453
beta	−41.875	−45.888
SSZ-33A[b]	−44.946	−38.300
SSZ-33B[b]	−46.221	−32.602

[a] Discover 2.8 from Biosym. [a] Polymorph A or B.

more than beta zeolite. Comparison of the normalized stabilization energies for both structures shows that *endo*-isomer **1** should promote formation of SSZ-33 while *exo*-isomer **2** should promote the formation of beta zeolite. These rationalizations are indeed in agreement with experiment. Likewise, even in the absence of modeling data for SSZ-31, we would suggest that *exo*-template **2** would be more likely to promote the ZSM-12 structure.

The normalized (for polymorph faulting) stabilization energies for template **1** in SSZ-33 and template **2** in beta zeolite are relatively close, within 3 kcal. This may explain why pure phase beta zeolite can be obtained even when the more favorable template **2** is only a minor component in the mixted template reaction. Once nucleation has been initiated (presumably by template **2**), it would not be unreasonable to expect that **1** could fill the pores in the zeolite beta phase and thus promote further crystal growth. In fact, considering stabilization energies of individual polymorphs, we see that beta zeolite polymorph B, occurring with 50% probability, is more stabilized by template **2** than SSZ-33 polymorph B, occurring with 70% probability and stabilized with template **1**.

These calculations show only the thermodynamic stabilization energy differences (ΔE) for the template isomers in the zeolite framework. Framework structures were taken from structure determinations in the absence of template or other adsorbates and structural relaxation was not included in the calculation. We presume on the basis of previous work[10c] that there is some relationship between stabilities of the final template-containing zeolite phase, which we have explicitly modeled, and the stabilities of the template-containing phases at or preceding nucleation which determine which structure will be preferred. Clearly there is a separate thermodynamic issue relating to the zeolite structures themselves. For instance, even though endo-isomer **1**/SSZ-33 polymorph A has the highest overall stabilization (except for ZSM-12), the experimental material contains 70% polymorph B. This may have a thermodynamic framework structural origin, which we have not modeled, or even a kinetic origin.

Table 8. Zeolite Product Results from Mixing the Contribution of Templates in the Synthesis of SSZ-33 with Seeding[a]

ratio 1/2	SSZ-33 by XRD	beta by XRD
90/10	100%	0%
85/15	100%	0%
80/20	100%	0%
75/25	100%	0%
50/50	major	minor

[a] See Table 5 for conditions.

The role of the templates for either nucleation or stabilization of crystal growth is further illustrated if the competitive experiments are run again and this time seeded with the apparently less favorable phase, SSZ-33.[25] The results are shown in Table 8, and it can be seen that it becomes possible to obtain pure phase SSZ-33 using smaller amounts of the more favorable template **1**. For example, as shown in Table 5 (unseeded competitive experiments), when the template **1/2** ratio is 75/25, the product is exclusively beta. Table 8 shows that this same mixture, when seeded with SSZ-33, results in formation of SSZ-33 as a single phase. Thus, one can see that by providing the nuclei for SSZ-33 crystallization, both templates can now participate in the crystal growth process, and we do not observe the product (beta) from nucleation by template **2**.

6. Issues in Host Lattice Structure Selection. A survey of the results using the tricyclodecane derivatives under favorable reaction conditions is shown in Table 4. While the list of nine templates is far from all-inclusive, three particular zeolites can be considered in relation to each other. Organic molecules deviating from "linearity" do not appear to make beta or ZSM-12. Products resulting from such templates (for example: **1**, **6**, and **7**) are very sensitive to the steric characteristics of the template: while *endo*-**1** gives SSZ-33 as product, related *endo*-derivatives **6** and **7** do not, even though they are in essence, only one methylene group larger. The diquat, **8**, while a mixture of isomers, certainly contains some endo substituents, and it is also ineffective in crystallizing new structures under these conditions. In contrast, "linear" templates **2**, **4**, and **9** all make beta or ZSM-12 (depending, on the lattice substitution). In this case, the extra methylene units do not preclude crystallization of these products. Beta zeolite and ZSM-12 then appear to tolerate more flexibility in the templates (especially along, the principal linear axis) than does SSZ-33.

As mentioned in the previous paragraph, crystallization of ZSM-12 or beta zeolite is very dependent on the concentration

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(25) We thank Professor M. E. Davis for the suggestion of this experiment.

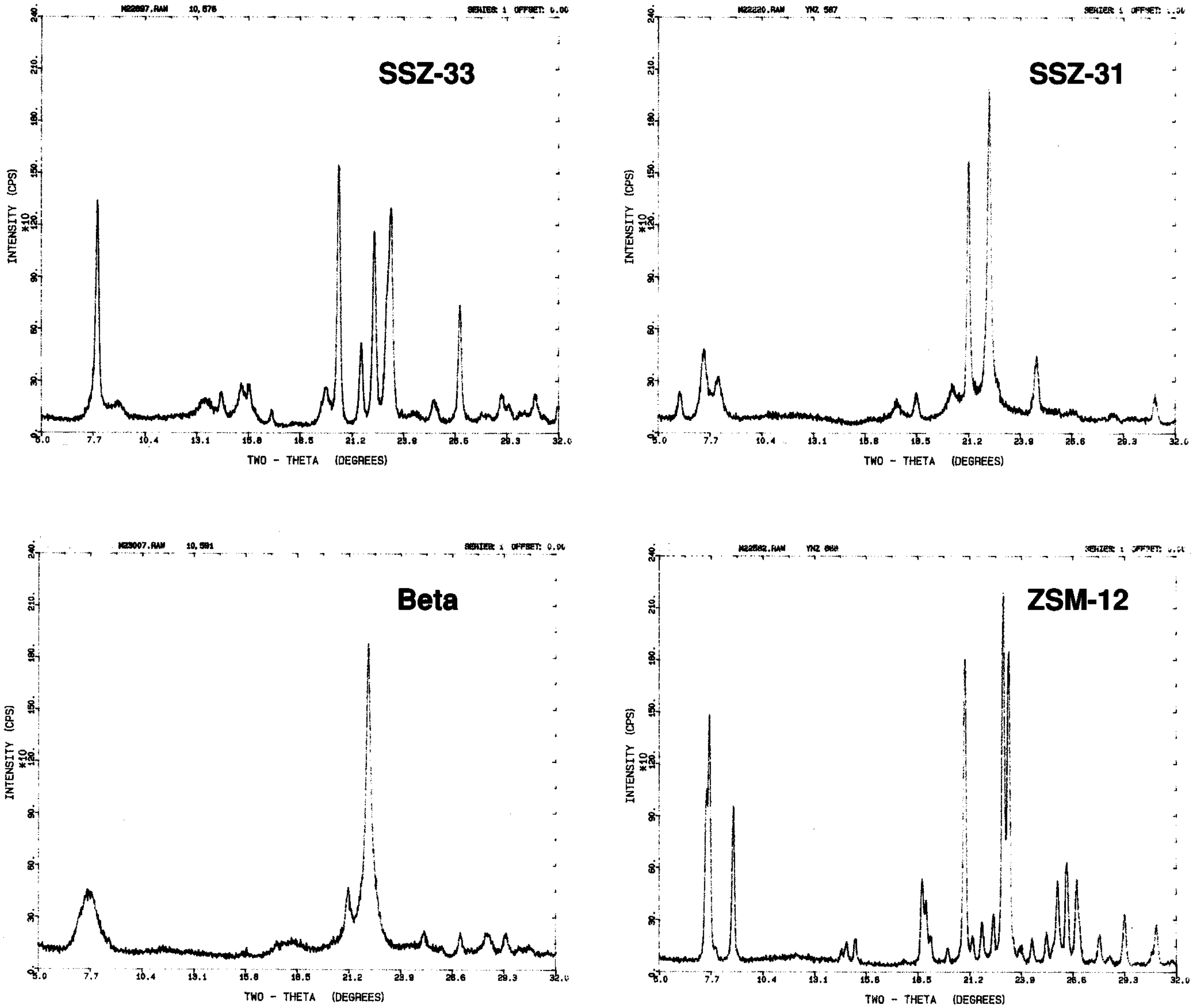

Figure 5. Representative X-ray diffraction powder patterns for the four principal borosilicate zeolites from organo-cations **1** and **2**.

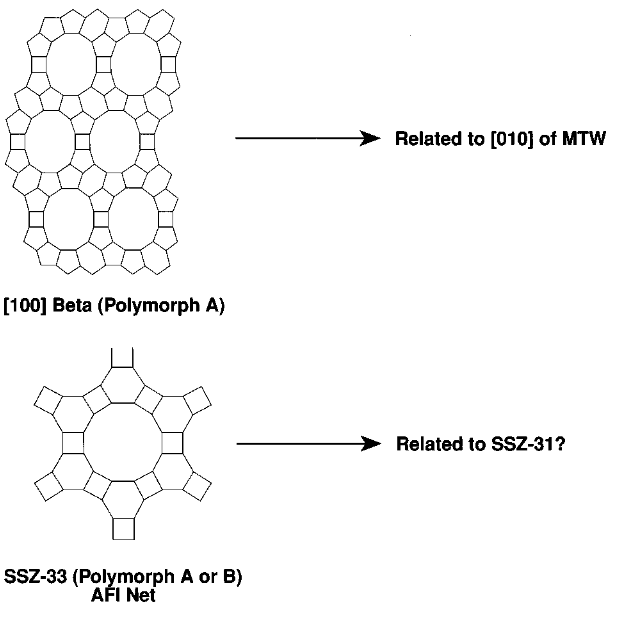

Figure 6. Two-dimensional nets yielding 12-ring apertures in beta and SSZ-33 zeolites. These two materials have other interpenetrating pore systems as well. But are these nets also found in the related one-dimensional pores of ZSM-12 and SSZ-31?

of the substituting element in the starting reaction mixture (in these cases, boron). As the concentration of boron is decreased, using the same linear organo-cations (**1** or **4**), the observed product changes from beta to ZSM-12 (Figure 3). Similarly, the *endo*derivative **1** yields SSZ-33 at high boron substitution and SSZ-31 as the boron concentration is decreased.

7. Beta Versus ZSM-12. The transition in crystallization products from zeolite beta to ZSM-12 can be observed in the scanning electron micrograph shown in Figure 8. The rod-shaped material has been determined to be ZSM-12 growing off of a core of beta zeolite (both phase identities were determined by electron diffraction). Presumably the beta zeolite crystallized first when the starting boron concentration was high. As the beta zeolite forms, the supply of boron is depleted from the reaction mixture, eventually resulting in an environment with a much lower B/Si ratio. This lower concentration of boron now favors the formation of ZSM-12 over beta, and, therefore, we observe the subsequent crystallization of ZSM-12. This may also illustrate a tendency for a product of high density to eventually recrystallize from a lower density product in a competitive crystallization field. This certainly has been observed for organic-free reactions in the form of "Ostwald ripening" or the Ostwald step rule.[26] In this comparison, beta zeolite has a higher microporosity as a multidimensional pore

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(26) Barrer, R. M. Hydrothermal Synthesis of Zeolites; Academic Press: San Diego, 1982.

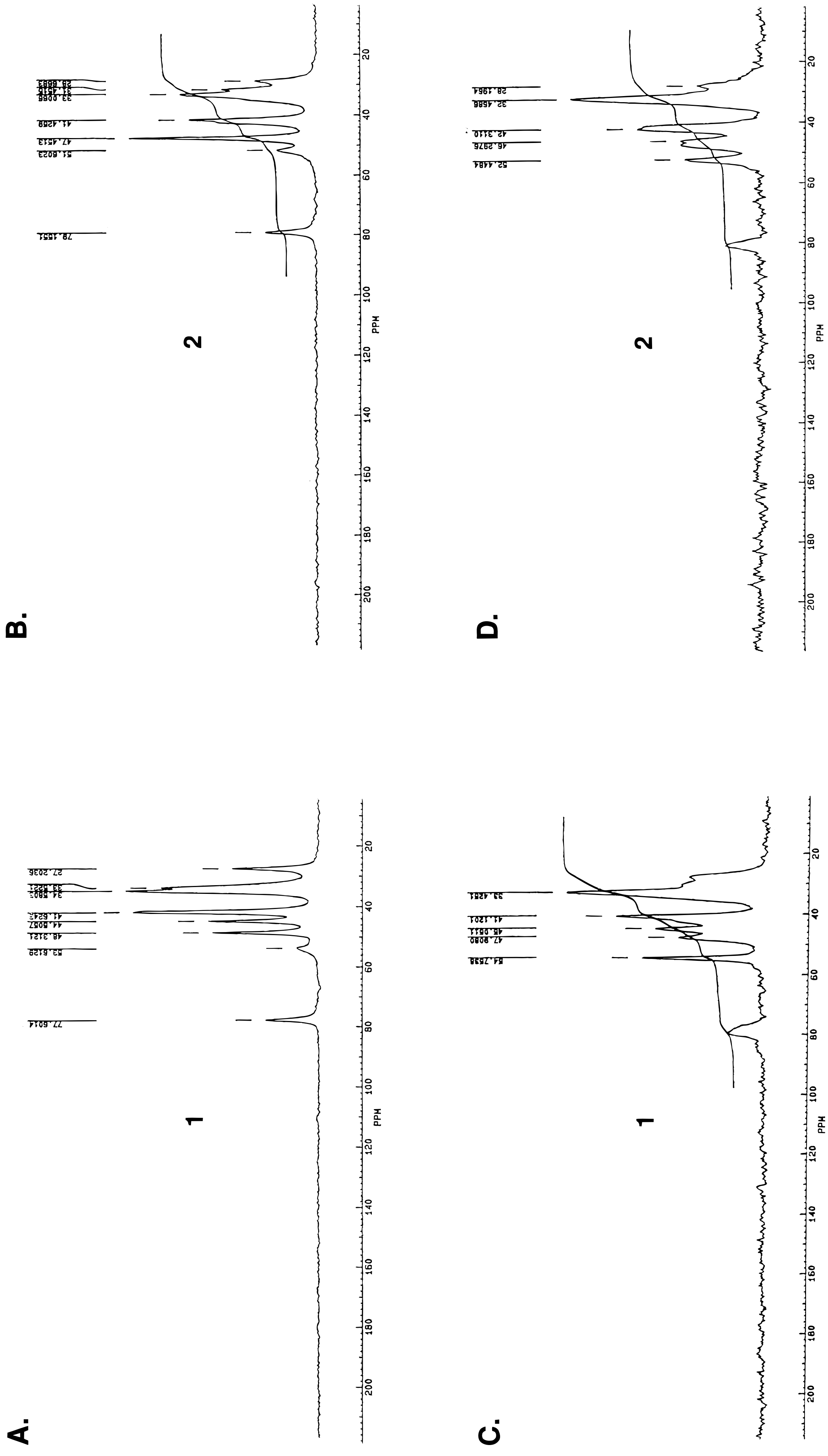

Figure 7. ^{13}C MAS−NMR spectra for (a) isomer **1** as iodide salt in the solid state, (b) the same condition for isomer **2**, (c) isomer **1** entrapped in the SSZ-33 product, and (d) the analogous condition for **2** in beta zeolite.

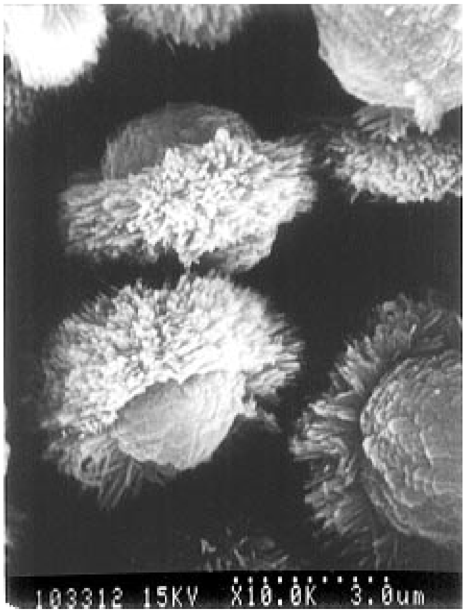

Figure 8. An electron micrograph which shows a center sphere with a systematic halo of needles protruding. Localized electron diffraction confirms that the core is beta zeolite while the needles are ZSM-12.

system as compared with ZSM-12. Therefore, beta zeolite is also the lower density phase.

The dependence of lattice substitution for beta or ZSM-12 crystallization has been observed with other "linear" organo-cations. For examples, using linked DABCO derivatives at low boron concentrations leads to formation of ZSM-12, but beta zeolite is the observed product upon increasing the starting boron content. For an even less structurally selective template, tetraethylammonium cation, the same trend was observed, a dependence on lattice-substituting element concentration.

Discussion

One of the goals in using organic molecules in zeolite synthesis is to obtain greater control over product phase selectivity. When using novel organo-cations as templates, the hope is that a new molecular sieve phase will be obtained. The results of this study emphasize the importance in considering the contributions of *both* the organic component and the starting, inorganic conditions in planning a synthesis reaction. We have demonstrated that for the organo-cations, the steric requirements appear to be the most important feature in determining, phase selectivity. With respect to the inorganic components, three factors must be considered: (1) the concentration of the trivalent element, capable of substituting for silicon in the lattice, (2) the concentration of hydroxide ion, which can dominate the silicate chemistry, thereby playing, a critical role in determining what product is formed, and (3) the concentration of the alkali cation itself which can also act as a template and dominate the course of crystallization.

At high OH^- concentrations ($OH^-/Si > 0.50$), most borosilicate products will not crystallize at all, owing to favorable solubilization of both silicates and borates above a pH of 11. Aluminates are less soluble at these high pH values, and therefore crystallization of aluminosilicates is favored under these conditions. As shown in Table 1, at a OH^-/Si of 0.65, only a few products are obtained. This limitation in observed product is due in part to the predominance of four- and six-ring silicate building units under these conditions. The cavity-containing products (SSZ-13) do incorporate the organic guest molecule, presumably to stabilize the large cages. If the template becomes too large to fit within the Chabazite-like cage, as they do in tricyclodecane derivatives (**1**, **2**, **6**, **7**, and **9**), mordenite becomes the observed product. Mordenite does contain some five rings in its structure and is considered a pentasil; however, it can form under similar reaction conditions in *the absence* of any organic component.[27] (The organic component was found within channels for these products.)

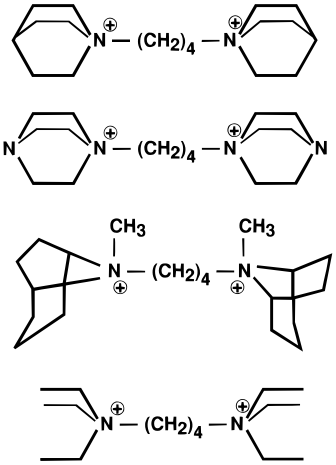

Figure 9. A representation of some of the sizable diquaternary ammonium compounds which produce SSZ-16 under conditions of high OH^-/SiO_2 (see Table 2).

Under these high $[OH^-]$ conditions, one other zeolite was observed with the diquaternary ammonium template. This product, SSZ-16, has small eight-ring pores but apparently a very large cavity.[28] When SSZ-16 is obtained, it usually requires a sizable diquaternary ammonium template. Figure 9 illustrates some of the other guests which have been found to produce it; note that all these templates have two bulky trialkylammonium groups linked by four methylene units. This zeolite is quite likely a member of the ABC-6 group of small pore/large cavity materials.[29] A structure solution, to that effect, has been proposed.[30] This would be an example of the cavity-containing, substitution-rich zeolites mapped out in Figure 3.

We have described several experiments where it was apparent that increasing the lattice substitution with boron favored the formation of intersecting channel systems. What is the controlling feature here? We have observed that these structures, in particular beta and SSZ-33, have increased populations of four-ring building units as compared to most zeolites with parallel nonintersecting channel systems. Substitution with aluminum gives a similar trend. Therefore, this observation is difficult to rationalize based simply on gel or solution chemistry. The aluminum oxygen bond is longer than the silicon−oxygen bond, and the boron−oxygen bond is shorter. On the other hand, each lattice substitution site introduces a negative charge to the framework and requires cationic balance. These cations are hydrated, at least in the early stages of crystallization. The arrangement of these hydrated, charged centers in the nucleation stage may help stabilize or promote the formation of four-ring building units, which, if included as part of the structure, might favor interconnecting, pore structures. High lattice substitution might result in interconnecting pore systems, but it may be the attendant cations (which balance the negatively charged framework sites) which are actually responsible for their formation. Further work is needed in this area to validate this hypothesis.

The interconnecting channel system in SSZ-33 presents something, of a puzzle. Table 9 shows adsorption data for six materials: SSZ-33, beta zeolite, ZSM-12, SSZ-31, Y, and

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[27] Breck, D. W. Zeolite Molecular Sieves; John Wiley and Sons: New York, 1974.

[28] Zones, S. I.; Van Nordstrand, R. A. *Zeolites* **1989**, *9*, 409.

[29] Smith, J. V.; Bennett, J. M. *Amer. Miner.* **1981**, *66*, 777.

[30] Lobo, R. F.; Zones, S. I.; Medrud, R. C. Submitted for publication.

Table 9. Adsorption Studies for Zeolites[a]

zeolite	N_2	*n*-hexane	cyclo C_6	2,2-dimethylbutane
Y zeolite	0.28	0.28	0.28	0.28
B beta	0.26	0.27	0.24	0.28
SSZ-33	0.20	0.20	0.20	0.20
MTW	0.12	0.12	0.10	0.11
SSZ-31	0.12	>0.10	0.09	0.10
ZSM-5	0.15	0.17	0.04	0.01

[a] Data obtained at 23 °C and $P/P_o = 0.14$ for hydrocarbons and at −177 °C for nitrogen. Values reported as cc/gm zeolite.

ZSM-5 (the last two are well-characterized multidimensional channel zeolites which are used in commercial applications). The largest adsorbate used was 2,2 dimethylbutane (DMB) which usually only enters the large (12-ring) pores. For SSZ-33 this value is as high as with the much smaller adsorbate, nitrogen. This gave us the impression that all of the porosity must be related to large pores. The proposed structure solution indicates a large and intermediate pore.[4] So the distance bounded by the intermediate 10-ring between adjacent 12-rings must actually be small. That is, there are not long 10-ring channel distances, which exclude the entry of DMB. The adsorbate packing, in the cavity intersections must see the zeolite as large pore, with packing virtually extending into the adjacent large pore.

Given what we have described for beta and MTW it is tempting to look for an analogous relationship for the SSZ-33 multidimensional channel zeolite and SSZ-31. The adsorption characteristics for the latter suggest a one-dimensional channel and large pore characteristics. The projection given for the 12-ring, in SSZ-33 is related to the AFI structure.[4,23] While SSZ-31 is certainly novel in comparison with AFI, we did find that template **1** can make the AFI structure in MAPO type chemistry.[31] So it can fit in this pore configuration; from this view it may be likely that SSZ-31 has a closely related structure.

To date only templates **1** and **5** have produced SSZ-31 from amongst this family of tricyclo[5.2.1.0$^{2.6}$]decane candidates. This once again reiterates the lack of flexibility for endo substituents. The exo isomer of **1** crystallizes MTW at high silica. But so do some of the other exo-substituted templates. In fact, we even found that two exo-substituted tricyclo[5.2.1.0$^{2.6}$]decanes, connected by a $(CH_2)_4$ chain between the nitrogens, will even make the MTW product (we have not yet determined whether this large, linear diquaternary template is intact within the zeolite pores). This result is conceivable given the previously described synthesis of this zeolite using a DABCO-based polymer.[32] In the search for new products the endo isomers, although failing to crystallize any product in some of our reaction attempts, may actually be better candidates for novel guest/host structures. In this regard, we are also exploring, organic synthetic routes which can change the endo/exo orientation of the tricyclo[5.2.1.0$^{2.6}$]-ring system. The previous work by Nakagawa on azapolycyclic tricyclodecanes generated these molecules primarily in the endo ring conformation. Once these templates are large enough (i.e., template **5**), the SSZ-33 and SSZ-31 structures could be generated under conditions analogous to the borosilicate runs for template **1**. In addition, a new zeolite, SSZ-37, was also found.[33] Once again, no substituent flexibility was observed; only one, discrete, rigid guest conformation was successful.

Conclusions

This study has highlighted some of the synergistic factors involved in the search for new molecular sieves via the development of guest/host structures. The organic chemistry of the guest organo-cation and inorganic factors relating to the gel chemistry leading to the final host lattice are both important. Each may dominate under selected synthesis ratios. The use of the tricyclo[5.2.1.0$^{2.6}$]decane family of guest molecules or templates can be entirely masked by too high an alkali concentration in the synthesis. Previously known phases, mordenite and SSZ-13 (a synthetic chabazite), dominated reaction products. At lower alkali metal levels and lower alkalinity the individual tricyclo[5.2.1.0$^{2.6}$]decane organo-cations showed much greater selectivity in terms of zeolites produced. Correlations began to emerge for the large pore zeolites crystallized and the spatial features of template **1**−**9**. Exo-substituted guests showed less size criticality in their product selectivity compared to endo substituted molecules.

The extent of boron as lattice substituent influencing the channel dimensionality of the product also was seen. High boron led to multidimensional zeolites SSZ-33 and beta, lower levels to MTW and SSZ-31. Some evidence was presented to consider the possibility that the high/low boron products are structurally related. The trends observed for borosilicate reactions have some precedence in earlier aluminosilicate reactions.

Finally, some of our experiments have demonstrated the importance of template structure at the nucleation stage with regard to phase selectivity.[10c] Both modeling work and experiments carried out with seeding showed that the energy differences can be small enough among some guest/host interactions that once having started the crystal growth of a given phase, often more than one space-filling, guest molecule can be incorporated.[24] This knowledge can aid in the design of future guest/host molecular sieve systems.

Acknowledgment. We thank Dr. D. M. Wilson for running the MAS NMR experiments. We also thank Dr. A. Rainis, Dr. C. Y. Chen, and T. F. Finger who built the adsorption micropore determination system and acquired the data. Dr. I. Y. Chan obtained the localized electron-diffraction data discussed. G. S. Lee synthesized some of the organo-cations studied. We thank Dr. Karl-Heinz Schoenwalder and Dr. Jurgen Weber at Hoechst A.G. for providing some of the template precursors. Finally, the support of Chevron Research and Technology Company is greatly appreciated.

Note Added in Proof: Recent structure work confirms that SSZ-31 is a large pore, one-dimensional zeolite with structural components related to not only AFI but to MTW as well (Lobo, R. F.; Freyhardt, C. C.; Tsapatsis, M.; Zones, S. I.; Chan, I. Y.; Chen, C. Y.; Davis, M. E. Manuscript in preparation).

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[31] Harris, T. V. Unpublished work.

[32] Davis, M. E.; Saldarriaga, C. J. *Chem. Soc., Chem. Commun.* **1988**, 920.

[33] Nakagawa, Y. U.S. Patent 5,254,514, 1993.