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STUDIES ON THE MECHANISM OF ZSM-5 FORMATION

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The nucleation of (Al-free) zeolite precursor gels was studied using X-ray diffraction, ^{29}Si FT-NMR, and ion exchange. Results suggest that in ZSM-5 nucleation, the channel intersections are first formed. These clathrate-like units, each containing essentially one TPA^+ cation, are initially randomly connected, but progressively "anneal" with rearrangement under the influence of OH^- ions to form the ZSM-5 framework.

Keywords: Nucleation of zeolite precursor, ZSM-5 nucleation by ^{29}Si NMR

1. Introduction

The crystallization of zeolites is generally believed to occur by one of two mechanisms: nucleation from solution, or nucleation from precursor gels. Proponents of solution nucleation [1–3] regard the gel phase simply as a source of nutrient, dissolving to provide the complex ions from which the crystal nuclei are formed. The structure of these complex ions are believed by some workers to resemble the secondary building units (SBU's) of Meier [4]. In gel nucleation, originally proposed by Flanigen and Breck [5], nuclei form directly in the solid gel phase, and crystallization proceeds through depolymerization and rearrangement of the gel network, mediated by OH^- ions. Barrer [6] has argued that while nucleation may occur in a gel, the higher density of the resultant crystal phase would cause the appearance of gaps due to shrinkage. In order to nourish the growing crystal, dissolution of the gel is necessary, and a solution ion transport mechanism would obtain. On the other hand the Flanigen-Breck mechanism permits the nutrient to be replenished through surface diffusion. Flanigen [7] later modified this view with the proposal that nucleation of low silica zeolites may be dominated by solution chemistry, while high silica zeolites such as the pentasils nucleate in the gel. For highly siliceous zeolites, an organic templating agent, such as a quaternary ammonium compound, is ordinarily required for crystallization. The template is presumed to exert a structure-directing role via H-bond interactions with the silicate framework. Flanigen's proposal was disputed by Derouane

et al. [8] who presented evidence that ZSM-5 could be grown either from solution or gel depending on the nature of the reactants and their method of preparation.

Experimental studies of zeolite crystallization have generally followed two approaches: kinetic studies, and speciation of precursors. It is well established that zeolite crystallizations are characterized by an initial induction period, during which it is presumed a critical concentration of nuclei is established [6]. This is followed by a period of rapid crystal growth, which gradually slackens with depletion of nutrient. At this stage, Oswald ripening may set in. Such observations, however, provide little information on the detailed chemistry of the nucleation process.

Characterization of zeolite precursors has focused mainly on the solution phase. The composition of silicate, and to a lesser extent aluminosilicate, solutions has been extensively investigated. There now exists a wealth of information on the structure, distribution and equilibria of complex ions in these solutions. The most detailed information available has been acquired through pulse FT-NMR techniques. This has been reviewed by Engelhardt et al. [9] and Bell [10]. Despite the extensive literature, a direct link between solution chemistry and the mechanism of zeolite formation has yet to be established. Persuasive arguments against the "SBU theory" were recently presented by Knight [11].

Much less is known about the precursor gels. A variety of techniques have been used to study the gel phase. These include X-ray and electron diffraction, and electron microscopy [12], Raman spectroscopy [13,14], and phosphorescence spectroscopy (with Fe^{3+} as tracer) [13]. These studies provided information on bulk properties such as phase composition, states of aggregation, and morphology. Gel transformation during crystallization of mordenite, ZSM-5, and faujasite has been observed using ^{27}Al and/or ^{29}Si NMR [9,15]. The crystallization of ZSM-5 has recently been studied by small-angle neutron scattering (SANS) [16]. With few exceptions [15] gel studies have been conducted on desiccated material. Drying may alter gel structure by promoting irreversible crosslinking (vide infra).

The present work is an exploratory study of high silica ZSM-5 crystallization in the presence of organic templates. Gel ion exchange properties were determined at various stages of crystallization. The wet gels were also examined by ^{29}Si Magic Angle Spinning NMR (MASNMR).

2. Experimental

Gel preparation and crystallization

Gel mixtures used in this study had the following composition:

$OH^-/SiO_2 = 0.1$

$H_2O/SiO_2 = 37–44$

$Na^+/SiO_2 = 0.6$

$R^+/SiO_2 = 0.1$;

R^+ = tetrapropylammonium (TPA^+), tetra ethylammonium (TEA^+), or tetra methylammonium (TMA^+).

Gels were prepared using two sources of silica: N-Clear (PQ Corp., 28.8% SiO_2, 8.9% Na_2O, 62.3% H_2O) and silicic acid, 99.9 + % (Aldrich). The following are typical preparations.

GEL I

TPABr (16.0 g) and 96% H_2SO_4 (15.4 g) were dissolved in 200 ml deionized water. This was added rapidly to N-Clear (125.6 g) diluted with 200 ml deionized water.

GEL II

Silicic acid (Aldrich) was dissolved in a solution of TPAOH (or TEAOH or TMAOH) and NaOH. H_2SO_4 (10%) was added to bring the OH^-/SiO_2 to the desired range.

The resultant mixtures were well-stirred, placed in polypropylene bottles with screw caps, and heated in a steam chest at 90–95 °C. Samples were periodically withdrawn and centrifuged, or filtered. A portion of each sample was dried at 100 °C and checked for crystallinity by X-ray diffraction (XRD). Elemental analyses were performed on the solid and liquid fractions. Typical solids analysis showed $SiO_2/Al_2O_3 > 2500$, while the liquid analyzed less than 500 ppm Si due to the low OH^-/SiO_2 utilized. Samples of the wet gel were examined by ^{29}Si MASNMR, and also subject to $[Pt(NH_3)_4]^{2+}$ exchange.

Ion exchange

The wet gel was washed with deionized water until free of sulfate, dispersed in aqueous 0.015 M $Pt(NH_3)_4Cl_2$ (1 g/50 ml), and gently stirred for 20 h at room temperature. In determinations of $[Pt(NH_3)_4]^{2+}/Na^+$ isotherms, the solution ionic strength was maintained constant by addition of NaCl. The ion exchanged gel was filtered, washed with deionized water until free of chloride, and dried in vacuo at room temperature overnight. Exchanged and unexchanged samples were analyzed for elemental composition.

X-ray diffraction

X-ray powder patterns were obtained on a Rigaku diffractometer with monochromatic Cu Kα radiation. Samples were step-scanned from 2.0 to 35.0 degrees 2θ, with 0.02 degree steps and 1.0 second counts.

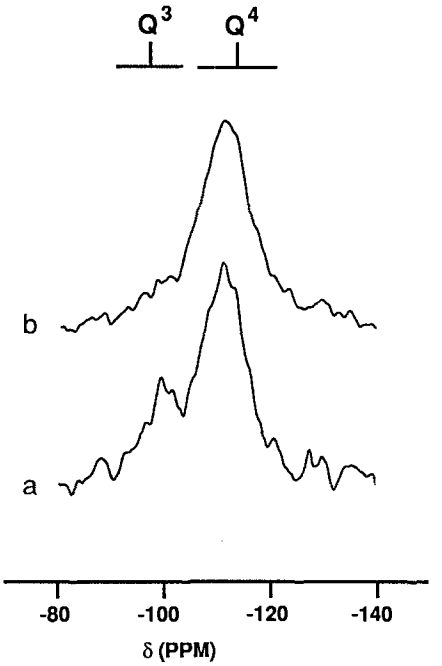

Fig. 1. Effect of drying on ^{29}Si NMR signal of gel: a) wet gel, b) same sample after drying at 120 °C, 16 hr.

NMR measurements

^{29}Si NMR spectra were recorded on a Nalorac NCC400 spectrometer equipped with a Doty MAS probe at a resonance frequency of 79.3 MHz. Samples were spun at ~ 2 kHz in sealed zirconia rotors described by Ginter et al. [17]. Spectra were obtained at room temperature using a single pulse excitation and 90° flip angle. Gel spin-lattice relaxation was not investigated in this work. Relaxation time was estimated by varying the recycle delay between 10 and 40 s and observing the increase in S/N. Based on these experiments a 20 s pulse delay was selected for the study. A total of 3600–4000 transients was collected on each sample. Line broadening of 100 Hz (50 Hz for highly crystalline samples) was applied prior to Fourier transformation. Fig. 1 shows the effect of drying overnight at 120 °C on the ^{29}Si MASNMR spectrum of a typical gel sample. Complete loss of the Q^3 component is seen.

3. Results and discussion

Typical GEL I XRD data are shown in fig. 2. It is seen that X-ray crystallinity is detectable after 2 days, about 70% crystallinity is attained in a week, and full crystallinity in 2 weeks. By comparison, GEL II samples (not shown) remained

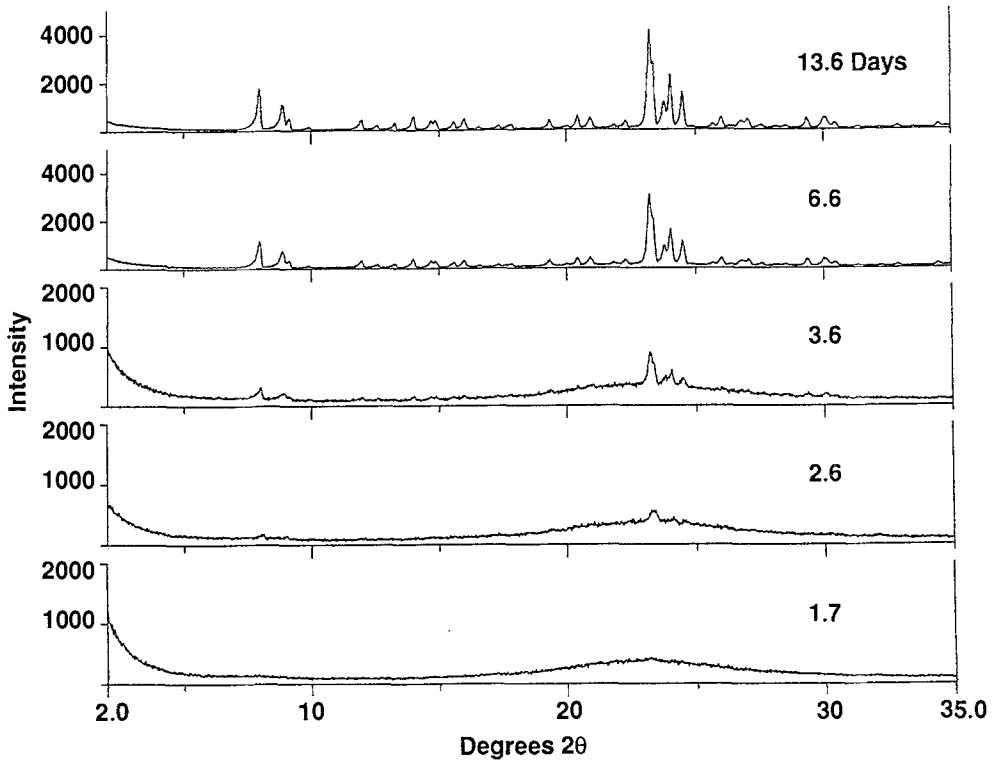

Fig. 2. X-ray diffraction patterns of ZSM-5 gels (GEL I) during crystallization at 90 °C.

X-ray amorphous after 1 week at the same temperature, indicating that N-Clear is a more reactive form of silica.

^{29}Si MASNMR spectra of the GEL I series appear in fig. 3. Spectrum A was obtained from the gel before heating, while the rest correspond to the XRD patterns in fig. 2. On account of the high viscosity and amorphous nature of these gels, their ^{29}Si spectra are dominated by broad, overlapping lines. The spectra exhibit two broad features associated with Q^3 [−95 to −104 ppm] and Q^4 [−104 to ca. −115 ppm] Si connectivities [9]. Peaks in the Q^3 region are due to silanol groups, or framework defects, while those in the Q^4 are attributed to Si connected to 4 T-atoms through O-atoms. Therefore the ratio of intensities of Q^3/Q^4 provides an indication of the progress of gel transformation. This is plotted in fig. 4, along with XRD crystallinity. It can be seen that the Q^3/Q^4 ratio decreases very rapidly compared to the crystallization rate, with the greatest change occurring during the induction period and the early stages of crystallization. Changes in the chemical shift of the centroid of the Q^4 feature are shown in fig. 5, also with the XRD crystallinity. An upfield shift is seen, occurring again in the early stages, levelling off with the onset of crystal formation. The upfield shift reflects increased shielding of the Si nucleus due to decrease in Si–O bond lengths and increase in Si–O–Si bond angles [9], which are consistent with increasing

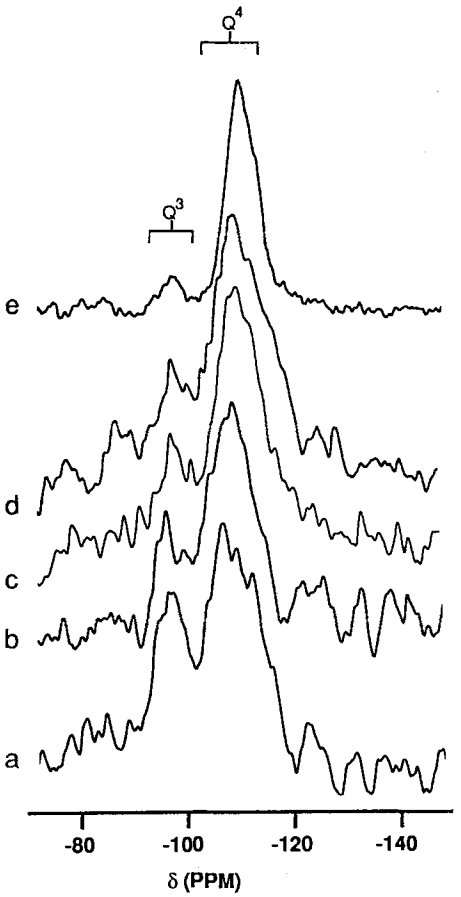

Fig. 3. ^{29}Si MASNMR spectra of ZSM-5 gels (GEL I) during crystallization at 90 °C: a) unheated gel, b) gel heated 0.6 days, c) 1.7 days, d) 2.6 days, e) 13.6 days.

crystallinity. In summary, ^{29}Si MASNMR results suggest that the major changes in gel structure occur during the early stages of reaction.

Fegan and Lowe [18], in a study of high silica ZSM-5 crystallization, examined the effect of base content of the reaction mixture on the base content of the final product, and found a linear dependence. This was attributed to base occlusion, where the cations are associated either with occluded OH^- ions or broken siloxane bonds (=Si–O^-HO–Si=), i.e. Q^3 defect sites, in the zeolite channel. Fegan and Lowe suggested that such materials should be ion exchangers despite the absence of Al. This was confirmed by Chester et al. [19] by ion exchange with $[Pt(NH_3)_4]^{2+}$, a cation which is selectively exchanged into ZSM-5 [20,21]. Silica gels are known to possess high affinity for polyvalent metal ions [22]. It seemed reasonable to assume that $[Pt(NH_3)_4]^{2+}$ exchange into ZSM-5 precursor gels might yield useful structural information, particularly since its size (commensurate with ZSM-5 pores) will subject it to ion sieve effects.

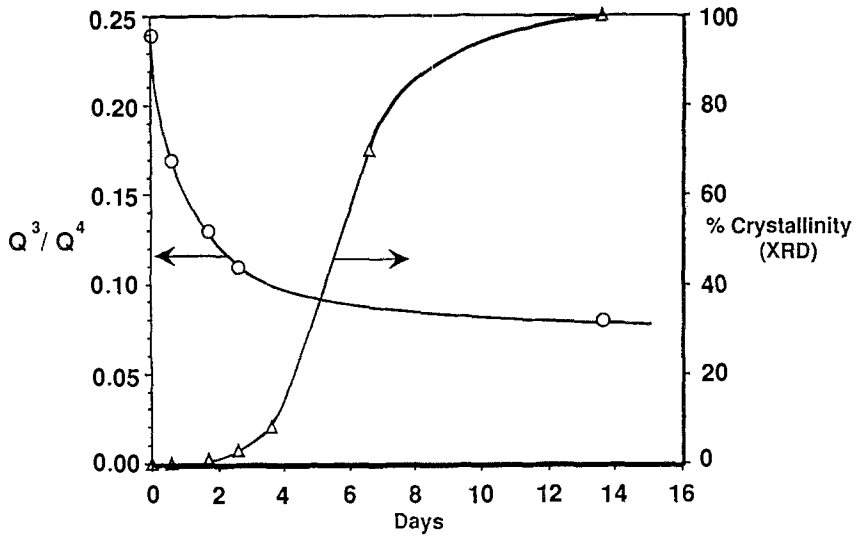

Fig. 4. GEL I variation of Q^3/Q^4 with X-ray crystallinity.

Ion exchange experiments were performed on both the GEL I and II series, the latter to obtain more information on the prenucleation period and to examine gels made with templates other than TPA^+. Ion exchange results are summarized in fig. 6. Here ion exchange capacity, expressed as moles Si per cation equivalent (exchangeable ions + unexchanged R^+) is plotted against time. The lower dotted line in fig. 6 represents the starting composition (Si/OH = 10). It is seen that the Si/equivalent ratio of both TPA^+ gels approaches a value of 20–24 very rapidly. The TEA^+ gel appears similar to the TPA^+, except that its Si/equivalent value is somewhat higher near the end. The TMA^+ gel attains a ratio of about 40, while

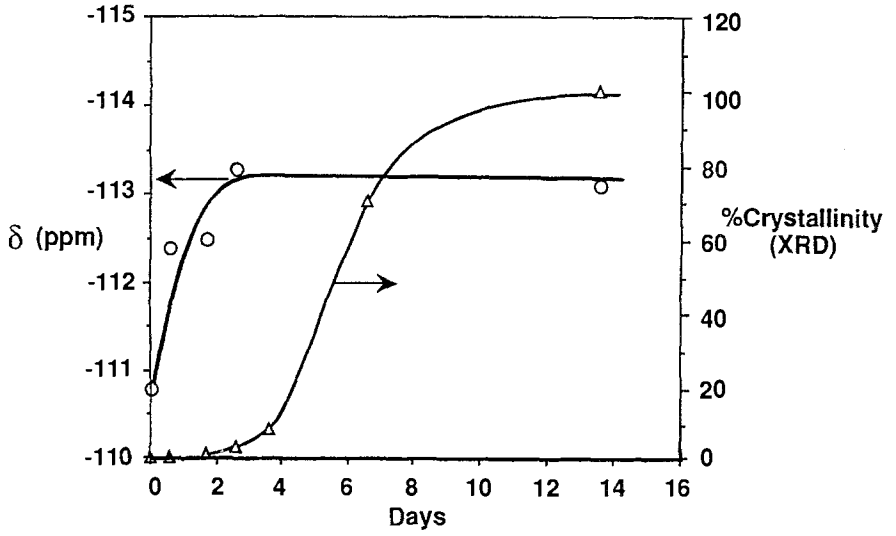

Fig. 5. GEL I variation of ^{29}Si Q^4 chemical shift with crystallinity.

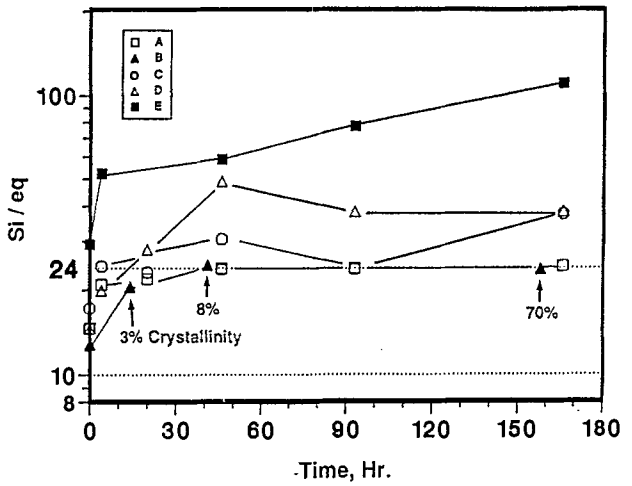

Fig. 6. Development of gel structure with time as reflected in template occlusion expressed as atoms Si per equivalent cation exchange capacity: A) TPA^+/Na^+ (GEL II), B) TPA^+/Na^+ (GEL I), C) TEA^+/Na^+ (GEL II), D) TMA^+/Na^+ (GEL II), E) Na^+ (GEL II). GEL II samples remained amorphous during this time.

for the template-free gel this ratio increases continuously to 100 showing it to be a dense phase. It will be noted that the number 24 corresponds to 1/4 of the number of T-atoms in the ZSM-5 unit cell [23].

An indication of ion sieve effects is seen in fig. 7, which shows Pt^{2+}/Na^+ exchange isotherms for two TPA^+ gels (GEL II). The 2 hr. gel shows high Pt

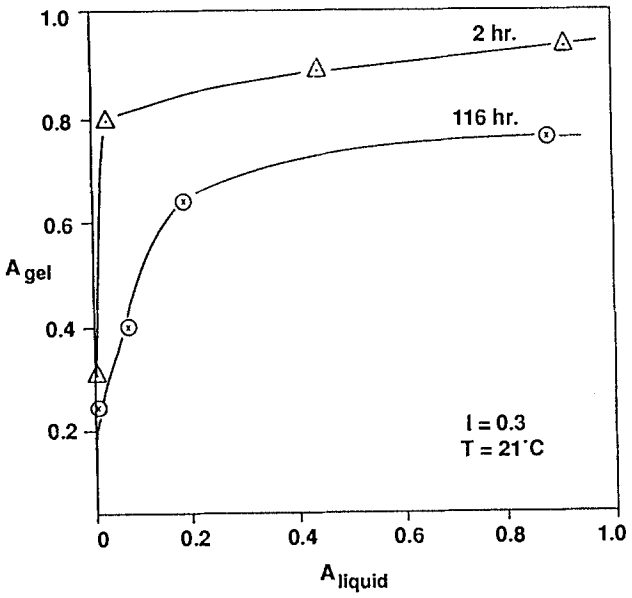

Fig. 7. $[Pt(NH_3)_4]^{2+}/Na^+$ exchange isotherms at 21° C of TPA^+/Na^+ gel (GEL I).

selectivity, while the 116 hr. gel shows around 75% selectivity due to its higher degree of polymerization and hence lower accessibility. The starting gels also exhibited a high degree of TPA^+ exchange. Ion sieve effects will be further discussed in a companion paper [24].

Based on the ion exchange and ^{29}Si MASNMR results we surmise that in TPA^+ gel system, embryonic structures are formed rapidly upon heating. The observed Si/equivalent ratio of 20–24 suggests that these rudimentary structures already bear a resemblance to the final crystalline product. A similar conclusion was reached by Henderson and White [16] from small-angle neutron scattering studies on TPA silicate gels. We conclude further that these structures resemble the channel intersections in ZSM-5. Inspections of the ZSM-5 structure [23] reveals that each channel intersection consists of 22 Si atoms. Moreover, each intersection can accomodate up to one TPA^+ cation [25], which seems to be ideally configured for inclusion. Since there are 4 intersections per unit cell, ZSM-5 is composed almost entirely of these cage-like units. The mechanistic picture emerging is therefore one where the zeolite channel intersections, or approximations thereof, are initially formed. These clathrate-like units, each

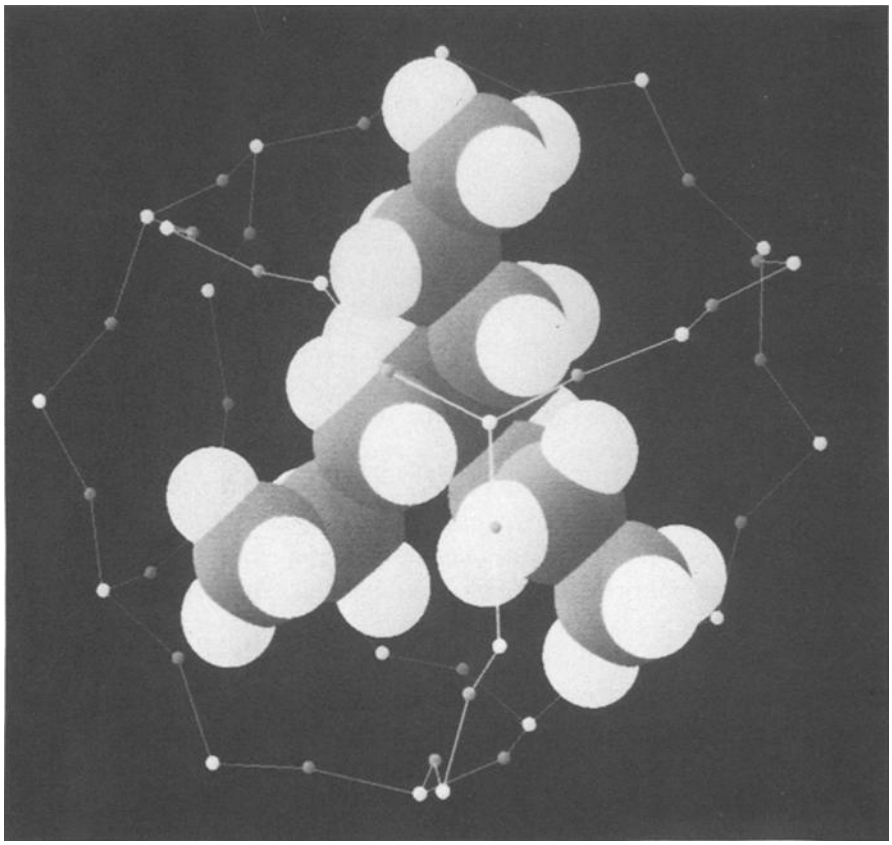

Fig. 8. Representation of ZSM-5 intersection containing a TPA cation.

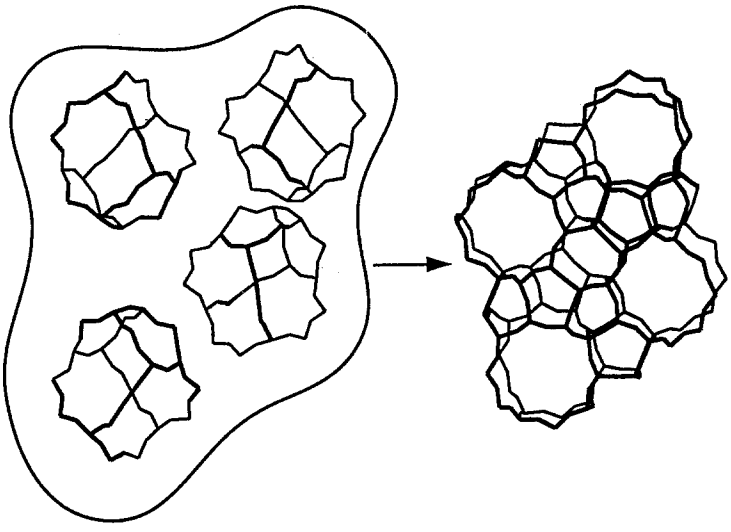

Fig. 9. Representation of ZSM-5 gel nucleation mechanism.

containing one TPA^+ cation, are at first randomly linked together, but in time become ordered or "annealed" through repeated cleavage and recombination of siloxane bonds, mediated by OH^- ion. Fig. 8 shows a representation of a single clathrate unit and fig. 9, the manner in which such units might combine to form ZSM-5.

The TEA^+ gel is similar to the TPA^+ in exchange properties, and functions also as a template for synthesis of ZSM-5 [26]. By comparison, the TMA^+ gel displays a Si/equivalent ratio significantly higher than 24, suggesting that it would not be effective as a template for ZSM-5. As already noted, in the absence of an organic template, Na^+ silicate gel forms a dense phase.

Drawing on the theory of hydrophobic solvation [27,28] a working hypothesis of templated ZSM-5 formation can be assembled. Aqueous solutions of tetraalkylammonium salts have been extensively investigated for their anomalous properties, such as large excess heat capacity and negative entropy of solution [28]. These and other effects [29] have been interpreted in terms of increased water structure in the neighborhood of solute molecules. The solute has been pictured as contained within a clathrate-like ensemble of solvent molecules which are in dynamic equilibrium with the bulk liquid [30]. Upon introducing silicate anions, it is not unreasonable to expect, in the presence of base, a dynamic exchange between water and monomeric silicate to occur in the vicinity of the template, with silicate ions progressively substituting for water in the clathrate structure, owing to the well-recognized structural similarity between water and silicate systems. To quote Weyl and Marboe [31], "Some properties of water and silica are so similar that the transition between hydrated silicic acids and the aqueous

$R^+ + nH_2O \rightleftharpoons \ldots \rightleftharpoons ch + H^+$
$ch + n(Na_xH_{3-x}SiO_4)^- + (n-1)H^+ \rightleftharpoons \ldots \rightleftharpoons cs + [n(2-x)-1]H_2O + nxNa^+ + (nx+1)OH^-$
$cs \rightarrow [\equiv SiOH^- \; OSi\equiv \rightleftharpoons \equiv SiOSi\equiv + OH^-] \rightarrow$ nuclei
ch = clathrate-like hydrate
cs = clathrate-like silicate
$0 \leqslant x < 3$

Scheme 1

matrix is a gradual one." The isomorphism between clathrate hydrates and certain framework silicates is exemplary. For example, Type I clathrate hydrate is isomorphic with the mineral melanophlogite [32], and Type II hydrate with ZSM-39 [33]. Our mechanism can therefore be summarized as in scheme 1. The species $H_3SiO_4^-$ has been identified [34] as the main vehicle of Si exchange in aqueous silicate solutions. The possibility of base occlusion [18] is not excluded.

4. Conclusion

Results of this study lend support to the Breck-Flanigen cation templating mechanism of zeolite formation. The hydrophobic effect and the isomorphism between water and silicate structure are invoked to formulate a working hypothesis of ZSM-5 nucleation, consisting of the following steps: 1) the formation of clathrate-like water structure around the template, 2) isomorphous substitution of silicate for water in these cages, which resemble ZSM-5 channel intersections, 3) progressive ordering of these entities into the final crystal structure.

Finally, it is recognized that the structure of the solvation sphere around the organic template will be influenced by factors other than geometry, such as pH, temperature, ionic strength, inorganic ions, etc., so that the same template may give rise to different zeolite phases under different conditions. Nevertheless, the notion of clathrate-like structures as primary units in the nucleation of zeolites may be general.

Acknowledgments

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