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The Role of Interfacial Energy in Zeolite Synthesis

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The thermodynamic factors playing a role in the synthesis of
silicon-rich zeolites are discussed. The Ostwald ripening
model for nucleation, as well as Ostwald's law of successive
transformations make it possible to describe kinetic phenomena
in terms of the relative stability of intermediate phases.
Theoretical and experimental evidence is presented to show
that the contribution of the interfacial free energy between
the large internal surface area in the micropores and the
intracrystalline liquor, to the chemical potential of the
zeolitic material, plays a crucial role.
A model for the elementary steps occurring in pentasil zeolite
formation is proposed.

INTRODUCTION

The presence or absence of particular cations in the zeolite micropore may in-
fluence the course of zeolite formation significantly. This has been most dramati-
cally demonstrated by the use of organic cations in the synthesis of silicon-rich
zeolites. Subtle changes in the structure of the cation can determine the zeolite
species formed. This led Flanigan [1] to suggest a template action on the part of
the organic cation. Changes occurring in the solution chemistry of silicates
support this hypothesis [2]. Organic bases have been found to strongly favour the
formation of particular double-ring silicate anions [3]. Ring opening and polymeri-
zation of such anions will result in silicon-rich zeolites. It will be shown that
this zeolite-formation mechanism makes it possible to predict the occurrence of
intracrystalline defects as found experimentally in ZSM-5 [4].

We will here consider the question whether such crystallization phenomena are
also affected by thermodynamic factors. Clearly, the stabilization of double-ring
silicate anions by organic bases occurs because it is favoured by energetics. The
alkylammonium - double-ring silicate salts are well known [3]. It follows from
elementary electrostatic considerations that lattices of large, negatively charged
anions are most stable if the anions are compensated by large, positively charged
cations.

Tetrapropylammonium ions occluded in ZSM-5 occupy well defined positions [4,5].
It has been suggested by Barrer [6] that they stabilize the zeolite lattice. Indeed
the chemical potential of the zeolite material in contact with its mother liquor
will contain a component attributable to the interfacial free energy between the
large internal surface area in the micropores of the solid and the intracrystalline
liquid. Such a term can be ignored for non-microporous systems with large particles,
since in these systems the number of atoms at the interface is several orders of
magnitude smaller than in the presence of an internal surface.

The presence of cations in the micropores, owing to their hydration energy,
reduces the energy required for the formation of the internal surface. Thus, for
instance, in water a high aluminium content of the zeolite framework will reduce

the interfacial energy contribution, stabilize the zeolite framework and hence favour crystallization.

In silicon-rich ZSM-5 one finds that the amount of organic ions incorporated is essentially independent of the alumina content and is such that a large proportion of the channel intersections are occupied. The unfavourable lyophilic-lyophobic interaction of water molecules and silica lattice is now replaced by the more favourable interaction of the organic cation with the silica lattice. Stabilization of zeolite phases will affect the kinetics of crystallization of zeolite phases will affect the kinetics of crystallization in two ways. If nucleation is rate limiting, the Ostwald ripening model predicts increased crystallization rates with increasing stability of the crystallization material. Secondly, Ostwald's transformation rule predicts that first the least stable material crystallizes and finally the most stable one.

We will present crystallization curves of ZSM-5 in the presence and absence of tetrapropylammonium ions, which demonstrate the importance of stabilization of the zeolite micropore lattice by organic cations.

It appears that the relative stability of the same zeolite lattices depends strongly on the alumina content. This agrees with a postulate of Mortier [7] predicting that five-rings are more stable for silicon-containing lattices than six-rings, but that the reverse holds for alumina-containing rings.

Semi-empirical quantumchemical calculations using Anderson's Atom Superposition and Electron Delocalization-Molecular Orbital (ASED-MO) method [8] adapted to the three-dimensional solid state [9] are used to calculate the relative stability of aluminium-free-faujasite, mordenite and ZSM-5. Initial results of three-dimensional electrostatic lattice energy calculations, including polarization effects, using a method developed by van Gool [10], will be presented, demonstrating that the order of the lattice energy of the zeolites mentioned above depends on their aluminium content.

ZEOLITE SYNTHESIS EXPERIMENTS

The ZSM-5 crystallization experiments were carried out at 190 °C in Teflon-lined autoclaves using the following molar composition:

40 SiO_2, 2.5 Na_2O, 1 Al_2O_3, 2.5 B, 1000 H_2O

In the organic-free crystallization B was Na_2O, whereas for the crystallization in the presence of tetrapropylammonium hydroxide (TPAOH), B was TPA_2O. After hydrothermal treatment the products were separated by filtration, washed with water and dried at 120 °C. The products were characterized by quantitative X-ray diffraction and elemental analysis (see Table 1).

Table 1. Elemental analysis of products from ZSM-5 crystallization experiments at 190 °C

	%w	Si	Al	Na	C	H	N
2.5 B = 2.5 Na_2O		39.2	1.6	2.7	<0.2	1.0	<0.3
2.5 B = 2.5 TPA_2O		38.2	1.4	0.7	7.1	1.6	0.7

The kinetic results are presented in Figures 1a and b. In the absence of TPA, ZSM-5 is formed, following by transformation to mordenite, quartz and analcime. In the presence of TPA a considerably faster crystallization to ZSM-5 takes place without successive transformations.

If ZSM-5 is crystallized in the presence of TPA using quartz as the silica source, it is found that up to 30 % of the quartz is converted into TPA-ZSM-5, which may indicate that the stability of ZSM-5 containing the occluded TPA cation is comparable to that of α-quartz.
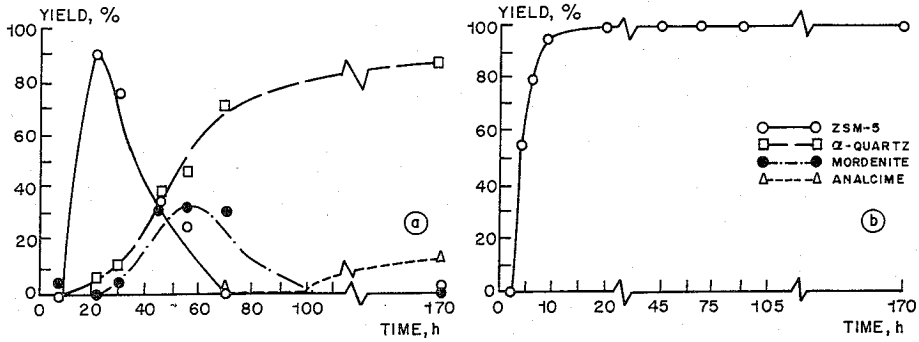
Fig. 1. ZSM-5 crystallization experiments
(a) "Organic-free" synthesis. (b) Synthesis in the presence of tetra-
propylammonium

   In the absence of TPA no ZSM-5 is formed with lattice Si/Al ratios smaller than
11. Mordenite is only formed with lattice Si/Al ratios between 5.0 and 10.
   If one applies Ostwald's law of successive transformations [11] to Figure 1a, one
concludes that mordenite plus quartz is more stable than ZSM-5 if no TPA ions are
occluded in ZSM-5. The data have to be interpreted with care since the aluminium
content of the mordenite phase is about twice as large as that found in the ZSM-5
phase. Two conclusions are possible: the mordenite (Si/Al = 10) phase itself is
more stable than ZSM-5 (Si/Al = 25), or quartz formation provides the driving force
for the conversion of ZSM-5.
   The presence of organic ions in the zeolite channels stabilizes the ZSM-5
lattice, explaining the increased nucleation rate of ZSM-5 and suppression of mor-
denite formation.

THEORETICAL CALCULATIONS
   The results of semi-empirical quantumchemical calculations using a version of
ASED-MO [8] method adapted to three dimensions are collected in Table 2. Details
of the calculation are presented elsewhere [9]. Since the ASED-MO method is based
on the Extended Hückel method, the calculations only account for covalent effects.

Table 2. Cohesive energies (U_c) calculated with the ASED-MO method[a]

Structure	U_c (kJ/mol)
Faujasite [13]	1819.4
Mordenite [14]	1858.9
Silicalite [5c]	1871.5

a. The references give the source of crystallographic data

Applied to α-quartz, the theory predicts a cohesive energy of 1845.9 kJ/mol, whereas
its experimental value is 2078.2 kJ/mol [23]. Table 2 lists calculated heats of
formation of aluminium-free faujasite, mordenite and ZSM-5 (silicalite). These

structures have been chosen because faujasite contains systems with even-numbered rings of tetrahedra, whereas mordenite and silicalite are lattices containing both even-numbered and uneven-numbered rings of tetrahedra. It is clear that the uneven-numbered ring systems are more stable than dealuminated faujasite. Silicalite is the most stable. The differences in the calculated cohesive energy are very small compared with the absolute value of the cohesive energy.

The calculated order of the stability can easily be understood. On average, faujasite has the largest Si-O bond length and the smallest bond angle φ in the Si-O-Si unit, mordenite has intermediate values and in silicalite the average Si-O distance is smallest. These trends are explained by the changing hybridization of the 2 s and 2 p orbitals on the oxygen atom as a function of bond angle φ. With decreasing bond angle φ the contribution of the oxygen 2 s-orbital to the Si-O bond strength decreases and hence the bond energy [9,12].

Initial results of electrostatic calculations, including polarization effects based on the method of van Gool [10], have been obtained for Si/Al = ∞ and Si/Al = 6. Substitution of Si^{4+} by Al^{3+} reduces the heat of formation of faujasite by 71.4 kJ/mol and that of mordenite by 117.6 kJ/mol. Now Al-containing faujasite becomes more stable than Al-containing mordenite, for which we found an energy difference of 42 kJ/mol.

Interestingly, the heat of formation of the Al-containing lattices is less than that of the Al-free lattices; nevertheless, in H_2O and in the absence of organic ions the Al-rich lattices are found to crystallize. This is readily understood when one considers the additional contribution to the free energies of the zeolites upon cation hydration. The free energies of alkali hydration in zeolites are only slightly less than in water [15], so adsorption of H_2O in the zeolite will be strongly exothermic because of hydration of the alkali ions. In Al-free material H_2O will only be physisorbed, explaining the driving force for the crystallization of high-Al-content zeolites from aqueous solutions.

ELEMENTARY STEPS IN PENTASIL ZEOLITE FORMATION

In a ZSM-5 forming solution, both at room temperature and at 100 °C double four-ring (D4R) and double five-ring (D5R) silicate anions are present [2b]. One finds a D4R/D5R ratio of 2.6 at room temperature. At higher temperatures partial hydrolysis occurs, but the relative amount of D5R increases.

The formation of ZSM-5 and ZSM-11 frameworks can be rationalized starting from D5R and monomer silicate and/or aluminate anions. There are several observations compatible with the idea of a D5R acting as a precursor for ZSM-5 formation. Nearly all reported ZSM-5 syntheses have been performed starting from solutions with an OH^-/Si ratio lower than 0.5. At such low OH^-/Si ratios significant amounts of D5R are formed [2b]. Furthermore, Mostowicz and Sand [16] have reported that, at constant TPA/Si ratio, the induction period becomes shorter and crystallization becomes faster with decreasing OH^-/Si ratio, consistent with our observation of increased amounts of D5R silicates [2b]. Romannikov et al. [17] have shown that in cases where besides ZSM-5, some analcime or mordenite can be formed, the selectivity towards ZSM-5 is determined by the OH^-/Si ratio.

As illustrated in Figure 2, a ZSM-5 structure built exclusively from D5Rs, would result in a lattice containing 2 empty tetrahedral positions (e.g. silanol nests) per D5R or 16 empty tetrahedra per idealized ZSM-5 unit cell: $Si_{96}O_{192}$.

The occurrence of intracrystalline defects in ZSM-5 is consistent with several experimental observations: the Al-independent cation exchange capacity found by Chester [18], the occlusion of 4 NaOH per ZSM-5 unit cell as proposed by Fegan [19], the presence of Q_3 type Si-sites as observed with ^{29}Si solid-state NMR [4,20], the 3720 cm^{-1} internal silanol frequency [21,24] and the realumination of silicalite with $AlCl_3$ [22].

Evidence for the existence of empty tetrahedral sites in the ZSM-5 framework is also found from the data of a series of ZSM-5 samples reported by Romannikov [17]. As shown in Figure 3, (Si+Al)/TPA ratios considerably smaller than 24 are found for ZSM-5 samples with low Al-contents, indicating the presence of Si-vacancies.

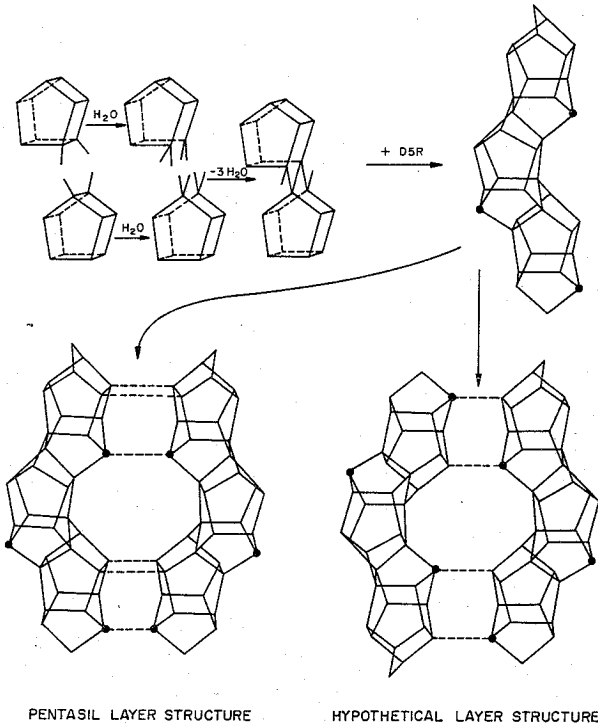PENTASIL LAYER STRUCTURE   HYPOTHETICAL LAYER STRUCTURE

Fig. 2. Formation of ZSM-5 via ring opening and polymerization of double 5-ring silicate anions.
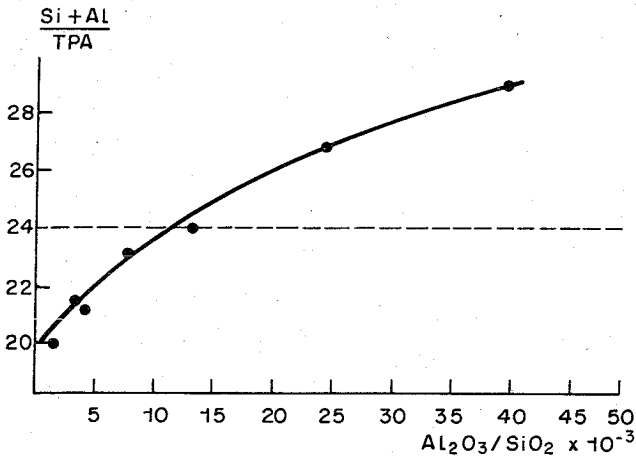. = isolated tetrahedral site

Fig. 3. TPA content of ZSM-5 samples as a function of the lattice Al-contents.
(Data taken from ref. 17)

Since the resulting silanol nests are hydrophilic, their presence will have a favourable interaction with occluded water and positively charged alkylammonium ions, which will reduce the interfacial energy.

CONCLUSIONS

The direct synthesis of silica-rich zeolites requires stabilization of the hydrophobic zeolite lattice. Organic cations occluded in the micropores of the zeolite perform this function in two ways: exclusion of water molecules from the micropores and adsorption of the organic ions to the oxygen atoms on the walls of the micropores built from silicon-oxygen tetrahedra. The latter explains the subtle structure-directing effects sometimes observed. In addition, the organic base molecules stabilize double-ring silicate anions in the solution that form the pentasil lattice by ring opening-polymerization reaction.

The relative stability of the zeolite framework is a sensitive function of its aluminium content.

Calculations show that Al-free ZSM-5 is more stable than Al-free mordenite and that Al-free faujasite is the least stable. Initial calculations for Al-rich systems show that for Si/Al ratios of 6/1 faujasite becomes more stable than mordenite. These results neatly illustrate the importance of the micropore interface. In the absence of water, Al-rich systems are less stable than Al-free systems. So, only hydration of the micropore cations by water, as occurs during the synthesis from water solutions, makes their crystallization energetically possible.

ACKNOWLEDGMENT

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