Relative stabilities of zeolitic aluminosilicates

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The use of organic bases in zeolite synthesis has constituted a breakthrough, enabling new zeolites to be made with lattice Al/Si ratios much lower than those obtained in the absence of organic bases. Apart from the change in Al/Si ratio there is a change in lattice structure: whereas at high Al/Si ratios structures built from even rings dominate, at lower Al/Si ratios systems containing a significant fraction of five rings can be made. In this paper we address ourselves to the question as to whether there is indeed a relation between lattice topology and Al/Si ratio found in the zeolite.

Barrer demonstrated that for the stability of porous structures the presence of "guest" molecules in the "continuous" structure is essential. In a recent paper, we interpreted the difference in stability between ZSM-5 in the presence and ZSM-5 in the absence of "guest" molecules in the "continuous" structure as a function of Al/Si ratio in the presence or absence of adsorbed water. Na⁺ ions are taken as the charge-compensating ions. Two types of approaches were followed to study the changes in heat of formation as a function of alumina content. In one approach, for a certain zeolite structure the Madelung and polarization energies are calculated for fixed lattice positions. The heat of formation due to ionic bonding is calculated both for the zeolitic aluminosilicate with varying amounts of aluminum and sodium ions and for the zeolitic silica, with the same framework distances as in the aluminum-containing material. The heat of formation is assumed to represent the contribution to the total heat of formation due to bonding stemming from the presence of aluminum and cations in a particular zeolite structure. This difference is added to the heat of formation due to covalent bonding of the silica polymorph as calculated by the extended Hückel method. The effect of hydration on the relative stabilities is estimated by using empirical data on hydration with water. In the second approach rigid ion lattice energy minimization calculations were used, with potentials parametrized to fit α-quartz. This technique was particularly useful to determine the stability of the structures whose energy had been calculated by the method discussed earlier. The presence of aluminum ions and cations as well as hydration is found to have a considerably larger influence on the relative stabilities of zeolites than covalent contributions. The predictions for the order of stability of faujasite, mordenite, and ZSM-5 as a function of Al/Si ratio is in qualitative agreement with the results of synthesis experiments.

### Table I: Heat of Formation Due to Covalent Bonding for Some Dealuminated Zeolites, Calculated by Using the ASED Method

<table>
<thead>
<tr>
<th></th>
<th>heat of formation, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>faujasite</td>
<td>905</td>
</tr>
<tr>
<td>mordenite</td>
<td>925</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>925</td>
</tr>
<tr>
<td>α-quartz</td>
<td>896</td>
</tr>
<tr>
<td>α-quartz (expt)</td>
<td>910</td>
</tr>
</tbody>
</table>

are linked via six-membered rings (Figure 1). Apart from six-membered rings there are four-membered rings. Mordenite has a channel-like pore structure in which the basic building blocks consist of five-membered rings. A view of the mordenite structure perpendicular to the main channels is shown in Figure 2. ZSM-5 is a pentasil zeolite. It is also composed of five-membered rings and its structure is shown in Figure 3.

In an earlier paper we described a simple quantum-chemical calculation method to obtain an estimate of the relative stabilities of zeolitic silicas. When we applied the method to dealuminated faujasite, mordenite, and ZSM-5, we found faujasite to be less stable than mordenite and ZSM-5. The differences between the calculated heats of formation of the three zeolitic silicas proved to be very small. The results of these calculations are reproduced in Table I. The absolute values of the results are different from the values given in the original paper, as more recent values for the heat of vaporization of Si (450 kJ/mol) and for the dissociation energy of O₂ (498 kJ/mol) were used. As these are constant terms, only the absolute values changed, the differences remaining the same. Whereas faujasite is found to be less stable than mordenite and ZSM-5, the latter two structures are found to be more stable than α-quartz. The last results indicate that the method used is too crude to allow a reliable prediction of the differences in covalent energy between these structures. Indeed recent STO3G ab initio calculations on silicate rings indicate that the differences...
in covalent energies are smaller than those found with the extended Hückel method.

Rigid ion lattice energy minimization calculations\(^6\) predict α-quartz to be the most stable of the silica polymorphs and a difference of 40 kJ/mol between α-quartz and dealuminated faujasite.

We followed two types of approach to study the changes in heat of formation as a function of alumina content. In one approach, for a certain zeolite structure the Madelung and polarization energies and the heat of formation due to ionic bonding are calculated both for the zeolitic aluminosilicate with varying amounts of aluminum and for the zeolitic silica. The difference between the two results for the heat of formation is assumed to represent the contribution to the total heat of formation of the zeolite structure stemming from the presence of aluminum ions and cations in this structure. This difference is added to the heat of formation due to covalent bonding resulting from a simple quantum chemical calculation 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. This procedure leads to heats of formation at zero aluminum content which are correct to within 10 kJ/mol. The work is an extension of earlier calculations of electrostatic fields and potentials not including polarization by Dempsey\(^7\) and Preuss.\(^8\)

For the electrostatic calculations we used the method and computer program described by Piken and Van Gool\(^9\) and Van Gool and Piken.\(^10\) Formal ion charges were used. The values of the polarizabilities\(^11\) were as follows: \(\alpha_{\text{O}} = 1.984 \text{ Å}^3, \alpha_{\text{Si}^{4+}}\) = 0.0256 Å\(^3\), \(\alpha_{\text{Al}^{3+}} = 0.0448 \text{ Å}^3\), and \(\alpha_{\text{Na}^+} = 0.128 \text{ Å}^3\).

In the second approach we used lattice energy minimization calculations to study the lattice energy as a function of aluminum content. These techniques enable the calculation of the stability of structures corresponding to minimum lattice energies.\(^12\) This calculation may be done in two ways: either the atomic positions only are adjusted until the minimum is obtained (constant volume minimization) or, additionally, the unit parameters are adjusted to remove any remaining strains in the lattice (constant pressure minimization). In our calculations relaxation to constant pressure has been used. The technique requires the specification of a starting structure, which may be based on experimental data, if available, and a set of interatomic potentials. The following potential model is used, in which the interaction of a pair of ions \(i\) and \(j\) is described by

\[
V_{ij}(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6
\]

Here \(q_i\) and \(q_j\) are the ionic charges and \(A_{ij}, \rho_{ij}\), and \(C_{ij}\) the short-range potential parameters. In the calculations discussed here, ions were treated as rigid and assigned formal charges. In order to be able to simulate framework relaxation it is necessary to include an extra term in the potential to take account of the directionality of the bonding of the oxygen ions with silicon or aluminum ions. This term, which defined for each OSi or OAl bond, takes the form

\[
V_{\text{body}} = \frac{1}{2} k (\theta - \theta_0)^2
\]

where \(k\) and \(\theta_0\) are constants.

The same parameters are those used earlier by Jackson and Catlow\(^8\) and were employed. They are listed in Table II.

### Madelung and Polarization Energy Calculation

In the calculations, we started with an existing zeolite structure and used the cell constants and the coordinates of the Al\(^3+\)/Si\(^4+\) ions, O\(^2-\) ions, and Na\(^+\) ions as given in the literature. For faujasite we used the data of Hseu,\(^14\) for mordenite and the data of Meier\(^15\) and of Mortier et al.,\(^16\) and for ZSM-5 the data of Baerlocher\(^17\) and of Chao et al.\(^18\) The distribution of the Al\(^3+\) ions over the Al\(^3+\)/Si\(^4+\) locations is not well-known, although it is generally accepted that Löwden’s rule precluding two aluminum ions being near-neighbors is obeyed. In our calculation the Al\(^3+\) ions were smeared out over the possible Al\(^3+\)/Si\(^4+\) ion locations, so that at those locations a fractional charge was present dependent on the Al/Si ratio. This simplification is rather drastic, but necessary due to the lack of knowledge about the positions of the Al\(^3+\) ions and justified by the fact that we are interested in the difference in heat of formation due to ionic bonding of a zeolite structure.

![Figure 1. Structure of faujasite.](image1)

![Figure 2. Structure of mordenite.](image2)

![Figure 3. Structure of ZSM-5.](image3)

### Table II: Rigid Ion Parameters for Interatomic Potentials\(^13,14\)

<table>
<thead>
<tr>
<th>Interaction</th>
<th>(A_{ij}), eV</th>
<th>(\rho_{ij}), Å</th>
<th>(C_{ij}), eV Å(^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(^2-)/O(^2-)</td>
<td>22764</td>
<td>0.1490</td>
<td>27.88</td>
</tr>
<tr>
<td>Al(^3+)/O(^2-)</td>
<td>1460.30</td>
<td>0.2991</td>
<td>0.000</td>
</tr>
<tr>
<td>Si(^4+)/O(^2-)</td>
<td>1584.167</td>
<td>0.3296</td>
<td>52.64511</td>
</tr>
<tr>
<td>Na(^+)/O(^2-)</td>
<td>1226.84</td>
<td>0.3065</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Three-Body Potential

<table>
<thead>
<tr>
<th>Interaction</th>
<th>(k), eV rad(^{-2})</th>
<th>(\theta_0), rad</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-T-O</td>
<td>4.5815</td>
<td>1.911</td>
</tr>
</tbody>
</table>


\(^12\) Tessmann, J R.; Kahn, A. H.; Shockley, W. Phys. Rev. 1953, 89, 890.


\(^18\) Smith, J. V.; Hseu, T. Ph.D Thesis, University of Washington, 1972; University Microfilms, no. 73-13835, Ann Arbor, MI.


\(^22\) Chao, K. J.; Lin, L. C.; Wang, Y.; Lee, G. H. Zeolites 1986, 6, 35.
and its dealuminated version. Using Van Gool's computer program we calculated the Madelung energy and the polarization energy of the zeolite structure. Next we subtracted the ionization energies, the heat of vaporization of Al, Si, and Na, and the dissociation energy of $O_2$, and found the cohesive energy with respect to the elements, called heat of formation due to ionic bonding of the structure. The calculation was repeated, but with the $Al^{3+}$ ions and $Na^+$ ions removed from the structure. The difference between the two results for the heat of formation due to ionic bonding was assumed to represent the contribution to the heat of formation due to the presence of aluminum and sodium ions in the structure. The total heat of formation of the structure was finally found by adding this contribution to the heat of formation due to covalent bonding resulting from the quantum chemical ASED method applied to the dealuminated structure.

In the last step of the calculation procedure the influence of hydration on the total heat of formation due to ionic bonding will be presented. The relative lattice energies of faujasite, mordenite, and ZSM-5 were compared at varying Al/Si ratios. These calculations were performed with an average charge corresponding to the Al/Si ratio. For the framework and cation positions the same data were used as earlier. The framework and cation positions were allowed to relax under constant pressure. Figure 8 shows the computed lattice energies for faujasite and mordenite as a function of Al/Si ratio. These detailed lattice energy calculations agree rather well with the approximate calculations discussed earlier. At Al/Si ratios larger than 0.2 the lattice energy of mordenite starts to decrease when compared to that of faujasite.

It appears that convergence of the calculations is only possible for a finite range of Al/Si ratios. This is shown in Figure 9. Calculations on ZSM-5 do not converge for Al/Si ratios larger than 0.1, mordenite 0.5, and faujasite 0.8. Also indicated in the figure are the maximum values of the Al/Si ratios for which those structures can directly be synthesized. The correspondence is quite reasonable.
with the results of synthesis experiments.

Appendix

Method for Calculating the Hydration Energy. In our calculations we have limited ourselves to the case that the cations present inside the channels and cages of zeolites are Na⁺ ions. The locations and number of Na⁺ ions in a unit cell of faujasite, mordenite, and ZSM-5 are given in Mortier’s review. The hydration of such cations gives a contribution to the total heat of formation of the zeolites. A simple method has been developed to calculate this contribution.

First the volume of a unit cell of faujasite, mordenite, or ZSM-5 was calculated. Knowing the porosity of these zeolites we determined their pore volume per unit cell and from this we calculated the maximum number of water molecules present in a unit cell. The result is as follows: for faujasite 236 water molecules, for mordenite 25, and for ZSM-5 60. For faujasite and mordenite these numbers are in very good agreement with the experimental data as given in Mortier’s review paper; there are no data about the possible water content of ZSM-5. Next we calculated for faujasite and mordenite the value of the ratio of the maximum number of water molecules to the maximum number of Na⁺ ions in a unit cell; this value is for both zeolites very close to 3. Therefore we assumed that each Na⁺ ion can hydrate three water molecules; if more water molecules per Na⁺ ions are present no further contribution to the heat of formation occurs. So for faujasite (Na₉Al₅Si₁₈O₄₆)·240H₂O there is a continuously growing contribution to the heat of formation, if x runs from 0 to 80; after that the contribution is constant. For mordenite (Na₆Al₄Si₈O₃₆)·24H₂O there is an increasing contribution from x = 0 to x = 8; for ZSM-5 (Na₆Al₄Si₈O₃₆)·60H₂O there is a contribution from x = 0 to x = 20. As the hydration energy is equal to about 420 kJ/mol of Na, we find that for faujasite it is given by (x/192) × 420 kJ/mol of SiO₂, for mordenite by (x/48) × 420 kJ/mol of SiO₂, and for ZSM-5 by (x/96) × 420 kJ/mol of SiO₂, in which x/192, x/48, and x/96 are the Al/Si ratios for the three zeolites.

A second, negative, contribution to the heat of formation due to hydration comes from the heat of evaporation of water, when during the synthesis stage it goes out of the solution and into the zeolite structure. As the heat of evaporation is about 42 kJ/mol of H₂O, we find that for faujasite it is (240/192)×24 = 25.5 kJ/mol of SiO₂, for mordenite (24/48)×42 = 21.25 kJ/mol of SiO₂, and for ZSM-5 (60/96)×42 = 26.25 kJ/mol of SiO₂.

In conclusion the net hydration energy is given by the following relations:

faujasite

\[ U_{hydr} = -52.5 \frac{x}{192} \times 420 \quad \text{for } 0 \leq x \leq 80 \] (1)

\[ U_{hydr} = 122.5 \frac{x}{48} \times 420 \quad \text{for } x > 80 \] (2)

mordenite

\[ U_{hydr} = -21 \frac{x}{48} \times 420 \quad \text{for } 0 \leq x \leq 8 \] (3)

\[ U_{hydr} = 49 \frac{x}{96} \times 420 \quad \text{for } x > 8 \] (4)

ZSM-5

\[ U_{hydr} = -26.25 \frac{x}{96} \times 420 \quad \text{for } 0 \leq x \leq 20 \] (5)

\[ U_{hydr} = 61.25 \frac{x}{96} \times 420 \quad \text{for } x > 20 \] (6)