II. Literature Review

A. Molecular Sieve Zeolites

1. Zeolite Synthesis

Zeolites are hydrated framework aluminosilicates formed under hydrothermal conditions by condensation polymerization in three dimensions. Zeolites are composed of infinitely extending 3-dimensional networks of AlO_4 and SiO_4 tetrahedra in which the oxygen atoms occur at the apices of the tetrahedra and the aluminum or silicon atoms occur in the center intertice formed by the oxygens. The tetrahedra in framework aluminosilicates are linked to each other in an apex to apex fashion wherein the apical oxygens are shared. In aluminosilicates the sharing of oxygen between contiguous tetrahedra can also occur in an edge to edge or face to face manner or in combinations of the two. Because all zeolites are framework aluminosilicates, the discussion will be limited to considering the factors which influence the framework structures.

Many factors influence the polymerization sequence in which zeolites are synthesized. The thermodynamic variables include temperature, pressure, and the overall starting batch composition of the reactor mixture. Kinetic variables also influence the products obtained during hydrothermal synthesis, because the reaction mixtures are generally heterogeneous and metastable. Nucleation appears to be kinetically determined as does Ostwalds rule of successive transformations.[6] During hydrothermal synthesis a competition usually exists between co-existing phases which are concurrently or successively polymerized. In accordance with Ostwalds rule, when competing phases appear, there is a tendency for the least stable phase to crystallize first and then be replaced by a more stable form again and again until the most stable product results. The kinetics involved in the crystallization of a zeolite phase are often determined by its prerequisite phase and the rate of dissolution or depolymerization. The nutrients involved in the polymerization of the zeolite often are made available only by the dissolution of a pre-existing less stable phase.

In addition to the thermodynamic and kinetic parameters outlined other factors also influence the nature and type of zeolite synthesized. These factors include the treatment of reactants prior to crystallization, the chemical and physical nature of the reactants, the influence of mineralizers and the templating effect of certain cations and additives. The chemical and physical nature of the initial starting materials can significantly influence the results of hydrothermal crystallization.[7,8,9,10,11,12]

The Mechanism of Zeolite Crystallization

Investigations of the mechanisms involved in zeolite crystallization have received extensive attention from many investigators over the past 20 years.[6,13,14,15,16,17,18,19,20,21,22,23,24,25,26] Regardless, many ambiguities still exist concerning the mechanism of crystallization including those concerning the autocatalytic kinetics of the crystallization process, the effect of alkalinity on the rate of crystallization, the specific nature of the induction period, the effect of seeding on reaction rate, and the effect of clathrating or templating cations.[22] Relevant questions still exists concerning the role of solid and liquid phases in the heterogeneous aluminosilicate systems responsible for the formation of zeolite crystalline phases.[23,24,25,26,27,28,29] Many excellent papers review in depth zeolite synthesis and serve to culminate the thoughts and expressions of these several hundred publications concerning zeolite synthesis which have emerged in the last two decades.[21,22,23,24,25,30,31] It is evident from these reviews that zeolite crystallization represents one of the most complex chemical problems in crystallization phenomenon. The myriad of reactions involved in zeolite crystallization including polymerization - depolymerization, solution - precipitation, nucleation - crystallization, declathration of certain zeolite precursors and the complex phenomenon governing aqueous colloidal dispersions add to the overall complexity of these systems. As is pointed out by Barrer and Cole,[32] the result of this inherent complexity is that "The art of synthesizing molecular sieve zeolites has developed more quickly than the chemical science which would properly account for their formation in nature and in the laboratory from an apparently simple aluminosilicate compositions."

The phenomenon of zeolite crystallization appears to be consistent with the simplicity principle proposed by Goldsmith.[33] In systems containing substances which can exist in the form of several polymorphs, those exhibiting most disorder or highest entropy will tend to crystallize first. The disordered form of an aluminosilicate gel is in a state of highest simplicity and entropy when compared to its ordered crystalline counterpart. During hydrothermal synthesis, in accordance with Goldsmith's simplicity princple, the formation and development of nuclei exhibiting maximum simplicity are preferred. Goldsmith states there is a gradual transition from simplicity to complexity and thereby, from maximum disorder to maximum order. Therefore, the nature of the phases present at a specific time during hydrothermal synthesis is governed by both thermodynamic and kinetic factors. A more complex structure which might be more stable under hydrothermal synthesis conditions is likely to require more time to evolve its complex ordering. Therefore, Goldsmith's principle simple states that the simplicist crystalline phase is kinetically favored and thermodynamically disfavored; whereas, the most complex crystalline phase is kinetically disfavored by thermodynamically favored. Fortunately, the nuclei of several metastable zeolite phases may develop before the nuclei of the most ordered structures. If not for this fact, synthesis of certain zeolites would not be possible.[34] According to Breck, "It is probable that many of the synthetic zeolites which do not have mineral relatives are nonequilibrium phases and do not exist when true equilibrium conditions prevail."

The existence of natural zeolite deposits of geologic origin and the fact that they have existed for millions of years does not necessarily indicate that they are equilibrium phases. Rather, it is more probable that the physiochemical environment in which they were formed changed over the eons in time in such a manner that further metamorphis could not occur. The geologic crystallization phenomenon was, therefore, quenched by a reduction in pH, a reduction in temperature, or the transition from an aqueous to anhydrous environment.

The schematic representation of the free energy relationships between the reaction mixture and various aluminosilicate phases is shown in Figure 4 . The initial reaction mixture is composed of components which first form the phase denoted A which may subsequently be converted to B or C given sufficient time. In the region of temperature where phases A or B both can form, the nucleation and growth rates are important because the metstable phase A which preferentially forms may transform to more stable phases B and C in succession.[36]

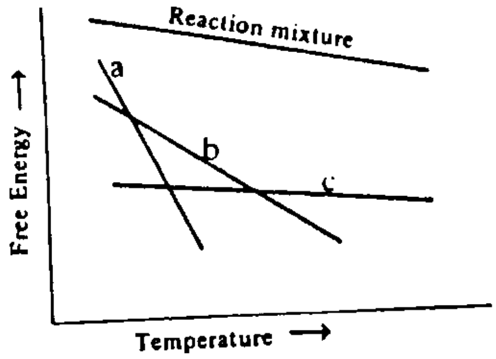


Figure 4. Schematic free energy relations between reaction mixtures and various zeolite phases, represented by a,b,c.[36]

In general the conditions used in zeolite synthesis are as follows:[37,38]

1. Reactive starting materials such as freshly coprecipitated gels, or amorphous solids.
2. Relatively high pH introduced in the form of an alkaline metal hydroxide or other strong base.
3. Low temperature hydrothermal conditions with concurrent low autogenous pressure at saturated water vapor pressure.
4. A high degree of super saturation of the components of the gel leading to nucleation of a large number of crystals. The term gel is used to denote a hydrous metal aluminosilicate which is prepared from either aqueous solutions, reactive solids, colloidal sols, or reactive aluminosilicate such as the dehydroxyllated residue structure of

metakaolin.[39] A substantial increase in fluid viscosity generally occurs the instant a dissolved sodium aluminate species and sodium silicate species are mixed. This gel formation is thought to occur by the co-polymerization of individual silicate and aluminate species by a condensation polymerization mechanism. The representative chemical reactions involved in the formation of gel and crystallization of zeolites in the Na_2O-Al_2O_3-SiO_2-H_2O system can be depicted as follows:

$$\begin{array}{l}
\mathrm{NaOH\ (aq) + Na\ Al(OH)_4\ (aq) + Na_2\ SiO_3\ (aq)} \\
\qquad\qquad \downarrow \quad T_1 = 25\ \mathrm{C} \\
\mathrm{(Na_a\ (AlO_2)_b\ (SiO_2)_c \cdot NaOH \cdot H_2O)\ gel} \\
\qquad\qquad \downarrow \quad T_2 = 25\ \mathrm{to}\ 175\ \mathrm{C} \\
\mathrm{Na_x((AlO_2)_x\ (SiO_2)_y) \cdot mH_2O + solution}
\end{array}$$

As shown in the first line of this overall reaction schematic there are three major components which lead to the formation of an aluminosilicate gel. The first component, typically sodium hydroxide, serves to contribute charge compensating cations and also adds hydroxyl ion to increase the pH of the system. The second and third major components are the aluminum source and the silicon source. Typical reactants employed as sources for each of these three major components are listed in Table 1.[41] The

Charge compensating cations	Aluminium	Silicon
Alkali metal hydroxides Alkaline earth hydroxides and oxides Other oxides and hydroxides Salts (fluorides, halides, carbonates, phosphates, sulphates, etc.) Organic bases and ammonium hydroxide, especially quaternary bases Silicates and aluminates Mixtures of two or more of the above.	Metal aluminates $Al(OH)_3$, Al_2O_3, AlO.OH Al alkoxides Al salts Glasses Sediments Minerals, especially clay minerals, felspathoids, felspars and other zeolites	Silicates and silicate hydrates Water glass Silica sols Silica gels Silica and other synthetic glasses Silicon esters Tuffs and volcanic glasses Minerals, including clay minerals, felspathoids, felspars and other zeolites Basalts and mineral mixtures Sediments Combinations of two or More of the above

Table 1. Some sources of cations, aluminum and silicon in zeolite crystallization.[41]

chemical and physical nature of the anionic form of aluminum which is soluble has been determined. Measurements of electrical conductance, hydrogen electrode data, electrometric titration, osmotic and cryptoscopic properties, viscosities, optical and dialysis behavior, and infrared and Raman spectra have shown that the anionic form of aluminum which exists in alakline solutions is $Al(OH)_4^-$.[42] This particular anionic form exists at moderate Na_2O concentrations in sodium aluminate solutions. At Na_2O concentrations exceeding 25 wt.%, the $Al(OH)_4^-$ anion dehydrates to yield AlO_2^-. Two possible dehydration steps are as follows:

$$Al(OH)_4^- \rightarrow AlO(OH)_2^- + H_2O$$

$$2Al(OH)_4 \rightarrow ((OH)_3Al - O - Al\ (OH_3))^{2-} + H_2O$$

Although existing evidence is not conclusive, the second of the above dehydration processes is considered more probable.[44] Dehydration of the $Al(OH)_4^-$ anion to AlO_2^- is likely to prevent the dehydration polymerization process from which zeolites are formed. Increasing alkalinity at constant temperature ($Na_2O \cdot H_2O = 2NaOH$) influences the crystallization kinetics in the same direction as increasing temperature at constant alkalinity. Studying the rate of crystallization of zeolite A from aluminosilicate gels with varying sodium hydroxide concentrations, Ciric found the rate of crystallization at constant temperature varied with the second power of the hydroxide concentration.[45]

$$\frac{dW_c}{dt}_T = K\ (OH)^2$$

The effects of increasing alkalinity at constant temperature; i.e., shortening the induction time and increasing the crystallization rate, occurs only within a certain stability field for a given zeolite. If the alkalinity is increased outside the stability field of Na_2O-SiO_2-Al_2O_3 ternary phase diagram, zeolite formation is slowed and prevented.

It is likely that the Al - O - Al bond formation occurring by the second dehydration mechanism above can only serve to reduce the rate of zeolite crystallization. According to Lowenstein's rule, no Al - O - Al bonds can occur within the zeolite framework. The formation of this aluminum hydroxide dimer therefore, would reduce the diffusion rate of the aluminum to the growing zeolite surface as it is a more bulky anion. Further, if one end of this dimer underwent dehydration polymerization with a surface silicic acid, a zeolite could not be subsequently formed unless the Al - O - Al bond was cleaved. Aluminate solutions are, therefore, relatively simple, as the $Al(OH)_4^-$ ions are the dominant anionic species. With silicate solutions, this is not the case and silicate chemistry is more complex in general because of the multitude of polymeric species which are known to occur.

Silica is used as an abbreviation for silicon dioxide in all of its forms;i.e., crystalline, amorphous, hydrated, or hydroxylated. The chemistry of silica is very similar to that of water. Silica and water are very much alike, they consist mainly of oxygen atoms with smaller hydrogen or silicon atoms interstices. In neutral or acidic solutions silica exists as the hydrated monomer $(SiOH)_4$. In basic solutions it exists as silicate ions.[46] "Some properties of water and silica are so similar that the transition between hydrated silicic acids and the aqueous matrix is a gradual one."[47] The solubility of silica particularly the amorphous forms has been extensively studied over the past 30 years. The dissolution of silica involves simultaneous hydration and depolymerization. The dissolution depolymerization reaction resulting in silicic acid is represented by equation 1.

$$1.\quad (SiO_2)_N + 2_N H_2O = N\ Si(OH)_4$$

$$2.\quad Si(OH)_4 + H_2O + OH^- = (H_2O)\ Si(OH)^-_5$$

$$3.\quad \frac{(H_2O)\ Si(OH)_5}{(OH)^-\ (Si(OH)^-_4} = 1.85 \times 10^4$$ [43]

$$4.\quad (SiO_2)_X + 2H_2O \underset{\text{DEHYDRATION}}{\overset{\text{HYDRATION}}{\rule{3cm}{0.4pt}}} (SiO_2)_{X-1} + (Si(OH)_4$$ [49]

Equation 2 shows the transformation from silicic acid in a basic medium to silicate anions. If the assumption is made that the concentration of the monomer $Si(OH)_4$ does not change with pH, the increased solubility of silica with increasing pH can be explained on the basis of the equilibrium constant shown in equation 3.[48] The overall reaction showing the dissolution and deposition of silica in water is shown in equation 4. The solubility of silica in water is defined as the concentration of $Si(OH)_4$ reached at steady state in the depolymerization - polymerization equilibrium. Certain materials have the capacity to catalyze the rate of dissolution of silica. "The catalyst is a material that can be chemi-adsorbed and increases the coordination number of a silicon atom on the surface to more than 4, thus weakening the oxygen bonds to the underlying silicon atoms." [50] The mechanism proposed for the dissolution of silica in the presence of hydroxyl ions is shown in Figure 5.[51]

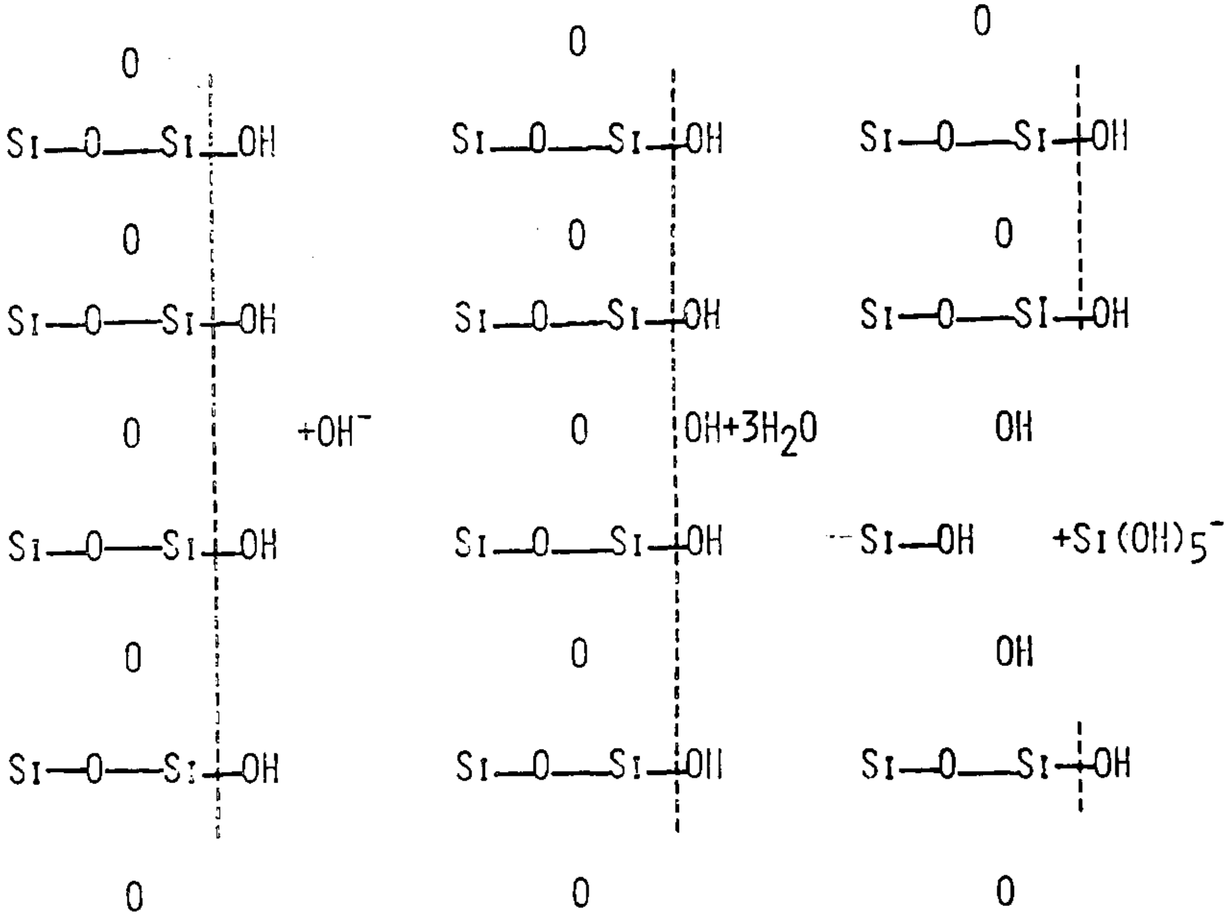


Figure 5. Proposed mechanism of dissolution of silica in water in the presence of hydroxyl ions. The dotted line represents the interface between silica on the left and water on the right.[51]

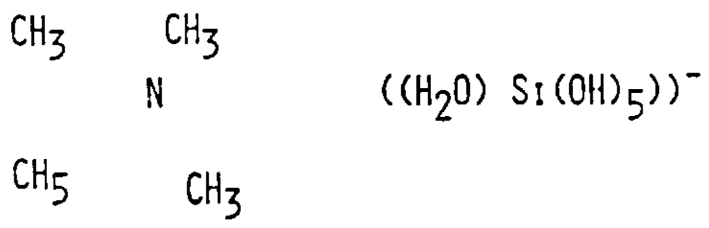
In Figure 5 the vertical dotted lines represent the interface between silica on the left and water on the right. On the silica's surface there are spaces between the oxygen ions sufficiently large to accommodate hydroxyl ions. The surface hydroxyl groups which are called silanol groups are exposed to the aqueous phase. Loss of a hydrogen from a silanol group causes the surface to be ionically charged. As is shown in Figure 5, the silicon atom which is removed from the silica's surface enters the solution as a silicate ion. If the solution pH is above 11 the silicate ion is relatively stable. If the pH is below 11 the silicate ion hydrolyzes to soluble silica $Si(OH)_4$ and OH^- ions.[50] If a solution cooling or becoming acidified, polymers form by dehydration polymerization. The polymerization of monomers or the deposition of silica can be represented by equation 5. In equation 5 N = the number of silicon atoms in a polysilicic acid molecule or particle or polymeric network: X = the number of OH groups per silicon atom in the polymer not exceeding four; M = the number of monomeric silicic acid molecules added to the polymer; P = fraction of the hydroxyl groups per monomeric silicic acid molecule that are converted to water during the polymerization reaction.[52]

$$5. \quad (Si_N O_{2N-(NX/2)} (OH)_{NX}) + MSi\,(OH)_4 =$$

$$(Si_{N+M}\, O_{2N-(NX/2)} + 2M_{(2-P)}\, (OH)_{NX+4(M-P)} +$$

$$2_{PM}\, H_2O$$ [47]

The presence of certain salts increase the rate of this solution of silica and the presence of others retard it. The rate of dissolution of quartz in aqueous sodium chloride solutions of concentrations 10^{-3}, 10^{-2} and 10^{-1} N was found to be 4, 14, and 67 times that of pure water.[52] Sasaki[53] found that both zinc and aluminum greatly inhibited the rate of solution of fused silica. He found that concentrations of 3.4×10^{-3} N aluminum and 5×10^{-3} N zinc completely inhibited the dissolution of silica in 0.1 N sodium hydroxide. Certain organic compounds strongly increase the solubility of silica. Myer and Yen[54] found that quinoline plus potassium hydroxide dissolved crushed quartz at a rate substantially faster than saturated aqueous potassium hydroxide. Strong quartennary ammonium bases like tetramethyl ammonium hydroxide dissolves silica rapidly forming the silicate salt.[55] The probable structure of this TMA silicate is shown below.



$$\begin{matrix} CH_3 & & CH_3 & & \\ & & N & & ((H_2O)\ Si(OH)_5))^- \\ CH_5 & & CH_3 & & \end{matrix}$$

The size of the silica particle can also influence its solubility. The Ostwald-Freundlich equation, applied to solubility is known as the Thompson-Gibbs effect. The

Ostwald-Freundlich equation is shown in equation 6, where Sr = the solubility of a particle of radius r. S1 = solubility of a flat surface or particle of infinite radius in nanometers. E = the interfacial surface energy (ergs centimeter^{-2}); B = molar volume which equals 27.2 cm^3 for amorphous silica. R = gas constant (8.3 x 10^7 ergs mole^{-1} DEG^{-1}. T = temperature (degrees Kelvin). The radius of curvature (cm) = 4. D = particle diameter (nanometers) and E = 104.6 (10^7) (r) log $\left(\frac{Sr}{S1}\right)$ at 25 C.[56]

$$6. \quad \frac{S_R}{S_I} = \mathrm{EXP}\ (2\ EVR^{-1}\ T^{-1}\ R^{-1})$$

OR

$$\mathrm{LOG}_{10}\left(\frac{S_R}{S_I}\right) = 2.85 \times 10^{-7}\frac{E}{T_R} = 5.7\ \frac{E}{T_D} \qquad {}^{56}$$

The variation in the solubility of silica with the radius of curvature of the silica surface is shown in Figure6 . In this figure the positive radii of curvatures are illustrated in cross section as particles and projections from a silica surface. The negative radii occur in the crevice between two particles or as depressions or holes in the silica surface.[57]

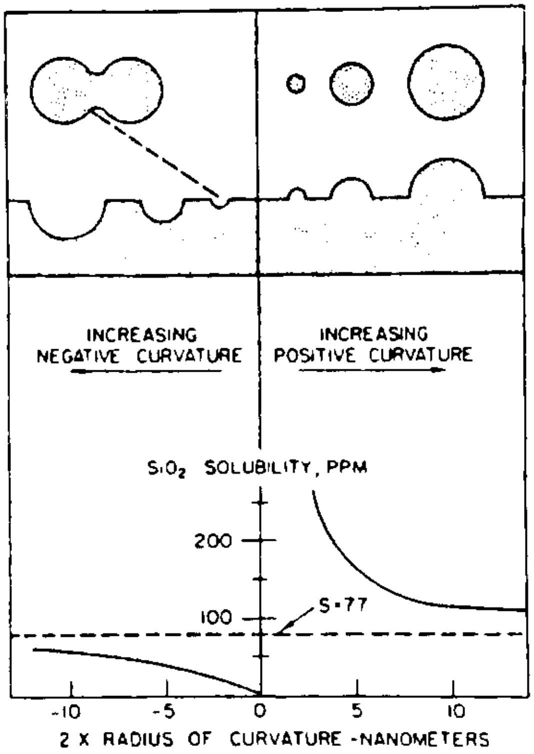
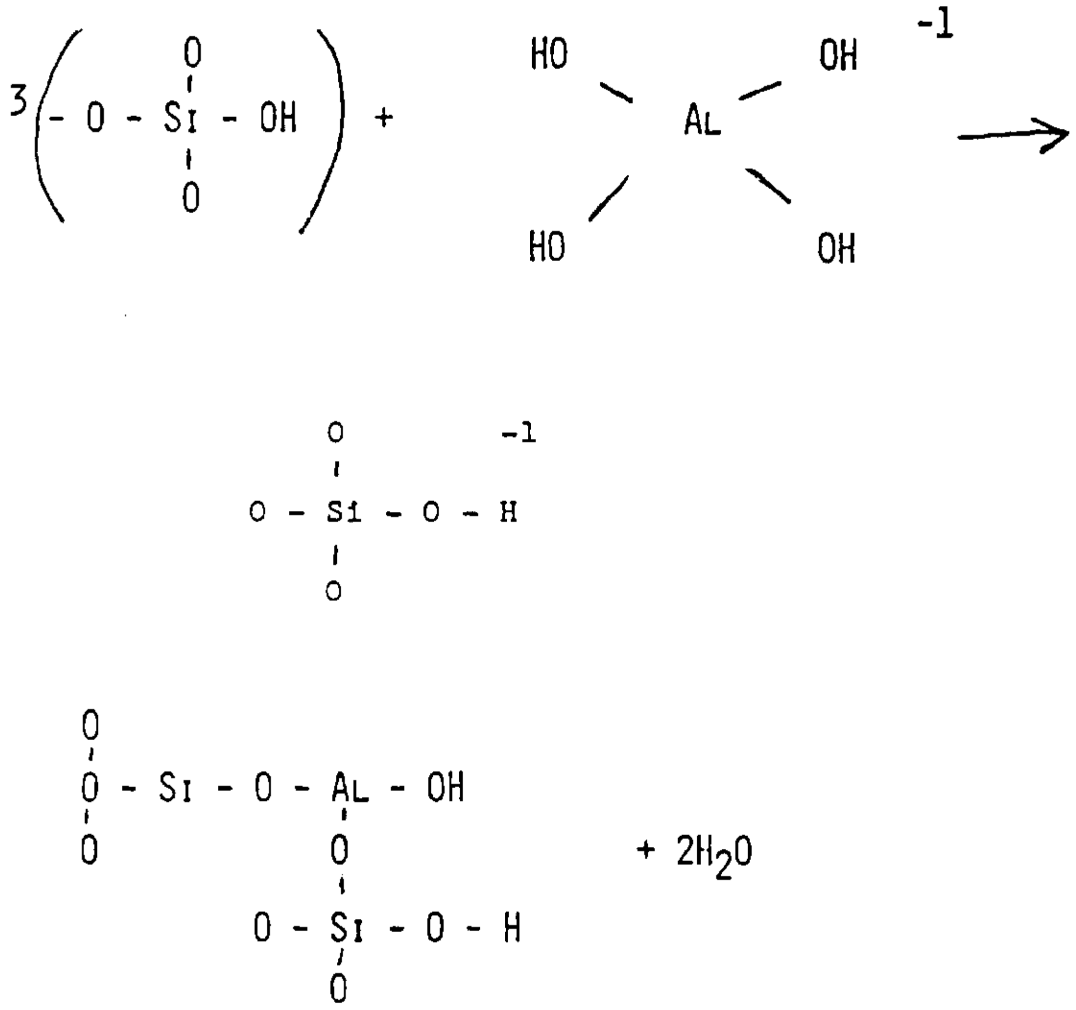


Figure 6. Variation in solubility of silica with radius of curvature of surface. The positive radii of curvature are shown in cross-section as particles and projections from a silica surface. Negative radii are shown as depressions or holes in the silica surface, and in the crevice between two particles.[57]

Having reviewed the mechanism of dissolution and polymerization of silica and the factors which influence its solubility one can now discuss the next stage of zeolite synthesis which is the formation of an aluminosilicate or silicate gel.

The dehydration polymerization mechanisms involved in the formation of aluminosilicate gels is very similar to that occurring in the gellation of silicic acid. "Since the aluminate ion $Al(OH)_4^{-1}$ is geometrically similar to $Si(OH)_4$, the ion can be inserted or exchanged into the SiO_2 surface, thus creating an aluminosilicate site having a fixed negative charge."[59] The polymerization reaction involved between an aluminate ion and three surface silanol groups is shown below[59]:



In 1948 Pauling pointed out that the incorporation of a four coordinated aluminum on a silica surface was anionic in nature and required the presence of a cation for stability.[59] The following year silica-alumina cracking catalysts were marketed.[61]

The steps involved in the dehydration polymerization from silica monomers to large particles, gels, or powders was represented schematically by Iler.[62] Figure 7 depicts the schematic representation of the polymerization of silica both for the case of basic aqueous solution and for the case in which flocculating salts or acids are present.

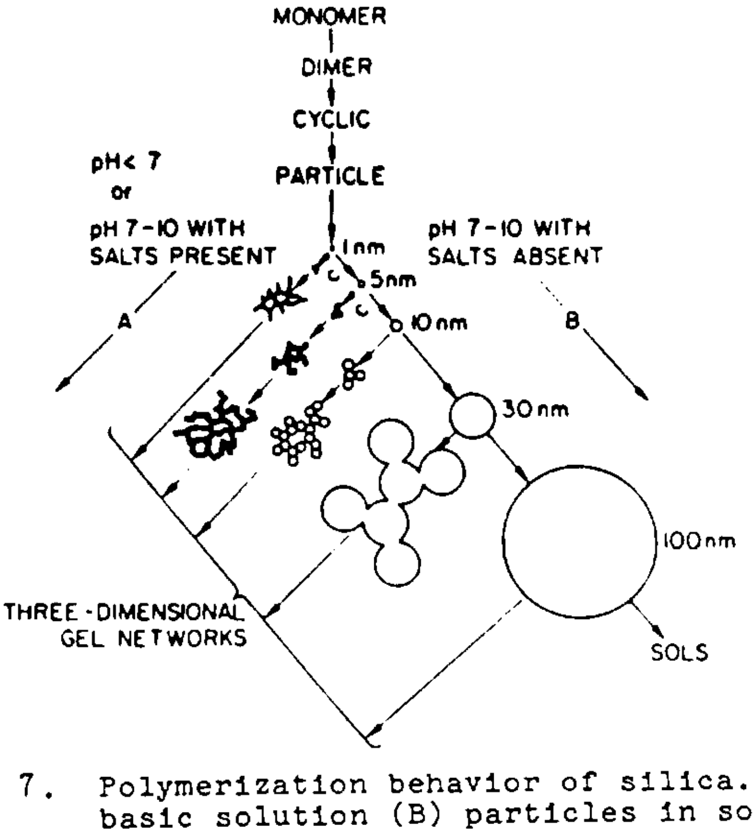


Figure 7. Polymerization behavior of silica. In basic solution (B) particles in sol grow in size with decrease in numbers; in acid solution or in presence of flocculating salts (A), particles aggregate into 3-dimensional networks and form gels.[62]

In a subsequent publication each successive step in the polymerization of a monomer to a gel is considered in detail. The major points Iler presents are herein summarized.[63]

1. Monsilicic acid is stable in water at 25 C at concentrations less than 100 parts per million. At concentrations in excess of 100 parts per million the monomer polymerizes by condensation to form dimers and higher molecular weight species of silicic acid.
2. The condensation polymerization of silicic acid involves an ionic mechanism. The rate of condensation is proportional to the concentration of OH^- ion if the pH is above 2 and is proportional to the hydrogen ion concentration below 2 pH.
3. The polymer is formed by condensation polymerization of silicic acid tend to possess a maximum of siloxane (Si-O-Si) bonds and a minimum of uncondensed Si(OH) groups. Condensation quickly leads to ring structures during the first stages of polymerization and later these ring structures, such as the cyclic tetramer, are linked together by the addition of monomers to form 3-dimensional molecules. When condensation is complete all internal silanol groups have been condensed such that the molecule is in its most compact state with silanol groups remaining only at the molecule

solution interface. A proposed mechanism for the formation of these cyclic tetramers is shown in Figure 8.

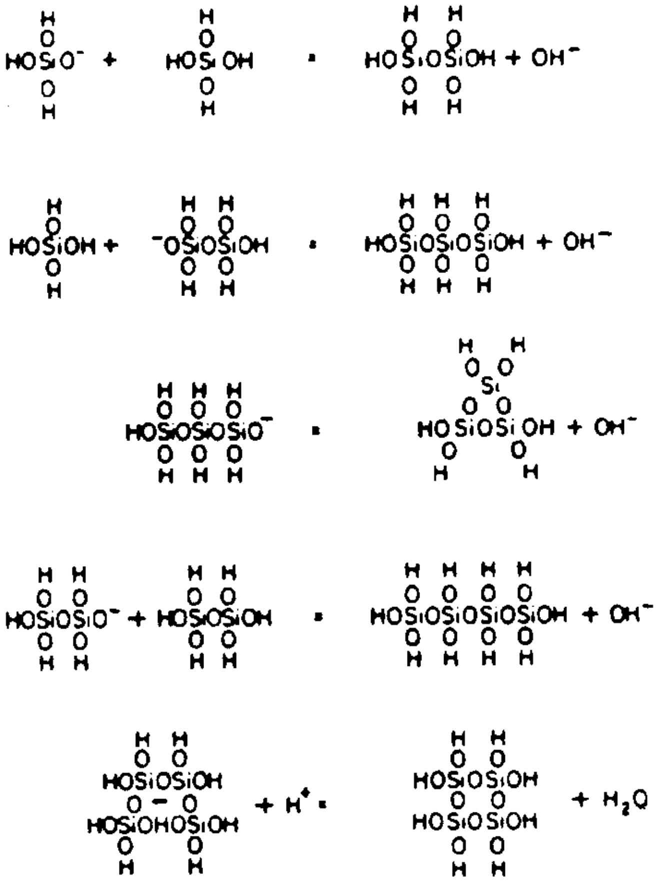


Figure 8. Conceivable steps in the polymerization of silica to cyclic species. However, consideration of bond angles makes the formation of cyclic trimer much less likely than cyclic tetramer.

4. The condensed particles have a solubility dependent on the radius of curvature of the surface. If the condensation occurred at room temperature uncondensed silanol groups may occur internally. If formed above 80 C and above pH 7 the compact state is almost anhydrous.
5. There are two basic processes of particle growth of silica growth in aqueous systems. The first involves the rapid growth of particles at the expense of the dissolved silicic acid to form large numbers of small particles. The second process is slower and may be negligible at low pH. This process involves the dissolving of the smaller particles to form aqueous silicic acid which subsequently recondenses contributing to the growth of the large particles.
6. Over a pH range of 7 to 10.5 silica particles are negatively charged and repel each other. The negative charge is caused by the loss of a small number of hydrogen atoms from surface silanol groups. The charged particles tend not to collide so that particle growth continues without aggregation. If charge repulsion is reduced by means of the addition of salt in concentrations greater than 0.2 N to 0.3 N, aggregation and gelling occurs. The mechanism involved in the aggregation

and gelling of silica by flocculating metal cations is shown in Figure 9.[64]

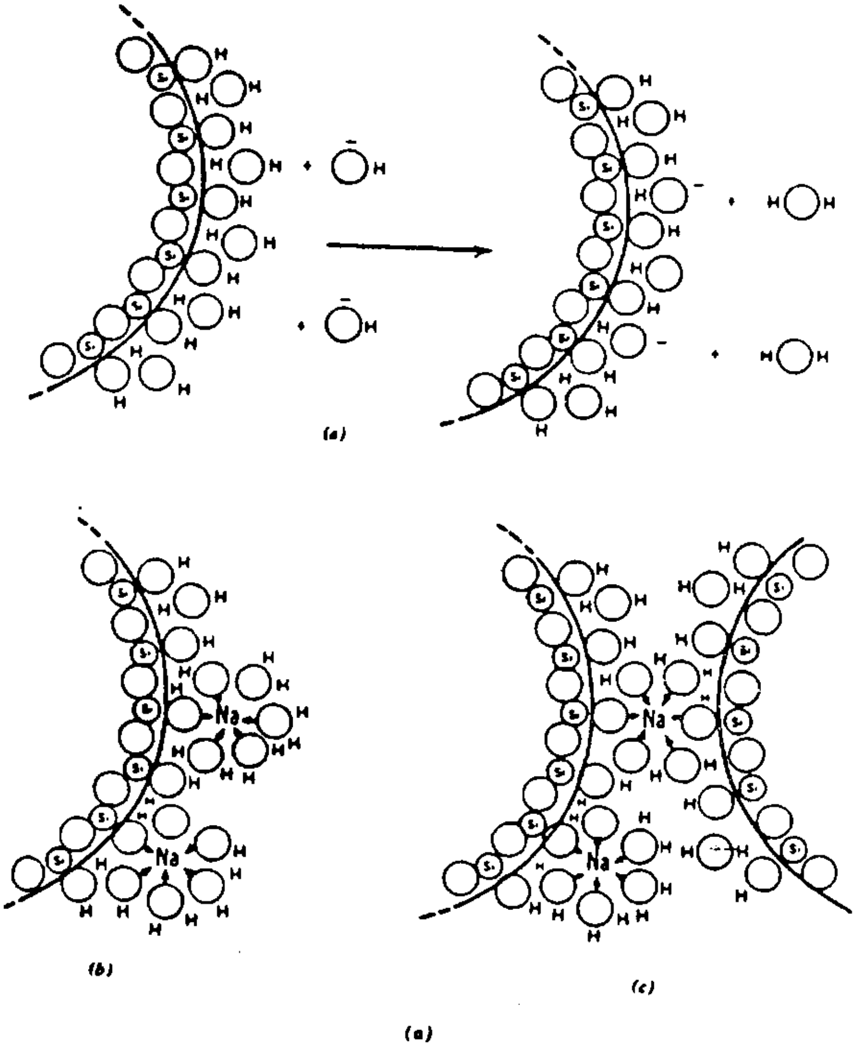


Figure 9. Possible bonding between silica particles through coordination with flocculating metal cations. (a) Hydroxyl ion transfers negative charge to water layer hydrogen-bonded to silanol groups on particle surface; equivalent to adsorption of hydroxyl ion; (b) hydrated sodium ion is adsorbed at negative site forming neutral complex; (c) collision with uncharged area of a second particle permits sodium ion to coordinate with oxygens of silanol and surface-bonded water, forming a coordination linkage between particles. Circles represent oxygen atoms. Colloidal particles are much large relative to atoms represented here. A number of sodium bridges may be formed.

In 1937 Morey and Ingerson proposed a mechanism for zeolite crystallization involving the formation of a solid amorphous precursor which is followed by a solution crystallization mechanism.[65] Zhdanov, who reviewed the aforementioned mechanism, proposed that a quasi equilibrium between the solid and liquid phases in the gel occurs and further nuclei form and grow in the liquid phase.[66] A schematic represenation of the depolymerization of the aluminosilicate gel structure by OH^- ions is shown in Figure 10. This figure also shows the silica and alumina tetrahedra regrouping around hydrated sodium ions to form the basic polyhedral units which agglomerate into the zeolite structure.[67] The overall mechanism is analogous to the solution mechanism proposed by Kerr.[68]

An excellent review of the mechanism of zeolite crystallization was given by Zhdanov.[66] In it he states that zeolites are crystallized from alkali aluminosilicate gels which are heterogenous colloidal systems containing both liquid and solid phases which differ considerably in their chemical composition. Certain common properties of these aluminosilicate gels also were reported. The composition of the solid gel phase is similar to that in the crystal lattice of the zeolite in that the silicon to aluminum ratio always is equal to or exceeds one and the sodium to aluminum ratio is approximately one. From this he concluded that aluminum was four fold coordinated within the gel. The solid portion

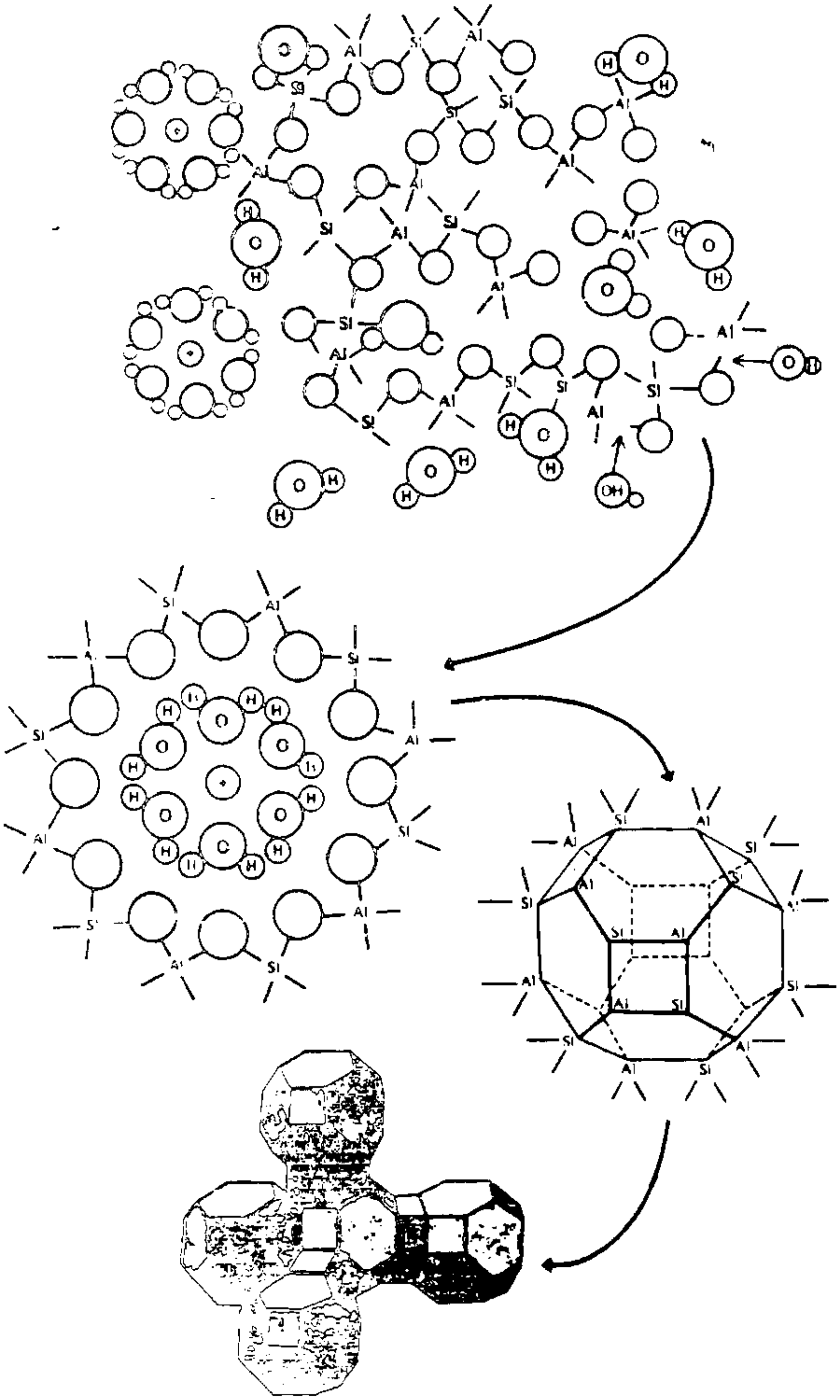


Figure 10. Schematic representation of the formation of zeolite crystal nuclei in a hydrous gel. The gel structure, center, is depolymerized by OH^- ions. Tetrahedra regroups about hydrated sodium ions to form the basic polyhedral units.[67]

of the gel constitutes a network structure containing complicated structural elements such as single, double, four and six membered rings and combinations thereof. A change in the silicon to aluminum ratio of the solid gel phase causes a proportional change in the silica to alumina ratio of .5, the silicon to aluminum ratio of the solid gel phase increases when the concentration of excess alkali is decreased (excess meaning greater than 1:1 sodium to aluminum). Zhdanov attributes this to a higher degree of hydroxylation of silicate ions with decreasing pH. For the same reason, the silicon to aluminum ratio of the zeolite crystals formed increases with increasing water content of the gel.

The specific contributions made by the liquid and solid phases of aluminosilicate gels in zeolite synthesis is still under debate. In the initial proposed mechanism of Flanigen and Breck, the importance of the solid phase of the gel as the locus of zeolite nucleation-crystallization and the heterogenous nucleation phenomenon were emphasized.[69] Tezek suggested that the discussion of zeolite synthesis in terms of nucleation and crystallization is oversimplified. Applying to zeolite crystallization his approach to complex precipitating bodies.[70,71] he proposed zeolite crystallization involves at least four subsystems; 1) formation of simple and polynuclear complexes, 2) embryonation as a state of aggregation of complexes, 3) nucleation as aggregate formation with a crystalline core and formation of micelles (primary particles), and 4) aggregation of primary particles into larger secondary structures through crystalline (oriented) aggregation. Although most references cited are in aggreement that the formation of a solid amorphous precursor preceeds zeolite crystallization, there is some debate as to which phase of the gel so separated is responsible for the crystallization of zeolites. Two mechanisms have been proposed. One supports the concept that zeolite crystallization occurs in the liquid phase and the second that zeolite crystallization occurs predominantly in the solid phase of the gel through an ordering of the aluminosilicate network. Khatami and Flanigen[23] observed the crystallization of zeolite X in the absence of a liquid phase. Interrupting the crystallization of zeolite X near the end of the induction period the liquid phase of the gel was removed and the solid phase dried in ambient temperature to a free flowing powder of composition $1.1\ Na_2O \cdot Al_2O_3 \cdot 2.7SiO_2 \cdot 4.6H_2O$. This dry powder which was initially x-ray amorphous showed 2% levels of crystalline zeolite X after 10 days at ambient temperature and 20% zeolite X after 47 days.

Culfaz and Sand[72] proposed a mechanism wherein nucleation occurs at the solid liquid interface. In this mechanism it is proposed that nucleation, mass transfer of species by surface diffusion, and zeolite crystallization occur in a boundary layer at the solid liquid interface. Support of this surface nucleation mechanism was given by Kerr[73] through the epitaxial growth which he observed in the cocrystallization of zeolite L, offretite, and erionite. As an increase in either the temperature or the alkalinity of these systems raises the solubility of the solid aluminosilicate phase it is likely the composition of the liquid phase in such heterogenous systems has an essential effect on crystallization.[22] Most references concur with what was originally stated by Zhdanov in 1965 "The nuclei of zeolites begin to form in the liquid phase of gels or at the interface of gel phases."[74]

The main supporting evidence suggesting zeolites form without the participation of the liquid phase are those experiments wherein zeolite formation occurred subsequent to the removal of a considerable part of the liquid phase. Equilibrium between solid and liquid phases of gels is, however, independent of the volume of solution.[22] Removal of a substantial quantity of the liquid phase will not lead to a change in the equilibrium and should not, therefore, have influence on the crystallization processes of such gels.[22] Even in situations where zeolites were found to crystallize from physically dry, free-flowing powders [23] it is conceivable that the condensation polymerization reaction itself contributed sufficient water to the system to produce a new aqueous boundary layer. The formation of zeolites at this boundary layer is consistent with the mechanism proposed by Culfax and Sand.[72]

The activation energy of zeolite crystallization corresponds to that of crystal growth.[22] The typical values for activation energies, i.e., 10 to 11 kcals per mole are equivalent to the energy necessary to break two hydrogen bonds.[22] It is proposed[22] that this activation energy might be that required for the dehydration of the silicate and aluminate ions in solution before the condensation reactions between the ions could take place. The rate of any crystallization process is determined by the rate of nuclei formation and the rate of crystal growth. The rate of zeolite crystal formation increases proportionally to the quantity of crystalline product present.[75,76] This autocatalytic rate of zeolite crystallization can be attributed either to an increase in the linear rate of crystal growth or an increase in the rate of nuclei formation during the crystallization period. Since the rate of crystal growth is maximum at the beginning of the crystallization process and gradually decreases as the process develops, acceleration of the crystallization rate must be attributable to the increase in the rate of nuclei formation after crystallization begins.[22] The period of time which elapses before the crystallization begins is called the induction period. The induction period begins when the silica and alumina gel constituents are mixed resulting in an amorphous dispersion of particles of the order of 100 to 300 angstroms in size.[23] During the induction period these amorphous particles grow to approximately 1000 A, after which time the first zeolite crystals appear.[23] In accordance with the aforementioned Thompson and Gibbs effect, nuclei form and dissolve during this induction period. Once one of the nuclei formed exceeds critical radius it will continue to grow in size marking the beginning of the crystallization process. Sand[77] found that increasing the alkali concentration in aluminosilicate gels leads to a decrease in both the duration of crystallization and crystal sizes. The rate of nucleation is, therefore, increased in direct proportion to alkali concentration. Crystal growth proceeds at the expense of the solid gel phase during the crystallization period. As the gel begins to become depleted, the crystallization rate slows down. The S-shaped nature of an autocatalytic reaction rate curve can, therefore, be explained as follows. If one plots weight% zeolite formed on the ordinate against time on the abscissa, one will observe that the rate curve is horizontal during the induction period. Following the induction period, the rate curve is concave upward. In this region the reaction rate is increasing due to the increasing amount of zeolite surface available to catalyze the synthesis reaction. Following this period is a relatively flat portion of the rate curve wherein the crystallization rate is mass transfer limited. Following this period the rate curve becomes concave downward because the reaction rate slows due to the depleted availability of nutrient.

In the early 1960s tetramethyl ammonium cation (TMA) was introduced as the first organic cation to be used in zeolite synthesis.[78,80] Tetraalkyl ammonium hydroxides were known to be strong bases but their effect on the mechanism of synthesis of zeolites is considerably more involved than that of simply contributing alkalinity to the system. In the following section the role of organic molecules in molecular sieve synthesis will be discussed.