

Computational studies of zeolite framework stability

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Chapter 42

Computational Studies of Zeolite Framework Stability

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For the purpose of determining the relative stabilities of topologically different aluminum-free tetrahedral networks, Hartree-Fock-level ab-initio calculations have been done of the relative stability of three-, four-, five- and six-unit $\text{SiO}(\text{OH})_2$ rings. Very small differences per T unit are found for the four-, five- and six-rings; however, the energy per T unit is unfavourable for the three-ring. Rigid ion lattice minimization calculations have been performed on Al-free as well as high-Al-content zeolite systems. The results will be discussed for ZSM-5, mordenite and faujasite structures. Very small energy differences, of the order of ~ 20 kJ/mol, are again found for the Al-free networks. Open structures have less favourable energy than dense structures due to decreased Madelung energy. Large changes in relative energy are found upon variation of the Al/Si ratio. Medium- and small-pore zeolites are much more sensitive to an increase in aluminum content than the wide-pore material. This should be ascribed to stacking of the cations in the channels of the zeolite. The implications of these results for zeolite synthesis are discussed.

The theoretical work to be discussed here has been initiated with the aim of providing support to fundamental studies of zeolite synthesis. Central to our discussion is the question whether a synthesis approach for new zeolites can be developed on the basis of guidelines generated by computational design.

For such an approach to be viable, certain fundamental physico-chemical knowledge about zeolites and their behaviour is essential. In particular, one needs to know:

- what zeolite structures are possible;
- what laws govern their synthesis.

Many leads on new zeolite structures are available in the open literature (1). We shall therefore concentrate on the second of the

two areas mentioned above, concerning the zeolite formation mechanism.

We are interested in the role of organic ions and organic molecules in zeolite synthesis. The use of organic molecules in zeolite synthesis mixtures in addition to inorganic bases is known to result in the medium-pore-size low-aluminum-content zeolites, such as ZSM-5, that revolutionized several processes of importance to the oil-refining and petrochemical industry.

Since, during synthesis, the organic molecules and ions become incorporated into the zeolite micropores in quantities much larger than required to neutralize the lattice framework, Flanigan (2) proposed that they act as a template around which the zeolite precursor molecules are formed. Barrer (3) proposed that adsorption of organic molecules during synthesis stabilizes the zeolite lattice. This second idea provided the starting point to our theoretical work. It can be understood on the basis of the following considerations.

The major characteristic of a zeolitic material that distinguishes it from a non-zeolitic one is its microporous structure, due to the presence of interconnected channels. This implies that, whereas the interfacial energy is a negligible quantity for large crystallites of non-porous materials, this is no longer more the case for a microporous system.

Consider, for instance, the interaction of the alumina-free silica framework of de-aluminated faujasite with water in the liquid phase. Per mol SiO_2 , 1.3 mol H_2O can be occluded. The heat of evaporation of water is 36 kJ/mol and the heat of adsorption -30 kJ/mol, so per mol SiO_2 there is an energy cost of 20 kJ.

It is of interest to compare this figure with the heat of immersion of aluminum-rich faujasite. For a compound with composition $\text{Na}_{80}\text{Al}_{80}\text{Si}_{112}\text{O}_{384}$ one calculates -122.5 kJ/mol (4), which is mainly hydration energy of intra-channel sodium ions.

So in the crystallization of microporous systems there is a balance between the energy cost of micropore generation and the energy gain because of interfacial stabilization by occluded molecules. Clearly there is no gain for porous aluminum-free systems in water, so they will not be formed unless a trick is used.

These notions can be given a more exact expression by the use of the rule of Gibbs:

$$d\mu_i = RT / a \cdot [\Sigma_i \theta_i \cdot d\ln(p_i)] \quad (1)$$

In this expression μ_i is the interfacial chemical potential, a the average surface area, θ_i the fraction of the surface covered by the adsorbed molecule i , and p_i the corresponding partial pressure. Expression (1) can be partially integrated, assuming Langmuir adsorption for the adsorbed molecules, to give:

$$\mu_i = RT / f \cdot [\ln(1 - \Sigma_i \theta_i)] \quad (2)$$

In expression (2), f^{-1} is the fraction of cavities present in the structure per mol SiO_2 . For instance, in silicalite f equals 24. Of course, crystallization of a microporous system completes with the formation of a dense system unless:

$$\mu_i < \mu^{\text{dense}} - \mu^{\text{zeo.lat.}} \quad (3)$$

In order to quantify this relation one needs information on the lattice energies of zeolites as a function of lattice topology and composition.

In the next sections calculations of the lattice energies of zeolites via several different computational approaches will be reported. Each approach is approximate; each has its own advantage(s).

To begin with, we shall discuss computations of the lattice energies of aluminum-free zeolites. We shall then go on to discuss the lattice energies of aluminum-containing zeolites. We shall conclude this paper with a discussion of the relevance of the results obtained to zeolite synthesis.

The Stability of Zeolitic Silica Lattices

Methods. Initial calculations were done using the semi-empirical Extended Huckel method (5). The purpose of these quantum chemical calculations was to explore the main electronic characteristics of chemical bonding in silica tetrahedral networks. The calculations showed that bonding can be considered covalent and can be considered to be due to localized SiOSi units.

Very small differences in bond strength between different silica polymorphs were found. Since the Extended Huckel Method is too approximate to calculate reliably the small differences in energy between low-density material, containing micropores, and high-density material without micropores, work was initiated to study the same problem but now with two rigorous techniques that are currently considered to be state of the art.

Hartree-Fock-level ab-initio calculations can provide reliable potential energy diagrams for small clusters. Such calculations can be applied to the zeolite lattice if the clusters are chosen carefully and use is made of the property that bonding is highly localized in these materials. Calculations were done using the GAMESS ab-initio package.

Since this approach does not account for long-range electrostatic potentials present in the extended material, the second approach chosen was the rigid-ion lattice energy minimization technique, widely used in solid-state chemistry. This method is based on the use of electrostatic potentials, as well as Born repulsion and bond-bending potentials parametrized such that computed atom-atom distances and angles and other material properties, such as, for instance, elastic constants, are well reproduced for related materials. In our case, parameters were chosen to fit α -quartz.

Results of Hartree-Fock Calculations. Using a STO3G basis set, calculations were performed on the open dimer (Figure 1) and 3-, 4-, 5- and 6-rings of C_{nv} symmetry (Figure 2), in which n stands for the number of $(\text{SiO})(\text{OH})_2$ units, the dangling bonds being saturated with H atoms. Figure 3 shows the equi-energy contours of the dimer as a function of bridging SiO length and SiOSi angle. The result fully concurs with results from similar work obtained by Gibbs et al. (6).

It can be seen that there is a steep increase in energy if the SiO distance starts to differ from its equilibrium value, but that the energy changes involved in angle variations are very small. The SiO bond strength is of the order of 450 kJ, whereas the change in energy with angle variation is only of the order of 20 kJ. The

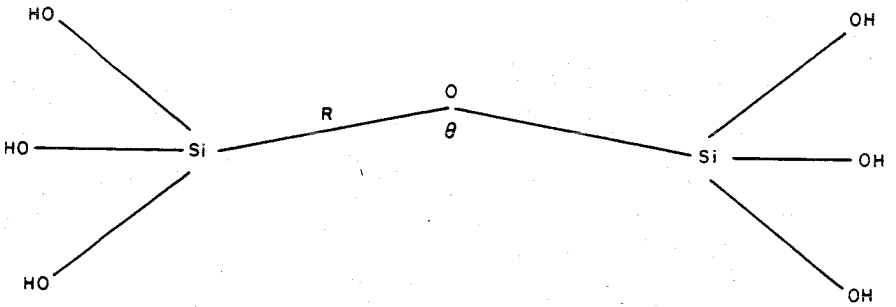


Figure 1. Dimer cluster; C_{2v} symmetry assumed.

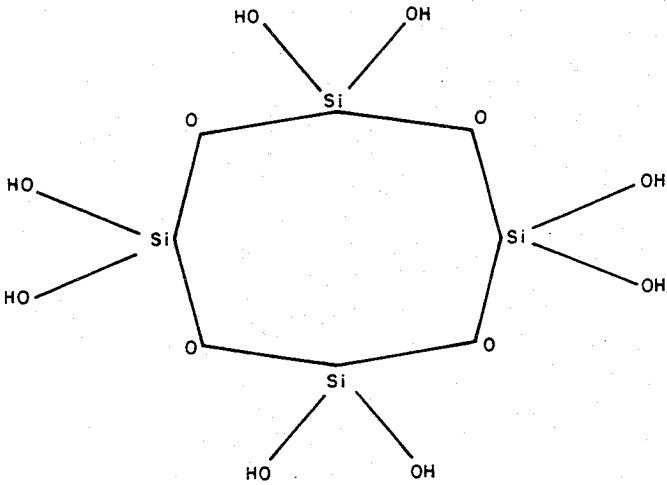


Figure 2. Ring structures; C_{nv} symmetry assumed ($n=3, 4, 5, 6$).

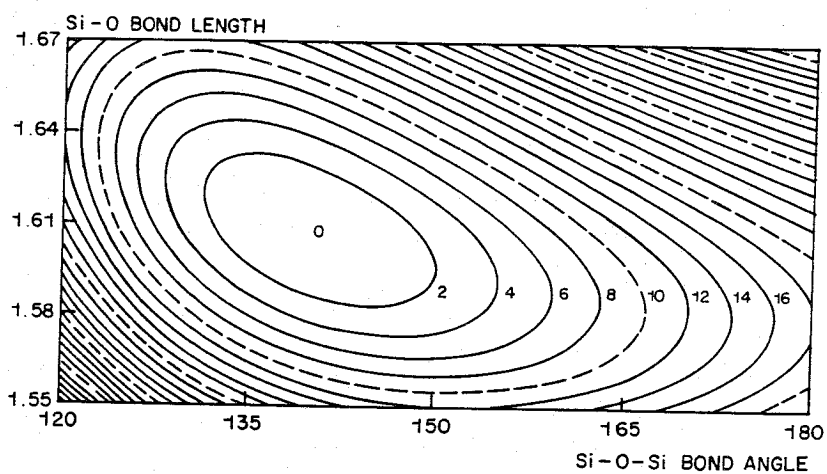


Figure 3. Total energy as a function of Si-O bond length and Si-O-Si bond angle. Contour lines in units of kJ/mol.

latter measurement agrees well with the very low rocking and torsional frequencies around the SiOSi bond measured by infrared experiments on zeolites (7). This implies that lattice deformation can take place at little energy cost as long as no SiO bonds are broken.

Tables I and II summarize the results found for the silicate ring clusters. Table I,A presents the computed total energies per $\text{SiO}(\text{OH})_2$ unit. Bond lengths and bond angles in the rings were optimized within the constraint of C_{nv} symmetry. As can be seen in Table I,A the energy difference between the 3-ring and the other rings is considerable. However, the energy differences per unit $\text{SiO}(\text{OH})_2$ of the 4-, 5- and 6-rings are computed to be within 1 kJ. Computed SiO distances and SiOSi angles are presented in Table II.

The reason for the instability of the 3-ring can be readily seen. Within the tetrahedra the OSiO angles differ from the optimum tetrahedral angles; in addition, the SiO distances appear enlarged. A clear trend in SiO distance as well as SiOSi angle is observed as a function of ring size: the SiO distance shortens, whereas the SiOSi angle increases. The relation between SiO distance and SiOSi angle is fully consistent with the potential energy diagram presented in Figure 1 and is due to changes in hybridization of the electrons on the O atom (5).

It is of interest to compare the extent to which geometry depends on ring size with the average bond lengths and angles observed in alumina-free zeolites with different numbers of rings. This comparison is given in Table III. A trend in angle and distance variation with increased amount of 5-rings compared to 4-rings similar to that observed in the calculations can be distinguished. The distances compare well; the average angle measured for mordenite and ZSM-5 appears somewhat large, though. This may be due to the difficulty in determining oxygen positions accurately.

Table I. Ring Structures

A. Total Energies				
n (Ring Size)	e/n (a.u.)			
3	-508.41206			
4	-508.41547			
5	-508.41578			
6	-508.41580			

B. Energy Differences in kJ/mol				
n	3	4	5	6
3	0.000			
4	-8.944	0.000		
5	-9.765	-0.820	0.000	
6	-9.806	-0.861	-0.041	0.000

Table II. Optimized Geometries for Ring Structures

	Distances in Ångstrom, angles in degrees			
	3	4	5	6
Si-O	1.662	1.602	1.595	1.592
Si-Si	2.942	3.042	3.063	3.067
Si-O-Si	130.1	143.5	147.5	148.8
O-Si-O	105.7	108.3	108.4	108.1

Table III. Comparison of Average Distances (Ångstrom) and Angles (Degrees) Calculated for a Few Zeolites with Different Ratios of n-Rings (nR)

	4R(%)	5R(%)	6R(%)	Distance	Angle
Faujasite(26)	70	0	30	1.61	142
Mordenite(22)	5	95	0	1.58	157
ZSM-5(20)	5	85	10	1.59	156

The results of these calculations are consistent with our earlier conclusions. As long as no 3-rings are present in the alumina-free material, differences in covalent energy are very small. The ab-initio calculations indicate that these differences do not exceed 1 kJ/mol.

Rigid Ion Lattice Energy Minimization Calculations. Table IV presents lattice energies derived from fully converged rigid ion lattice energy minimization calculations. Again one notices the small difference in energy between dense and open structures. The dependence on density (ρ) is presented in Figure 4.

The lower energy of the more open structures relates to the decrease in Madelung energy. However, as Figure 2 shows, local topological effects also play a role. See, for instance, the difference in energy calculated between zeolite A and faujasite.

Table IV. Calculated Rigid Ion Lattice Energies of Aluminum-Free Zeolite Lattices

Zeolite	Lattice Energy, kJ/mol
Faujasite	-11914
Mordenite	-11931
Zeolite A	-11931
Silicalite	-11945
Sodalite	-11949
α -Quartz	-11959

Discussion of Alumina-Free-Lattice Calculations. Two main conclusions emerge from the results presented so far. Firstly, the energy differences between tetrahedral networks with different ring systems are very small, except when the networks contain 3-rings not found in nature.

This is a very significant conclusion because it is widely believed (9) that, in order to synthesize systems with 5-rings, such as ZSM-5, the only requirement is to synthesize systems low in alumina. Both our quantum-chemical and our electrostatic lattice calculations contradict this theory. The calculations show, for example, that sodalite, which contains only 4- and 6-rings and no alumina, is more stable than ZSM-5, in which 5-rings predominate. This agrees with recent experimental work relating to the synthesis of high-silica sodalite (10).

Secondly, the decrease in lattice energy with increasing microporous volume reaches a maximum at 45 kJ/mol, the difference between α -quartz and faujasite, faujasite being the zeolite with the largest micropore volume.

Expressions 2 and 3 show that, in order to overcome this energy difference, the micropore cavities should be largely filled with adsorbed molecules. As mentioned earlier, in cases where low-alumina-content materials have been directly synthesized, high values for θ_i are invariably found. This confirms Barrer's postulation. The dominant interaction that governs narrow- and medium-pore zeolite synthesis is the strong interaction of the occluded organic molecule with the micropore wall.

Of interest with respect to this hypothesis is the significant difference in heat of paraffin adsorption between the medium-pore zeolite silicalite and large-pore, de-aluminated faujasite. The heat of paraffin adsorption is much smaller in the case of the de-aluminated faujasite, which has so far had to be prepared by an indirect route, than for silicalite, which can be synthesized direct in the presence of an organic molecule. The difference, which increases with chain length, is of the order of 5 kJ/mol per CH_2 unit, and may be ascribed to the optimum fit of hydrocarbon and channel in the case of the medium-pore zeolite (11, 12).

^{13}C solid-state NMR studies on occluded organic ions by ourselves (13) and others (14) have provided further evidence for the strong interactions between occluded organic molecule and micropore wall mentioned above. We have also reported lattice stabilization of silicalite (ZSM-5) by occlusion of tetrapropylammonium ions (15). It is therefore very unlikely that a synthesis procedure can be defined for the preparation of highly siliceous forms of large-pore (12-ring or larger) zeolites such as faujasite direct.

Variation of Zeolite Lattice Composition

The changes in heat of formation as a function of alumina content were studied via two different approaches.

One approach (4) is to calculate, for a certain zeolite structure, the Madelung and polarization energies for fixed lattice positions. The heat of formation due to ionic bonding is calculated both for the zeolitic aluminosilicate with varying amount of aluminum and

sodium ions and for the zeolitic silica, with the same framework distances as in the aluminum-containing material. The difference between the two heats of formation is assumed to represent the contribution of the total heat of formation due to ionic bonding stemming from the presence of aluminum ions and cations in a particular zeolite structure.

In these calculations averaged charges on the intra-tetrahedral lattice cation positions were used. The difference between the two heats of formation due to ionic bonding is added to the heat of formation due to covalent bonding resulting from the simple Extended Huckel Method for zeolitic silicas in order to arrive at the total heat of formation of the zeolite structure as a function of the amount of aluminum.

For the calculations we used the method and computer program described by Piken and Van Gool (16,17).

Adsorption of water into the pores of a zeolite structure may contribute considerably to the total heat of formation because of hydration of the cations present in the pores. Using empirical data on hydration with water we have estimated the magnitude of this effect (4).

The second approach involves the use of the rigid ion lattice energy minimization method discussed earlier. This technique proved especially useful for determining the stability of structures following calculation of their energy by the method discussed in the previous paragraph. The charges of aluminum and silicon were again averaged.

Results of Madelung and Potential Energy Calculations. Figure 5 gives the heat of formation due to ionic bonding for faujasite, mordenite and ZSM-5 in the presence and in the absence of Al^{3+} and Na^+ ions. Lattices with the same lattice constant are compared. SiO and AlO distances used are values extrapolated from low- and high-Al-content zeolite crystallographic data. The results for the total heat of formation computed in the way explained earlier are given in Figure 6. A decrease in the heat of formation with increasing aluminum content is observed. In the final step of the calculation the effect of hydration of the cations was taken into account. The results are presented in Figure 7.

Changing the aluminum content has a significant effect on the relative stability of zeolite structures with very different topology. While the heat of formation of the wide-pore zeolite is affected very little, the heats of formation of the medium-pore zeolites fall significantly.

Results of Lattice Energy Minimization Calculations. Relative lattice energies of faujasite, mordenite, silicalite and sodalite were compared. For the framework and cation positions of faujasite and sodalite the same data were used as before, from Hseu (18) and Olson (19), and Baerlocher (20) and Chao (21), respectively. For mordenite and sodalite the data of Meier (22) and Mortier (23) (on mordenite) and Baerlocher and Meier (24) (on sodalite) were used. The starting unit cells for faujasite and mordenite have the chemical composition $\text{Na}_x[\text{Al}_x\text{Si}_{48-x}\text{O}_{96}]$. For sodaite and ZSM-5 we used $\text{Si}_{12}\text{O}_{24}$ and $\text{Na}_x[\text{Al}_x\text{Si}_{96-x}\text{O}_{192}]$. The framework and cation positions were allowed to relax under constant pressure. Parameter values used and details of the calculation can be found in (25).

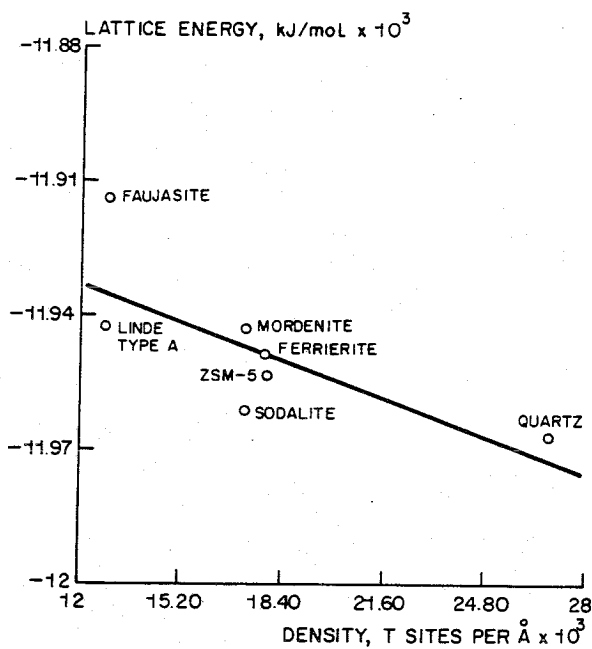


Figure 4. Lattice energy as a function of density.

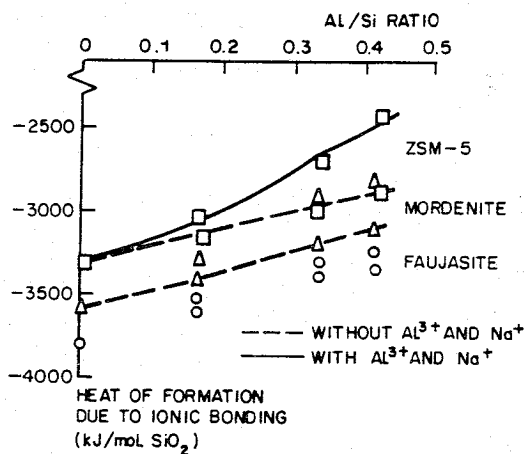


Figure 5. Influence of Al/Si ratio on heat of formation due to ionic bonding.

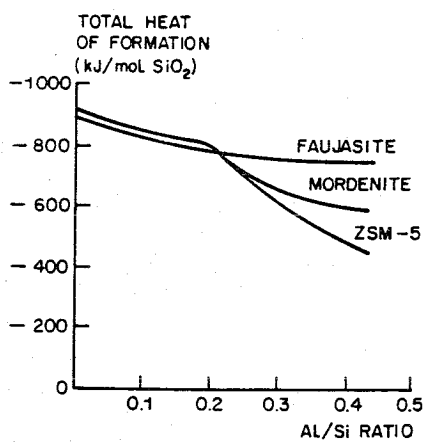


Figure 6. Total heat of formation as a function of Al/Si ratio without effect of hydration.

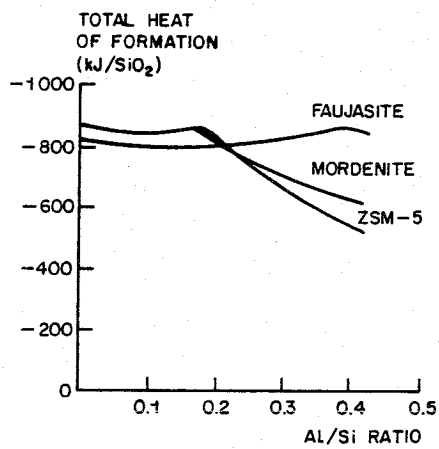


Figure 7. Total heat of formation as a function of Al/Si ratio with effect of hydration.

Figure 8A shows the computed lattice energies for faujasite and mordenite as a function of Al/Si ratio. These fully converged calculations agree very well with approximate calculations discussed earlier. At Al/Si ratios larger than 0.2 the lattice energy of mordenite starts to decrease compared to that of faujasite. Figure 8B shows computed lattice energies for ZSM-5 as a function of Al/Si ratio. Only the first two calculations are fully converged to an energy minimum. The calculations for Al/Si > 0.05 correspond to calculations where no energy minimization is performed.

It appears that convergence of the calculations is only possible for a finite range of Al/Si ratios. This is shown in Figure 9. The maximum Al/Si ratio at which calculations converge is 0.05 for ZSM-5, 0.5 for mordenite and 0.8 for faujasite. Also indicated in the figure are the maximum Al/Si ratios which can be obtained by direct synthesis.

Discussion of the Calculated Al/Si Dependence. Both approaches show very clearly the great changes that occur in relative energy upon variation of the Al/Si ratio. Whereas the electrostatic contribution to the total energy is very small for the Al-free material, it becomes significant for Al-containing materials. The greater sensitivity of the medium-pore zeolites than the wide-pore material to the increase in aluminum content has to be ascribed to the stacking of the cations in the channels of the zeolite. For instance, it is shown in Figure 10B that a ZSM-5-type structure cannot accommodate sodium cations at a Si/Al ratio of 1.4, because the cations become so close that strong repulsive interactions take place. In addition, such low Si/Al ratios result in unfavourable channel positions having to be occupied. As can be seen in Figure 10A, for a Si/Al ratio of 11 the sodium cations are much less clustered together, so that repulsion is far less.

Impact on Zeolite Synthesis Strategies

We have presented evidence that the interaction of molecules or ions occluded in the micropores between themselves and with the zeolite wall plays a decisive role in the thermodynamics of zeolite formation.

It has been shown that the alumina-free zeolites are hydrophobic and hence interact unfavorably with water. This renders them thermodynamically unstable in aqueous solution with respect to dense phases. Only when organic molecules are occluded does water penetration decrease and the favourable interaction of occluded molecules with the zeolitic silica micropore wall become dominant. This is a means whereby the alumina-free zeolites may become thermodynamically stable.

We have also discussed the fact that a good fit between the organic molecule and zeolite wall is required for such a favorable interaction. This implies that synthesis techniques employing organic molecules may be expected to yield aluminum-free zeolites with pore dimensions of the order of the dimensions of the organics used.

It follows from the calculations on the lattice energy as a function of Al/Si ratio that synthesis of new wide-pore zeolites would require a different strategy. We have found that increasing

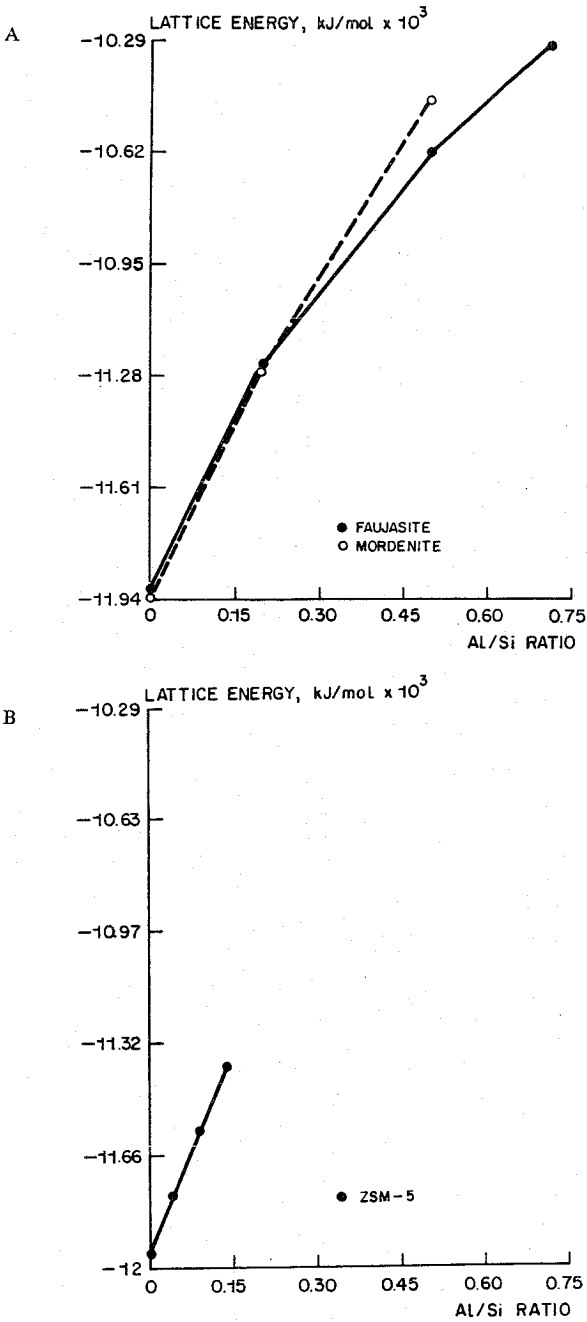


Figure 8. Lattice energy as a function of Al/Si.
 A: Faujasite and mordenite.
 B: ZSM-5.

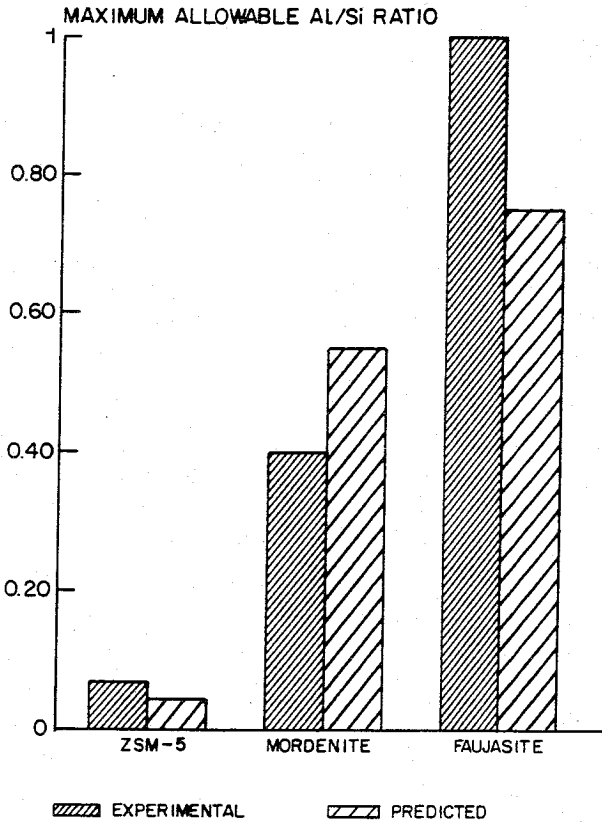
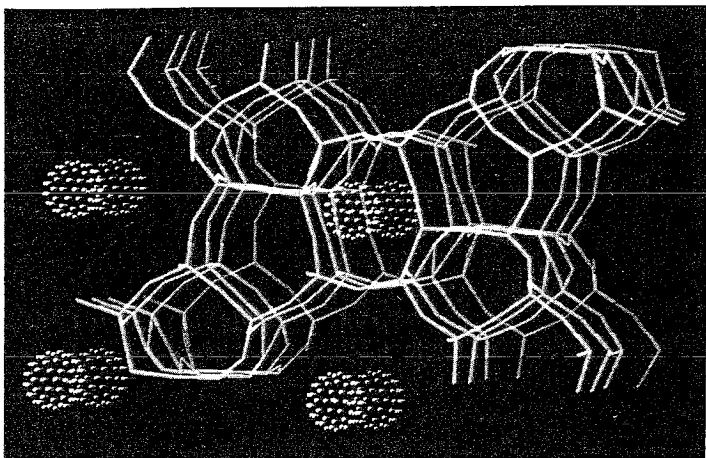


Figure 9. Experimental and predicted maximum allowable Al/Si ratios.

A



B

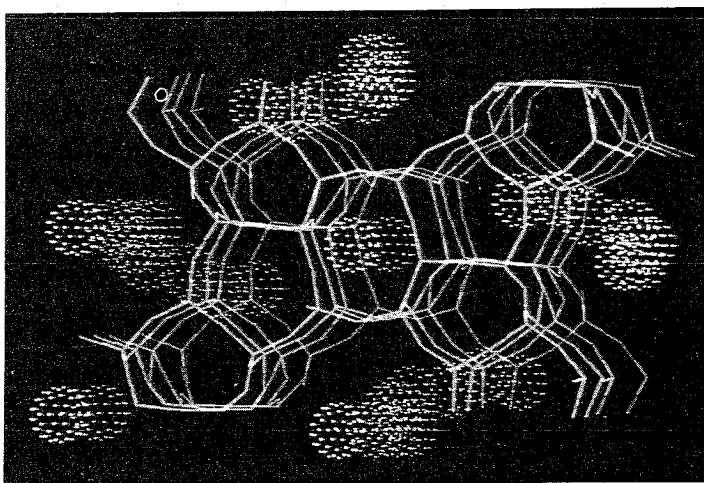


Figure 10. Sodium distribution in ZSM-5.

A: Si/Al = 11.

B: Si/Al = 1.4.

isomorphic substitution of cations of a lower valency for Si in the tetrahedral zeolite framework causes large-ring structures to stabilize with respect to dense structures. In small- to medium-pore zeolites, the cations which will have to be introduced in the micropore channels in order to compensate for the negative charge on the zeolite lattice and to maintain charge neutrality will interact with each unfavorably other if the concentration of low-valency cations in the lattice is high. In wide-pore zeolites the repulsion is less; moreover, more favorable channel positions may be available than in the more dense zeolites.

In the search for wide-pore zeolite synthesis conditions, therefore, efforts should be concentrated on the field where zeolites are produced with a large amount of isomorphous substitution.

Lattice energy calculations can assist in assessment of which cations are to be chosen in the zeolite lattice or channels in order to stabilize the structure.

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