

《解説》

FACTORS AFFECTING THE SELECTIVITIES OF ORGANO-CATION GUEST MOLECULES IN THE SYNTHESIS OF HIGH SILICA ZEOLITES

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Abstract

This paper examines the ability to use new organo-cations in the search for new high silica zeolite structures. A strong correlation can be found for the space-filling demands of the organic guest with the available space in the host lattice. For this reason it is sensible to construct rigid guest molecules. However, spatial factors are not enough. We therefore also examine the role of lattice-substituting elements in the outcome of the synthesis experiments. Experimental work on probing thermodynamic and kinetic issues for the directing function of the guest molecule in the synthesis is also presented. One emerging feature is the importance of van der Waals interactions from guest to developing host at the nucleation stage.

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Zeolite catalysts have an increasing role in the successful manufacture of a variety of chemical- and petroleum-based products. Manufacturing countries throughout the world are watchful for opportunities involving enhanced selectivity, reactivity, or lifetime for these inorganic, crystalline oxides used as catalysts. The discovery of new structures, which are then tested as catalysts, is an event which researchers in the field look forward to. The discussion given in this paper attempts to outline some of the approaches taken at Chevron Research and Technology Company to tailor organic guest molecules which, in concert with other variables, can influence the host lattice which eventually crystallizes.

Over time some very good guest/host correlations have been observed. Two such examples are given in Figure 1. In these examples there is a high degree of space-filling by the guest throughout the extent of the host lattice. After the pioneering discovery of the MFI material from the use of TPA (tetrapropylammonium cation) as template, much research was devoted to both understanding this process and to finding new high silica products. A large variety of organic molecules have been explored as templates for zeolite synthesis and a sampling is given in Table 1. While discoveries have been made using all of these types of templates, we have preferred to concentrate on the use of quaternary organo-cations, particularly with respect to finding new high silica zeolite structures. Quaternary ammonium salts provide a fixed charge which allows us to span a range of inorganic conditions. Table 2 describes some of the issues which must be considered when one is using organo-cations as templates or guests in zeolite synthesis. In this review we will discuss some of these issues in greater detail.

* The authors wish to thank Kiriye Nakagawa for providing this calligraphy.

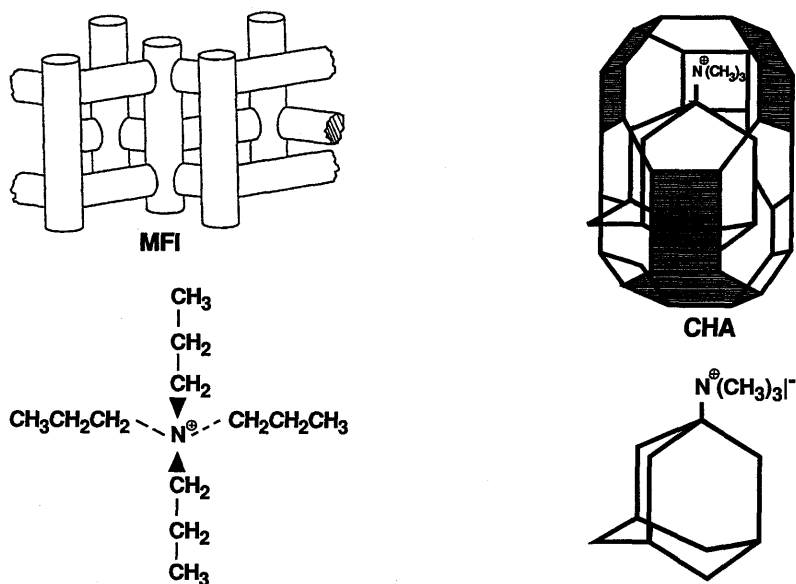


Figure 1 - Two zeolite structures which are produced over a wide range of conditions with the guest molecules shown. The "guests" fit the void regions of the zeolites very well.

TABLE 1

SYSTEMS OF ORGANIC MOLECULES

- Symmetric Tetra-alkylammonium Salts
- Free Amines (OH^- , F^-)
- Free Amines (PO_4^- , F^-)
- Micelles (MCM-41 Type)
- Hydrophilic, Charge (ECR Reactions)
- Diquats (ICI)
- Cyclic Quats
- Rigid, Polycyclic, Hydrophobic
- "Nonaqueous" Reactions
- Polyethers (Crowns)

TABLE 2

ISSUES

- Size
- Charge(s)
- Stability
- Solubility
- Concentration Effects
- Side Reactions

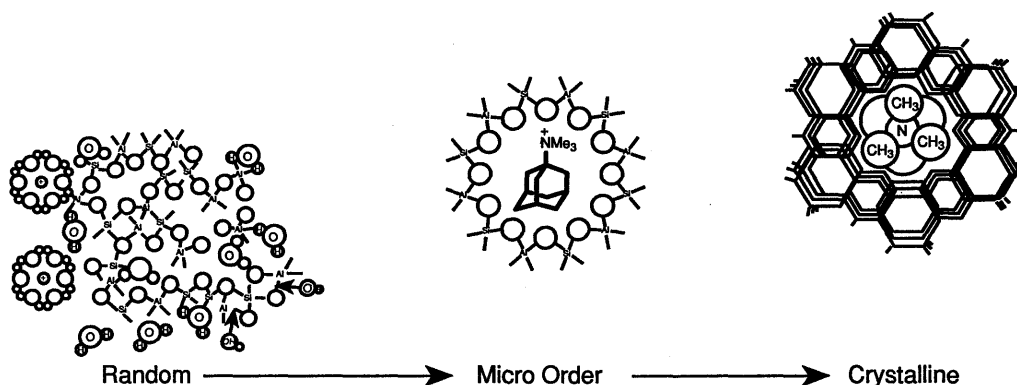


Figure 2 - A representation of the increase in order during zeolite crystallization in the presence of an organo-cation guest.

One of the parameters of particular interest is the size of the guest molecule. This can be manipulated to some degree (see below) to influence the pore sizes of the resultant molecular sieve. Once we build some conformational rigidity into the guest we can also hope to influence the dimensionality of the pore system. An idealized representation of this process is illustrated in Figure 2. Understanding the details of crystallization selectivity is also an objective of our studies.

Product Selectivity Factors

Over time a few trends have emerged. Figure 3 shows a pyramid representation of the size of the guest, represented as a sum of heavy (carbon and nitrogen) atoms, contrasted with the variety of zeolite structures made. Most of the zeolites are abbreviated as their IZA code or by patent identifiers. What is observed is that the smaller quaternary ammonium guests yield a variety of structures but the selectivity narrows with larger guests. It appears that the requirements for inclusion into an emerging pore system become more demanding as the template size is increased. Zeolites such as MEI (ZSM-18) or SSZ-26 can only be made if a particular guest molecule is used (1). It can be seen that to accommodate a larger guest molecule, the arrangement of the silicate subunits loses a great deal of flexibility. For some guests, no crystalline arrangements have been found. On the other hand, it is interesting to note that some zeolites with at least one large pore channel system (12-ring or a diameter greater than 6.5 Å) are relatively guest-insensitive. A variety of organo-cations have been found to work, and candidates with a long principal axis appear to work best. This can be seen in Figure 3 for MTW and Beta (BEA) zeolites.

By synthesizing guest molecule candidates and then using them in a series of zeolite reactions, we have determined that their size and conformation is not enough to determine the zeolite product outcome. Another key determinant is the lattice substitution. Figure 4 shows a variety of zeolites formed with respect to the C/N⁺ ratio of the guest (which is a rough measure of guest size). The data is also broken up into two Si/Al regimes. In the first group with a higher degree of lattice substitution, large pore and small pore zeolites tend to dominate with intermediate pore materials absent. It appears that in this group there is either the formation of cage structures with small pores (i.e., CHA), or larger pore materials which more than likely will have channel branching.

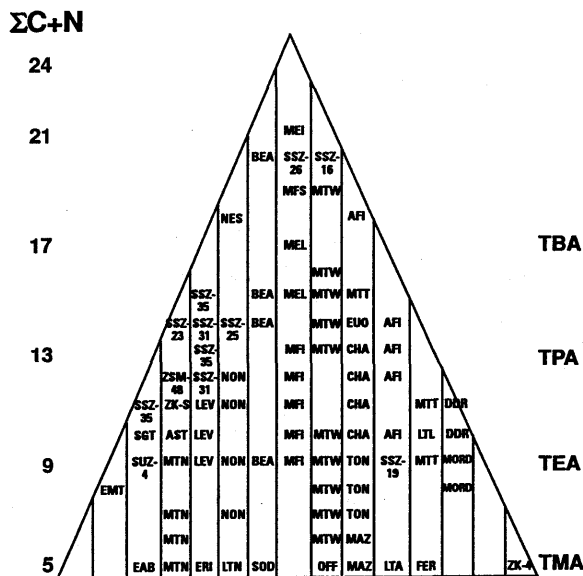


Figure 3 - A graphic representation of the variety of zeolite structures made versus the size of the guest (from summing carbon and nitrogen atoms). The codes given are from either the Atlas of Zeolite Structures or from the patents and papers where the materials appear. The far right margin indicates the level where symmetric tetralkyls like tetramethyl ammonium, etc., would appear.

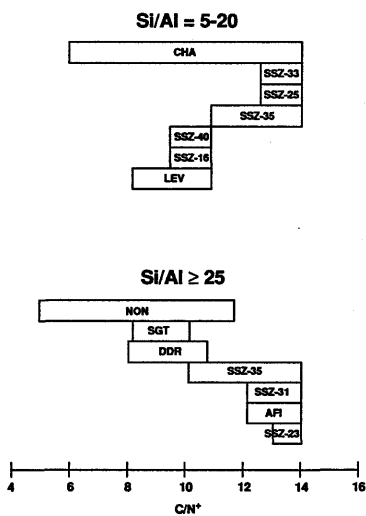


Figure 4 - The range of zeolite materials made as a function of template size and viewed in two different Si/Al regimes. The novel SSZ (Social Synthetic Zeolite) materials are from the authors' research at Chevron Corporation.

Moving to the higher Si regime, two new types of materials emerge. Their formation becomes sufficiently favorable that they represent barriers to be overcome. If the guest molecules are small enough, cage structures which have no pores at all form: clathrasils are the product (2). If the guests become larger in size, then the large pore zeolites which form tend to be one-dimensional. Three of the four zeolites shown in Figure 4 made from

templates with $C/N^+ > 10$ are known to have a principal one-dimensional large pore. We have previously described this trend for medium-pore aluminosilicates (3). Recent work from our laboratory indicates that borosilicate chemistry follows similar trends.

Some Energetics Considerations

Professor Barrer at Imperial College has attempted to describe thermodynamic considerations for guest-host formation. His derivation follows from the Gibbs-Duhem relationship (4). While this is certainly a consistent and attractive picture, particularly for guest adsorbates like water, a few issues puzzled us with regard to the larger organo-cations we were studying. First, a recent paper by Navrotsky, which examined the enthalpies of formation for a variety of high silica zeolite structures, as determined by high temperature calorimetry, indicated that the values were not very different from each other (5). In fact, the enthalpies appear to be relatively *structure insensitive*. This surprised us because we imagined that our guest-host complex might represent an energy minimum in a sea of possible structures in the zeolite synthesis reaction.

The second feature that caught our attention was the possibility that the guest-host problem might be quite complex in terms of the solvation of the guest by water prior to "solvation" by the lattice. What might be the energy associated with that step? This problem is illustrated in Figure 5 where we show, by analogy, that if our thermodynamic product is a candy-coated peanut, then one of our energy steps is to remove the shell from peanuts before we can place them into the new lattice. The energy associated with "shell removal" might actually be favorable and a driving force towards crystallization if the organo-cation is not well solvated by water in high ionic strength media. The largely covalent, nonpolar environment of a silica lattice might be preferable to the surrounding high pH solution.

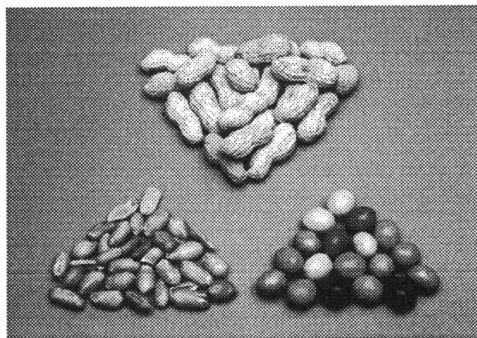


Figure 5 - The solvation of a solute in solution can be considered as analogous to a nut in a shell. The shell must be removed before encasing the nut in a new "lattice," in this case a candy coating.

We attempted to test this concept in an indirect manner. We had noticed that small organo-cations are very well solvated by water and that high concentrations of solute can be achieved. This is less the case as the organo-cations become larger with a fixed single charged nitrogen. If given the opportunity to reside in a less polar environment, to some degree these cations will migrate from water to a solvent like chloroform. In Figure 6 we plot the transport percent versus C/N^+ for a series of organocations. In general, values below 10 reside largely in water but by 16 the transport over to the $CHCl_3$ phase is very high. In the center are several points, all from molecules with a C/N^+ value of 12.

We gained a different insight into this problem by exploring a reaction where all the organo-cations, under the same conditions, make the same crystalline structure. A variety of molecules can make the caged clathrasil, Nonasil (NON), in reactions without any lattice substitution. We then performed computer modeling on the energetics of guest-host interactions in this system (8). A plot of stabilization energy versus C/N^+ shows a trend of increased energy as the organo-cation becomes larger for a fixed cage size (see Figure 7). Interestingly, there are a few low energy points even as the organo-cations were becoming larger. The fit wasn't as favorable even though Nonasil was the eventual product obtained.

The most interesting relationship emerged when we plotted the stabilization energies versus rates of reaction. In this case, when all candidates are directing towards the same crystalline product, the most favorable stabilization energies give the fastest rates, as shown in Figure 8. In the computations, the stabilization energies appear to be dominated by van der Waals interactions from guest hydrogen to host oxygen atoms in the cage. As the guest molecule's size is increased, these contacts should increase in both number and strength to the point where the guest can no longer be accommodated within the Nonasil cage. In the crystallization experiments we view this favorable interaction as influencing nucleation. The following additional observations support this: (a) In the fastest crystallizing systems the average crystallites are larger, an indication that once nucleation starts, crystallization is quite favorable and rapid. (b) By choosing a slower reaction, with a less favorable calculated stabilization energy, and adding seed crystals, the crystallization rate more than doubles. This indicates that by providing nucleation sites, it no longer matters that the calculated stabilization energies are not as favorable. We can imagine then that in the zeolite crystallization, the more favorable the van der Waals interactions, the more likely germ nuclei (9) will be stabilized, which will propagate the crystallization.

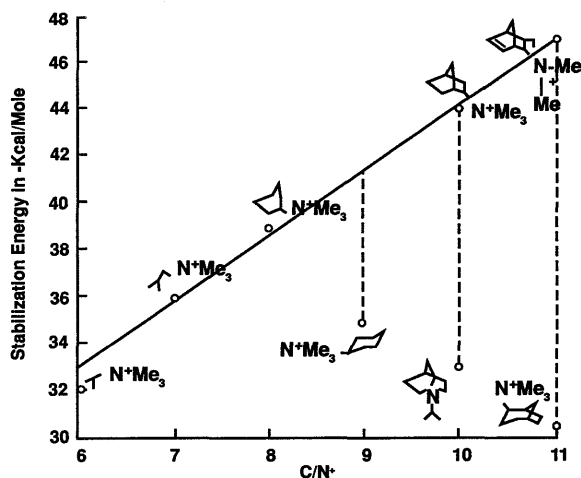


Figure 7 - A plot of stabilization energy versus guest size for a series of organo-cations which all make Nonasil.

Examples of Using of These Concepts

Two problems will be used to illustrate how these concepts can be put into effect. In the first instance, we'll consider how the tailoring of a given organo-cation can be useful in producing a novel zeolite with designed features. Earlier, we had mentioned that molecules with a single principal linear axis were effective in producing

the one-dimensional MTW zeolite and the length of the guest did not seem to be a critical variable (see Figure 3). Our hypothesis was if we wanted to introduce a second pore system into a zeolite product, we needed a "break" in the linear orientation of the guest molecule. By synthesizing a diquaternary propellane molecule, containing three fused rings, we now had such a candidate. In addition, we found that it was necessary to work at a sufficiently high lattice substitution. Under these conditions, then, a novel zeolite, SSZ-26, was produced (10).

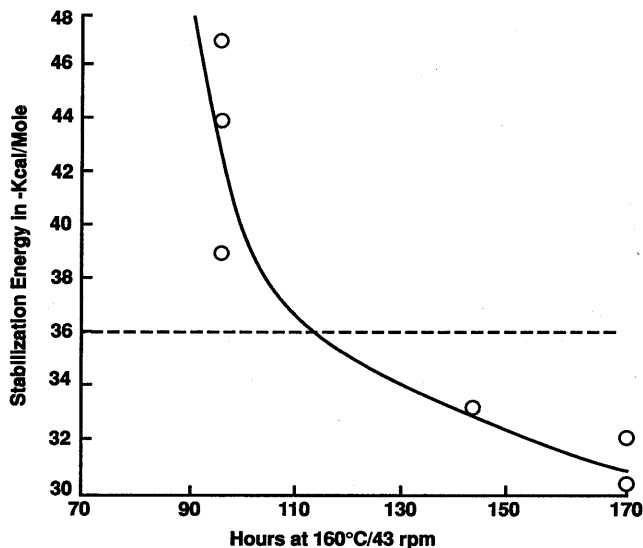
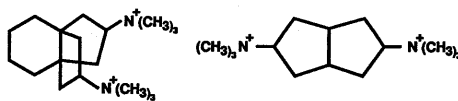


Figure 8 - The stabilization energies, from Figure 7, versus crystallization times for Nonasil from several guest molecules.

Table 4 shows the propellane structure contrasted with a more linear analog which makes MTW. In the table we can also see that the N_2 micropore volume for SSZ-26 is almost double that of the one-dimensional MTW. Recent work carried out together at Chevron, Caltech, and Arizona State University confirmed that the structure of SSZ-26 is indeed multidimensional, containing both 10 and 12 rings (11). This is the first zeolite of this type synthesized with both pore types accessible to reactants and it places the material in between the commercially useful ZSM-5 (MFI) and beta zeolites with respect to void volume.

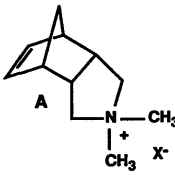
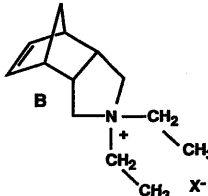
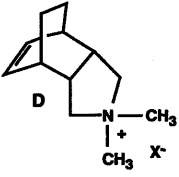
TABLE 4



Zeolite Produced	SSZ-26	MTW
Micropore Volume	0.20 cc/g	0.12 cc/g
Product SiO_2/Al_2O_3	20-70	>50

A second example arises from developing a strategy to "fine-tune" small structural changes into a given guest structure. Nakagawa et al. have shown that by employing Diels-Alder organic synthesis methodology they can make rigid polycyclic organo-cations which are quite useful for large pore zeolite synthesis (12). The modifications can be introduced into either of the reacting rings before the cyclo-addition reaction, or alterations can be made when quaternizing the nitrogen of the pyrrolidine ring. In Table 5 several related guest structures are shown as well as the corresponding product selectivity with and without lattice substitution. It can be seen that this approach, combining several of the key features we have discussed in this article, has led to the preparation of several new large pore zeolite phases; we next hope to realize their commercial benefits.

TABLE 5

	Diels-Alder Structure		
			
All-Silica	NON	MTW	SSZ-31
Aluminosilicate	CHA	MTW	SSZ-37*
Borosilicate	NON	MTW	SSZ-33*

*Large pore and multidimensional.

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