

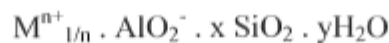
Chapter 2. Literature Review

2.1. Zeolite

2.1.1 Background

Zeolites (Greek, zeo, "to boil", lithos, "a stone") are aluminosilicates that have well-defined porous structures. The term was originally coined in the 18th century by a Swedish mineralogist named Axel Fredrik Cronstedt who observed, upon rapidly heating a natural mineral that the stones began to dance about as the water evaporated. Using the Greek words which mean "stone that boils", he called this material as zeolite [24].

Strictly speaking, zeolites are defined as crystalline microporous aluminosilicates with pore structures consisting of sharing TO₄ tetrahedra, where T is Si or Al. Zeolites can be described with the following empirical formula [25]:



Where

M – counter ion

n – counter ion valence

x – silicon/aluminum ratio

y – content of hydrate water

Owing to the well-defined pore structure, zeolites are also known as "molecular sieves". The term molecular sieve refers to a particular property of these materials, i.e., the ability to selectively adsorb molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the diameter of the pore channels.

2.1.2. Structure

The flexibility of the zeolite Si-O-Si bond explains the fact that about 200 structures have been determined. Indeed, there is little energetic difference (10-12 kJ/mol) between these remarkable porous silicates and higher density phases such as quartz. More than 150 zeolite types have been synthesized and 48 naturally occurring zeolites are known.

The structure commission of the International Zeolite Association (IZA) provides up to date classification by framework type. Each framework is assigned a three-letter code, recognized by the IUPAC Commission on Zeolite Nomenclature [26]. According to the IZA structure commission, zeolite frameworks can be thought to consist of finite or infinite (i.e., chain- or layer-like) component units. The primary building units are single TO_4 tetrahedra. The finite units which have been found to occur in tetrahedral frameworks are shown in Figure 2.1. These secondary building units (SBU), which contain up to 16 T-atoms, are derived from the assumption that the entire framework is made up of one type of SBU only. A unit cell always contains an integral number of SBU's. In some instances, combinations of SBU's have been encountered. However, it should be noted that the SBU's are only theoretical topological building units and should not be considered to be or equated with species that may be in the solution/gel during the crystallization of a zeolitic material [26].

Zeolites can be also classified on grounds of their pore openings and the dimensionality of their channels. Thus, one distinguishes small pore zeolites (eight-membered-ring pores), medium pore zeolites formed by ten-membered rings, large pore zeolites with twelve-membered-ring pores and extra-large pore zeolite category. This classification simplifies comparisons in terms of adsorptive, molecular sieving and catalytic properties.

Two important and industrially relevant structures, MFI and FAU are depicted in Figure 2.2. The channels in the MFI structure are formed by 5-1 building units linked together. These building units render a framework of zigzag 10-membered ring channel ($5.1 \times 5.5 \text{ \AA}$) and intersecting straight 10-membered ring channels ($5.3 \times 5.6 \text{ \AA}$).

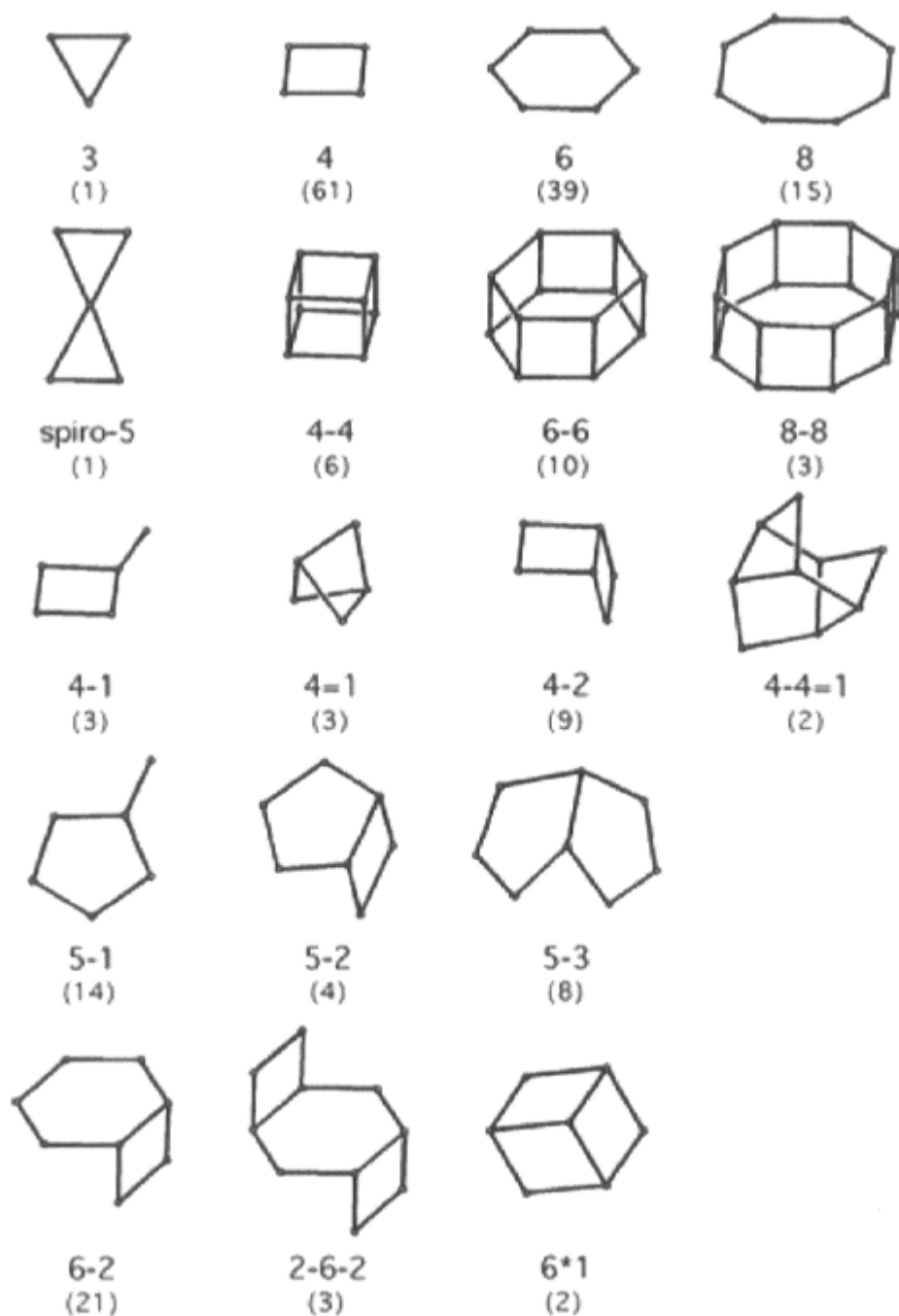


Figure 2.1. Secondary building units and their symbols. Number in parenthesis indicates frequency of occurrence

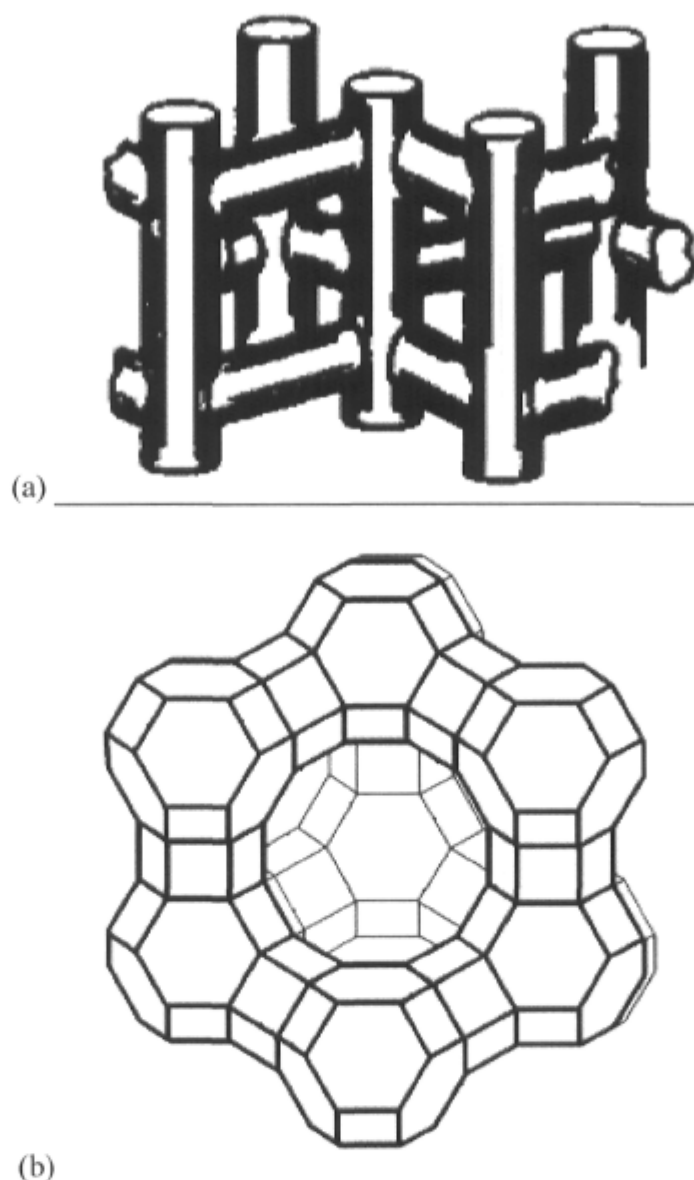


Figure 2.2. (a) MFI and (b) FAU structures

The FAU structure (structure of zeolite Y) is made up of 6-6 SBUs. In addition, it is possible to consider the sodalite cage, a truncated octahedron that has eight hexagonal and six square faces, as basic structure of zeolite Y. The FAU structure is formed when half of the octahedral faces are joined together to form hexagonal prisms. The spherical internal cavity generated when eight sodalite cages are joined is called the α -cage (or supercage) and is about 13 Å in diameter. Entry into the spherical α -cage can occur through four identical openings that are 7.4 Å wide. The dimensions of Y zeolite allow reasonably large

molecules to penetrate the internal pores, since compounds may extend through a prism into two connecting α -cages.

2.1.3. General properties of zeolites

As mentioned above, the presence of Al in the structure of zeolites results in the formation of anion sites within the framework. Charge neutralization may occur by either protonation or by interaction with a metal cation or a hydronium ion. Thus, both Brønsted and Lewis acidities may be present within the zeolite framework. The protonation of the Al-O-Si oxygen center can result in Brønsted acidity in the zeolites structure. Lewis acidity is typically related to the compensating metal ions and defects in the aluminosilicate framework. Brønsted acid sites in zeolites can change into Lewis acid sites through dehydroxylation on heating [27].

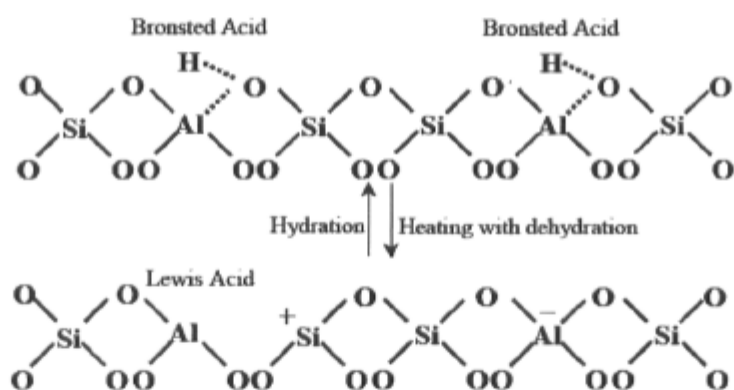


Figure 2.3. Inter-conversion of Brønsted and Lewis acid sites [27]

Although zeolites are usually considered acid catalysts, cation substitution with Rb and Cs, as well as metal doping, creates a basic zeolite [28]. The presence of heavy metal cations is believed to increase the negative charge on the aluminum center, which is transferred to the adjacent oxygen atom, creating a basic site [29,30].

The hydrophobicity is an important characteristic of zeolites since it can have a profound influence on their chemical reactivity. Zeolites containing charges are normally hydrophilic materials that, depending on the framework Si/Al ratio, can be more or less selective adsorbents for polar or nonpolar molecules. However, silicalite-1 which is a pure silica zeolite is a highly hydrophobic material. In contrast, FAU zeolite with the Si/Al ratio between 2 and 5 is a highly hydrophilic adsorbent. It is then clear that the polarity of a given zeolite could be controlled by controlling the Si/Al ratio by direct synthesis or by postsynthesis treatments, and this, together with appropriate control of the number of silanol groups by synthesis or postsynthesis treatments should make it possible to prepare zeolite catalysts within a wide range of surface polarities [31].

2.1.4. Applications

Since their successful introduction as commercial molecular sieves in 1954, synthetic zeolites have grown to an estimate \$1.6-1.7 billion industry of which detergents represent the largest volume (in terms of mass) [32]. LTA-type zeolites have been used to substitute phosphate compounds in the water softening process in laundry. However, the largest market value for zeolites is in refinery catalysis. FCC (Fluid Catalytic Cracking) catalysts account for more than 95% of zeolite catalyst consumption and consist of various forms of zeolite Y. MFI-type zeolites are the second most used catalyst, primarily because they are added to FCC catalysts for octane number enhancement. Zeolites are also employed in the drying and purification of natural gas, separation of paraffins and desulfurization processes. Zeolites are also used in fine chemicals production such as oxidation and acylation [32].

Zeolite science appears to be a mature science and is still a very dynamic field. Discoveries of new zeolites continuously open new areas of development. New trends at the beginning of this century include environmental applications such as De-NO_x catalysis and hydrocarbon storage in vehicles powered with diesel or gasoline engines, and biopharmaceutical applications. Zeolites can also be used in the nuclear industry for radioactive waste storage. Applications of zeolite material science still play an important role in many areas of technology.

2.2. Nanozeolites

2.2.1. Background

Nanozeolites are a type of zeolites which have narrow particle size distribution with sizes of less than 200 nm [33]. Compared to “ordinary” zeolites of which the particle diameters are of micrometer order, nanozeolites represent very small particle size, the narrowness of their particle size distributions (often monodisperse) and especially, the fact that they are composed of discrete particles (single crystal) rather than aggregates.

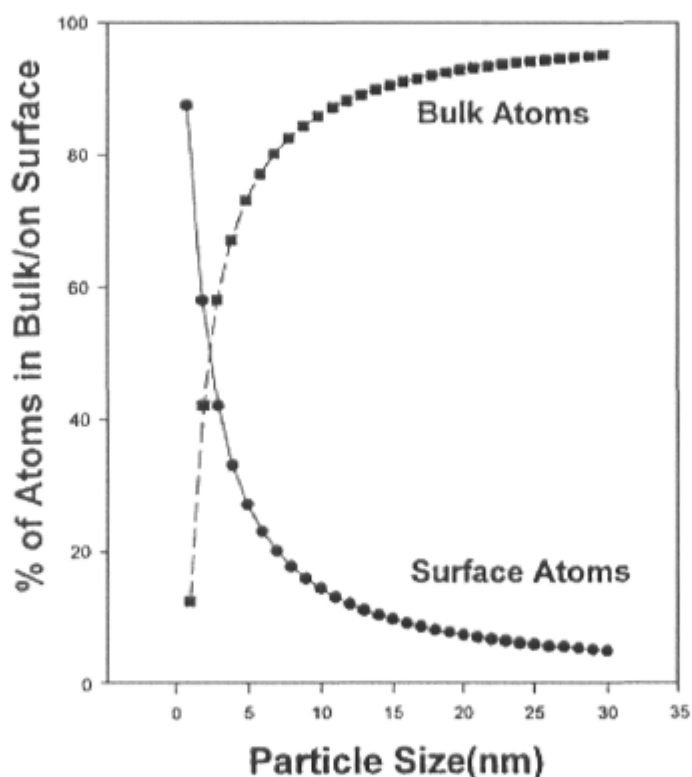


Figure 2.4. Calculated surface to bulk atom ratios for spherical nanocrystals [37]

One of the advantages of nanozeolites is their higher external surface area. The external surface is of vital important in numerous processes, including adsorption and catalysis. For example, in the fluidized catalytic cracking (FCC) process, the commercial catalysts are manufactured by dispersion of 1 micron FAU and MFI zeolites in an amorphous alumina-silica matrix. For cracking to occur, gas oil molecules must pass

through the matrix and reach the surface of the zeolite crystals. The molecules then diffuse through the micropores of zeolites until they reach an active site. Due to the zeolite structure, molecules larger than 7.4 Å cannot reach active sites located inside the zeolites. This problem can be avoided by replacing the micrometer-sized zeolites with the corresponding nanozeolites. The substitution could lead to a decrease in the diffusional resistance and an increase in the external surface area, hence raising the number of active sites available for large molecules [34-36]. Zeolite particles in the 10-100 nm range can bring in new applications of zeolites. The huge surface areas of the nanosized materials dictate that many of the atoms are on the surface, thus allowing good “atom economy” in surface-gas and surface-liquid reactions. Figure 2.4 illustrates the calculated numbers of atoms on spherical solid nanoparticles (iron) that are surface or bulk (interior) atoms. The ratio of atoms available on the surface increases as the crystal size decreases. A 20 nm particle has about 10% atoms present on the surface. This feature demonstrates that it is necessary to be very small in order to benefit from the atom economy desired [37].

Besides the improvement on the external surface areas, nanozeolites have been found to be excellent “building blocks” for constructing structured materials [38]. Hierarchical porous materials with controlled porosity microstructure are of great interest for catalysis and separation applications [39-43]. These porous structures can be fabricated by templated self-assembly of silicalite nanocrystals (nanosilicalite-1) and the structures so obtained include long zeolite fibers, micro-patterned zeolite films and micro-macroporous zeolite structures. The use of preformed zeolite nanocrystals for preparation of supported zeolite films and membranes is one of major applications of nanozeolites. The small size of nanozeolites offers high homogeneity and intactness of the zeolite layer and reduces the number of defects in the film, such as crack and pinholes.

2.2.2. Synthesis

A number of nanozeolites with different structures have been synthesized such as FAU, MFI, LTA, MOR... Most of them were prepared using clear solutions or gels, however, other methods such as confined space synthesis and synthesis using growth inhibitor have been found to be useful to synthesize these materials.

2.2.2.1. Synthesis from clear solutions

The synthesis of nanozeolites from clear solutions was first discovered by Shoeman et al. [45] and Verduijn [76]. Since then this method has been widely used in the synthesis of nanozeolites (Table 2.1).

Table 2.1. Molecular sieve types synthesized in nanosized form, synthesis conditions, and crystal size [33]

Type	Molar composition of the clear synthesis solution (S) or gel (G)	Temp, °C	Crystal size range, nm	ref
FAU	5.5Na ₂ O:1.0Al ₂ O ₃ :4.0SiO ₂ :190H ₂ O (G)	60	20-100	44
LTA	2.0-2.3(TMA) ₂ O:0.2-0.5Na ₂ O:Al ₂ O ₃ :3.4SiO ₂ :370H ₂ O (S)	100	230-240	45
	1.2(TMA) ₂ O:0.42Na ₂ O:Al ₂ O ₃ :3.62SiO ₂ :246H ₂ O (S)			46
FAU	2.46(TMA) ₂ O:0.04Na ₂ O:Al ₂ O ₃ :3.4SiO ₂ :370H ₂ O (S)	100	100	
	1.576(TMA) ₂ O:0.044Na ₂ O:Al ₂ O ₃ :3.62SiO ₂ :246H ₂ O (S)			46
FAU	0.15Na ₂ O:5.5(TMA) ₂ O:2.3Al ₂ O ₃ :10SiO ₂ :570H ₂ O (S)	100	40-80	
LTA	1.12-3.6SiO ₂ :1.0Al ₂ O ₃ :1.5-7(TMA) ₂ O:0.007-0.28NaCl:276-500H ₂ O (G)	100	50+130-900	47,48
FAU	3.4SiO ₂ :0.83-1.7Al ₂ O ₃ :2.3(TMA) ₂ O:0.1NaCl:300H ₂ O (G)	100	80	49
FAU	4Na ₂ O:0.2Al ₂ O ₃ :1.0SiO ₂ :200H ₂ O (G)	25	100-300	49
FAU	1.00Al ₂ O ₃ :4.35SiO ₂ :1.40-3.13(TMA) ₂ O(2OH ⁻):0-2.40(TMA) ₂ O(2Br ⁻): 0.048Na ₂ O:249.00H ₂ O (S)	100	32-120	50
FAU	2.46(TMA) ₂ O:0.032-0.43Na ₂ O:1.0Al ₂ O ₃ :3.40SiO ₂ :370H ₂ O:13.6EtOH (S)	100,130,100+130	75-137	51,52
LTA	6.1-15.8SiO ₂ :Al ₂ O ₃ :17Na ₂ O:0.9-6.5(TMA) ₂ O:389H ₂ O:3 ⁺ PrO ₂ (~S)	80	50-100	53,54
LTA	0.3Na ₂ O:11.25SiO ₂ :1.8Al ₂ O ₃ :13.4(TMA) ₂ O:700H ₂ O (S)	22	40-80	55
LTA	0.22Na ₂ O:5.0SiO ₂ :Al ₂ O ₃ :8.0(TMA) ₂ O:400H ₂ O (S)	63	130	56
SOD	14(TMA) ₂ O:0.85Na ₂ O:1.0Al ₂ O ₃ :40SiO ₂ :805H ₂ O (S)	100	37	57
ZSM-12	1.52(TMA) ₂ O:0.53Li ₂ O:0-0.08Na ₂ O:3.4SiO ₂ :315H ₂ O (S)	100	49-108	58
GIS	1Al ₂ O ₃ :4.17SiO ₂ :2.39(TMA) ₂ O:253H ₂ O (S)	100	30-50	59
OFF	2.78(TMA) ₂ O:0.47-0.98K ₂ O:0-0.5Na ₂ O:Al ₂ O ₃ :9.90H ₂ O:91H ₂ O (n.s.)	85	45-60	60

OFF	10SiO ₂ :1.0Al ₂ O ₃ :110-220H ₂ O:0.12Na ₂ O:0.5K ₂ O:3-4.5(TMA) ₂ O (G)	100	30-250	61,62
MOR	6Na ₂ O:2Al ₂ O ₃ :30SiO ₂ :780H ₂ O+seeds (G)	150	63	63
LTL	10-12.5K ₂ O:1.0Al ₂ O ₃ :16-40SiO ₂ :250-450H ₂ O (S)	140-190	30-70	64
LTL	10K ₂ O:1Al ₂ O ₃ :20SiO ₂ :400H ₂ O (S)	175	50-60	65
LTL	8.0K ₂ O:Al ₂ O ₃ :20SiO ₂ :200H ₂ O (n. s.)	72.5,82.5,92.5	30-75	66
LTL	0.005BaO:0.25K ₂ O:0.08Al ₂ O ₃ :1.0SiO ₂ :15H ₂ O (G)	170	140	67
BEA	Al ₂ O ₃ :16-400SiO ₂ :5.16-105(TEA) ₂ O:240-6400H ₂ O (G)	140	10-200	68
BEA	0.48Na ₂ O:9TEAOH:0.25Al ₂ O ₃ :25SiO ₂ :295H ₂ O (S)	100	60	69,70
BEA	SiO ₂ :0.2(TEA) ₂ O:11.8H ₂ O (S)	100	100	71
MFI	5-9TPAOH:0-0.3Na ₂ O:25SiO ₂ :0-0.25Al ₂ O ₃ :480-1500H ₂ O (S)	98	130-230	72
MFI	1Al ₂ O ₃ :60SiO ₂ :21.4TPAOH:650H ₂ O (S)	170	10-100	73
MFI	9TPAOH:0.16Na ₂ O:1Al ₂ O ₃ :50Si:300-495H ₂ O:0/100EtOH (S)	165	15-60	74
MFI	Al ₂ O ₃ :60SiO ₂ :11TPAOH:900H ₂ O (S)	70,90	10-20	75
MFI	0/0.53Na ₂ O:0.62-1.52(TPA) ₂ O:10SiO ₂ :60/143H ₂ O (S)	50,60,80	25-80	76
MFI	9TPAOH:0/0.1Na ₂ O:25SiO ₂ :480/1500H ₂ O:100EtOH (S)	98	95-180	77
MFI	0.01-0.443TPAOH:20-80H ₂ O:TEOS (S)	115	>90	78,79
MFI	9TPAOH:25SiO ₂ :480H ₂ O:100EtOH (S)	60,80,60+100,80+100	60-80	80
MFI	3-13TPAOH:25SiO ₂ :480H ₂ O:100EtOH (S)	95	>100	81
MFI	3.0/4.5/9.0TPAOH:16NaOH:50SiO ₂ :495/2000H ₂ O:100EtOH (S)	60-98,165	20-1000	82
MFI	0.27Na ₂ O:5TPAOH:25SiO ₂ :420H ₂ O (S)	22+230	130-260	83
MFI	9TPAOH:25SiO ₂ :0.13Na ₂ O:595H ₂ O:100EtOH (S)	60,100	60-170,100-300	84
MFI	9TPAOH:25SiO ₂ :0.13Na ₂ O:595H ₂ O:100EtOH (S)	22+60,22+100	55-160,70-230	85
MEL	0.55Na ₂ O:1.26(TBA) ₂ O:10SiO ₂ :150H ₂ O (S)	67.5,90	50-200	86
MEL	SiO ₂ :0.3TBAOH:4.0EtOH:18H ₂ O (S)	22+100	90	87

MEL	0.35TBAOH:1.0TEOS:12H ₂ O (S)	60-90	114	87
MFI	9TPAOH:0.25TiO ₂ :25SiO ₂ :404H ₂ O:100EtOH (S)	100	85	88
MFI	0.36TPAOH:0.06TiO ₂ :1.00SiO ₂ :16.2H ₂ O:4EtOH:0.24BuOH (S)	22+175(mw)	<100	89
AFI	0.7-1.1(TEA) ₂ O:0.6-1.0Al ₂ O ₃ :1.1P ₂ O ₅ :50H ₂ O (G)	160, 150-160(mw)	50-300	90,91
AFI	1(TEA) ₂ O:1Al ₂ O ₃ :1.32P ₂ O ₅ :110H ₂ O (G)	90,110,160(mw)	80-600	92
AEL	1.6 <i>i</i> -Pr ₂ NH:1.3-1.73P ₂ O ₅ :1.1Al ₂ O ₃ :35/70H ₂ O:0/0.8-1.2HF (G)	160,200	100-800	93
AEI	1Al ₂ O ₃ :3.16P ₂ O ₅ :3.16(TEA) ₂ O:186H ₂ O (S)	100,150,170	120-240	94

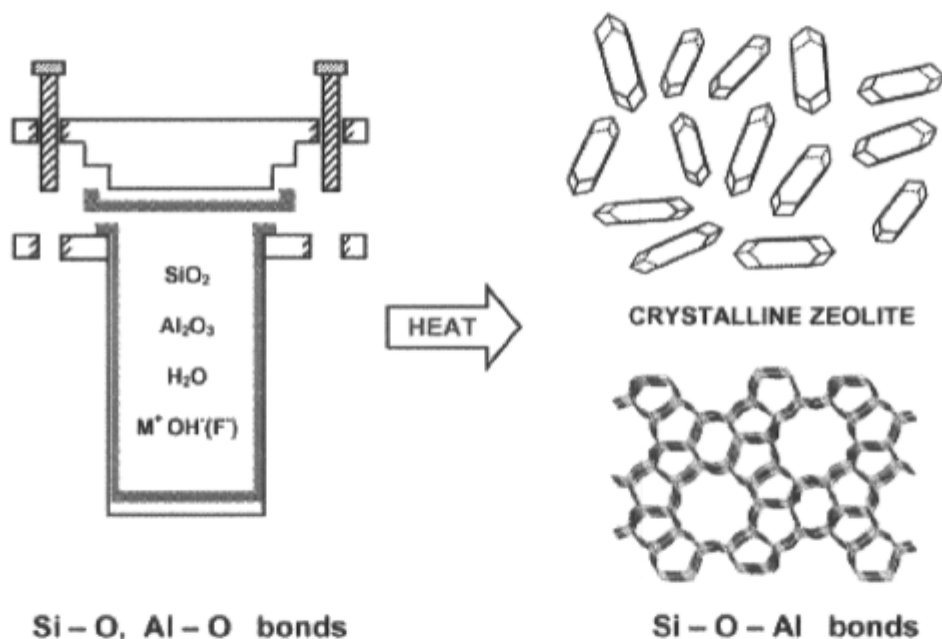


Figure 2.5. Synthesis of nanozeolites from clear solutions [95]

A typical synthesis of nanozeolites using this method can be described as follows (Figure 2.5):

- Amorphous reactants containing silica and alumina are mixed together with a structure directing agent (SDA) source, usually in a basic (high pH) medium, resulting in a clear solution.

- The aqueous reaction mixture is heated, often (for reaction temperatures around 100 °C) in a sealed autoclave.

- For some time after raising to synthesis temperature, the reactants remain amorphous.

- After the above “induction period”, crystalline zeolite product can be detected.

- Gradually, essentially all amorphous material is replaced by an approximately equal mass of zeolite crystals (which are recovered by filtration, washing and drying).

Crystallization Mechanism of nanozeolites from clear solutions

Although the crystallization mechanism of zeolites has not been well understood, it has been accepted that the synthesis of nanozeolites in clear solution involves the assembly of very tiny species present in the pre-crystallized solution. For example, in the crystallization of silicalite-1, an all-silica and hydrophobic zeolite, it was revealed by de Moor et al. [96] that hydrophobic silicates and structure directing agents (SDA) are assembled by hydrophobic interaction, which results in the formation of primary units (ca. 2.8 nm) in the solution prior to nucleation. Subsequently, the nucleation occurs via aggregation of primary units. The primary units are also incorporated directly into the crystalline phase during crystal growth. As a result, nucleation and subsequent crystal growth mechanisms are described by a cluster aggregation scheme (Figure 2.6). Further study was carried out by Jacobs et al. [97-101]. The silica species in an aged clear sol (which crystallizes silicalite upon heating) were extracted. The resulting powder was characterized by a wide variety of methods leading to the identification of constituent "nanoslabs" having dimensions $1.3 \times 4.0 \times 4.0$ nm and having the MFI structure with nine intersections per particle, each constituent unit containing a TPA cation (Figure 2.7a). Aggregation of precursor units leads to larger particles measuring up to $15.6 \times 8 \times 8$ nm

and ultimately to the crystalline colloidal MFI-type material which forms the final product of the synthesis (Figure 2.7b). Hence, the authors proposed that the formation of the final silicalite-1 crystals is resulted from stacking the nanoslabs.

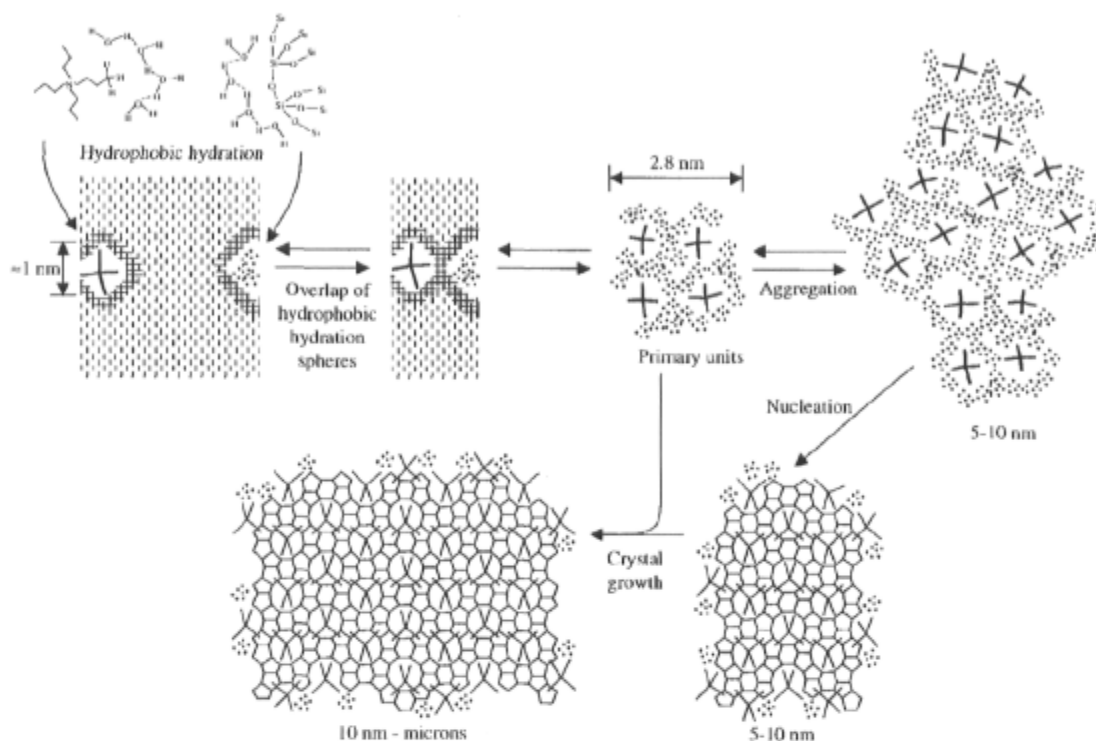


Figure 2.6. A scheme for the crystallization mechanism of silicalite-1 [96]

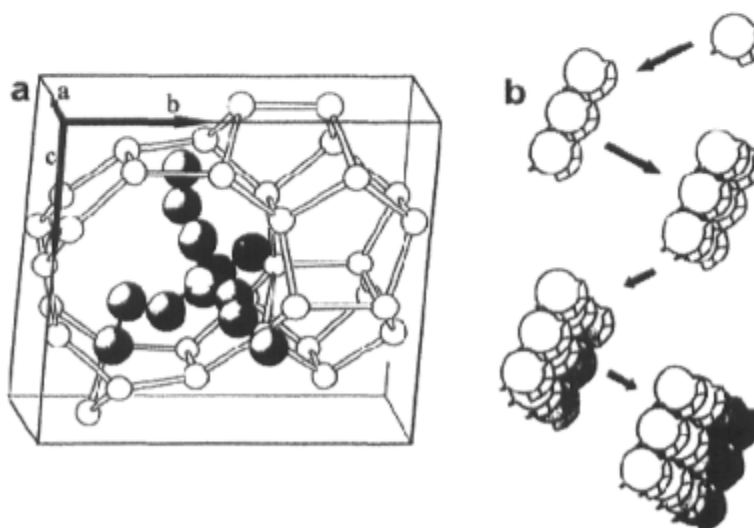


Figure 2.7. The "nanoslab" hypothesis: (a) the precursor unit containing one TPA cation and (b) schematic representation of nanoslab formation by aggregation of precursor units, as determined by XRS and GPC [100]

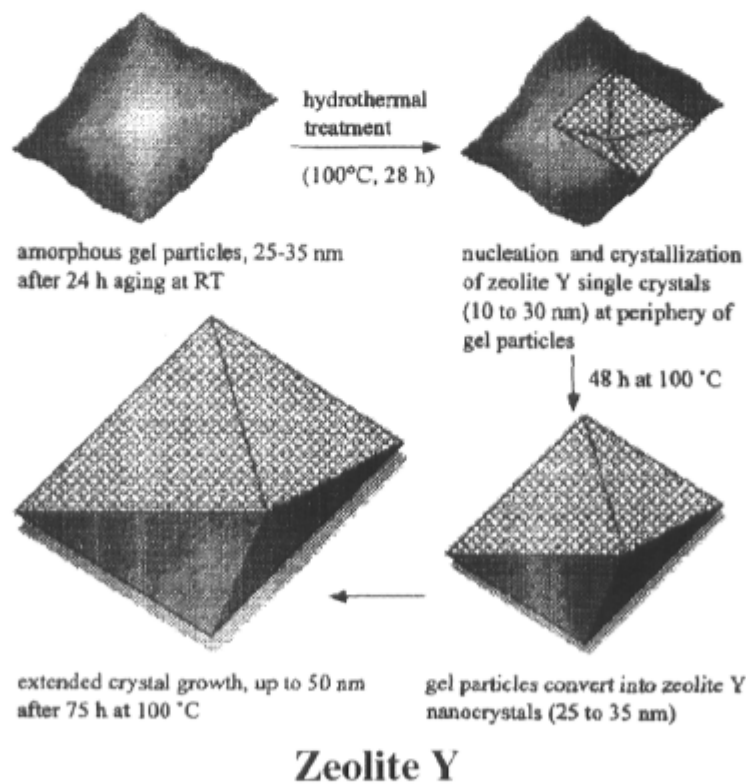
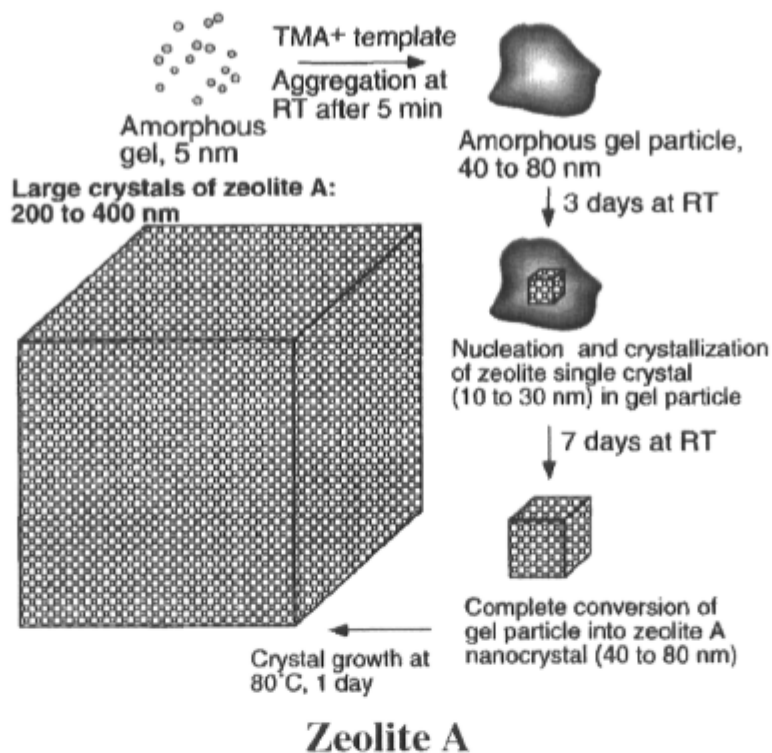


Figure 2.8. Nucleation and growth model of zeolite A and zeolite Y as represented by TEM [47,102]

In the crystallization of hydrophilic zeolites (low Si/Al zeolites) using clear solution method, the presence of nanosized amorphous gel particles in the pre-crystallized solution were also found [47,102]. From the TEM observations, Mintova et al. [47,102] revealed that, these amorphous gel particles have different sizes, depending on the starting materials and the zeolite structure. The particles in the synthesis of nanozeolite A were about 5 nm whereas, those in the synthesis of nanozeolites Y were 25-35 nm. The authors proposed that the mechanism involved the aggregation of these particles (Figure 2.8).

Parameters affecting the crystal size

From the perspective of crystallization theory, the crystal size is a function of the ratio between rate of nucleation and rate of growth [103]. Thus, to obtain nanozeolites, one should optimize the following conditions: (i) attaining very high nucleation rates and (ii) providing stabilization of nucleated entities. The first condition is controlled by many parameters such as temperature, alkalinity, aging... whereas, the second one depends chiefly on the role of SDAs. Here is a brief review of these parameters.

- Temperature: a low crystallization temperature (80 – 100°C) is often applied. This is because temperature raises growth rate more than nucleation rates. However, it should be noted that a too low temperature usually results in poor crystallinity, low efficiency, and longer crystallization time.

- Aging: the aging of the synthesis mixture at room temperature has significant influence on the nucleation rates. This is due to the fact that nucleation rate is favored at room temperature, but the growth rate is negligible, and thus the nuclei prevail until the temperature is raised.

- Alkalinity: the concentration of OH⁻ ions strongly increases the solubility of silicate species. In general, smaller zeolite crystals tend to be formed at higher alkalinity.

- The concentration of the clear solution strongly affects the degree of saturation of the system. At lower supersaturation, growth is favored at the expense of nucleation.

Dilution of the solution can cause large crystals to form. Hence a high concentration is a desired parameter.

- The solubility of the silica source plays an important role in the synthesis of nanozeolites. Smaller crystals are formed from monomeric silicate solutions than by dissolution of colloidal silica.

- Metal cations usually facilitate the crystal growth. Hence, they should be present in the synthesis solution at low concentration. For example, it has been found that sodium is the growth-limiting nutrient in the formation of Y-type zeolite [45, 104]. The crystallizations of Y-type and A-type zeolites are very sensitive to sodium content. In some cases, a small variation in this factor results in the formation of a different crystal phase, for the synthesis of zeolites with the clear synthesis gel having molar composition of $2.46 (\text{TMA})_2\text{O} : x \text{Na}_2\text{O} : 1.0 \text{Al}_2\text{O}_3 : 3.40 \text{SiO}_2 : 370 \text{H}_2\text{O} : 13.6 \text{EtOH}$ ($0.03 < x < 0.43$), the sodium concentration of the batch is crucial for controlling which zeolite phase crystallizes. Greater $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio (0.43) in the batch favors the formation of zeolite A with a higher yield of 56.5% after a shorter crystallization time. Lower $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio (0.03) in the batch produces smaller zeolite Y crystals with a lower yield of 8.1% after a longer crystallization time.

- Structure directing agent (SDA): SDAs are often quaternary of the type $[\text{R}_4\text{N}]^+\text{OH}^-$ (where R is an alkyl group, typically CH_3 , C_2H_5 , C_3H_7 or C_4H_9). The presence of SDA in the synthesis solution helps assist the formation of a desired zeolite structure. Furthermore, SDA is responsible to the stabilization of silicate subcolloidal particles [105] as well as the nanozeolites [97]. In the synthesis of nanosilicalite-1 using tetrapropylammonium hydroxide (TPAOH) as SDA, it was revealed [97] that, there were two different environments for the TPA^+ cation: (i) TPA^+ occluded in the channel intersections and (ii) TPA^+ adsorbed on to the external surface of the particles. Bulky quaternary ammonium cations adsorbed on to particle surfaces provide steric stabilization, preventing aggregation upon collision. In an aqueous medium, zeolite particles will acquire a negative surface charge due to dissociation of the surface silanol groups. Such a surface charge will cause organic cations in the surrounding solution to align along the particles' surface, creating an electric double layer. This stabilizing barrier of bulky organic cations restricts the close

approach of similar particles, such that the attractive potential between them is insufficient to cause aggregation or flocculation.

2.2.2.2. Synthesis using growth inhibitor

The synthesis of nanozeolites using growth inhibitor is in fact derived from the synthesis from clear solution. In this method, an organic additive other than SDA is introduced to inhibit the growth process, thus resulting in small zeolite crystals. The reactivity of the additive and its content in the synthesis mixture are two significant factors. The additive should be able to adsorb onto or react with the surface of the silicate particles, thus protecting them from further aggregation. If the concentration of the additive is too high, zeolite might not be obtained since there would be not sufficiently free aluminosilicate species for the formation of zeolite structure. In contrast, if the concentration is too low, the inhibition effect might be inadequate.

Hosokawa and Oki [106] revealed that, a nonionic surfactant (polyoxyethylene lauryl ether, C12E6) and polyethylene glycol (PEG 600) were able to act as growth inhibitors in the synthesis of nanosized A-type zeolites. The inhibitor was added with the synthesis mixture prior to crystallization. TEM investigation showed that the resulting zeolite A was in the form of aggregated 30 – 40 nm particles, which was nearly similar to the size of the aluminosilicate precursor species available in the synthesis gel prior to crystallization. This observation indicated that the growth of the zeolite crystals should be almost inhibited.

The introduction of a growth inhibitor can be postponed until viable zeolite precursors become prevalent. Thus the undesired interference of the inhibitor in the formation of precursors is avoided. This approach was developed by Naik et al. [107] for preparation of nanosilicalite-1. The procedure involves: (i) prepare a clear solution that is known to produce colloidal TPA-silicalite upon extended hydrothermal reaction; (ii) subject the solution to hydrothermal condition but stop before the appearance of colloidal silicalite; (iii) protect the TPA-silicalite precursor nanoparticles with cationic surfactant (CTABr) and collect them as flocculated mass; (iv) convert the precursor/surfactant hybrid

into nanocrystals via high temperature steaming. A steaming temperature of 150 °C was found enough to convert the collected precursor into nanocrystals. The obtained nanocrystals were smaller than 30 nm. However these particles are hard aggregated and cannot be redispersed in water.

Recently, Serrano et al. [108] have reported the use of organosilane as the growth inhibitor. Organosilane is a good silylating agent which has been widely used for the functionalization of zeolites. According to the author, MFI and beta zeolites were successfully synthesized, using phenylaminopropyl-trimethoxysilane (PHAPTMS). The synthesis is based on reducing the growth of zeolite crystals by silanization of the zeolitic seeds to hinder their further aggregation. Typically, the synthesis of MFI zeolite is as follows: a clear solution of TPA-aluminosilicate was produced. The precursor solution was precrystallized under reflux with stirring (100 rpm) at 90 °C for 20 h. Then, the zeolite seeds obtained were functionalized by reaction with PHAPTMS at 90 °C for 6 h. Finally, the resulting solution was subjected to hydrothermal treatment at 170 °C for 5 days. However, as investigated by TEM analysis, the MFI sample obtained consisted of particles of about 300 – 400 nm which were formed by aggregate of ultra small primary units of 10 nm. Having that large size, the sample was hardly considered as true nanozeolite.

2.2.2.3. Confined space synthesis

In the field of zeolite science, the term “confined space” was first used by Jacobsen et al. [17-18] in 1999 to describe a novel method for zeolites synthesis which allows preparation of nanosized zeolites crystals with a controlled crystal size distribution. The principle of confined-space synthesis is to synthesize the zeolite inside the mesopores of an inert matrix. The maximum crystal size is limited by the diameter of the mesopores as shown in Figure 2.9.

The zeolite gel is introduced into the mesopores of the matrix by sequential incipient wetness impregnations the matrix with the gel precursor solution. For the synthesis of ZSM-5, the carbon black was impregnated to incipient wetness with a clear solution of TPAOH, H₂O, NaOH and ethanol. After aging for 3 h at room temperature, the

carbon black was subjected to hydrothermal treatment at 180 °C for 48 h in an autoclave. The product was then recovered by calcination to remove the matrix [17].

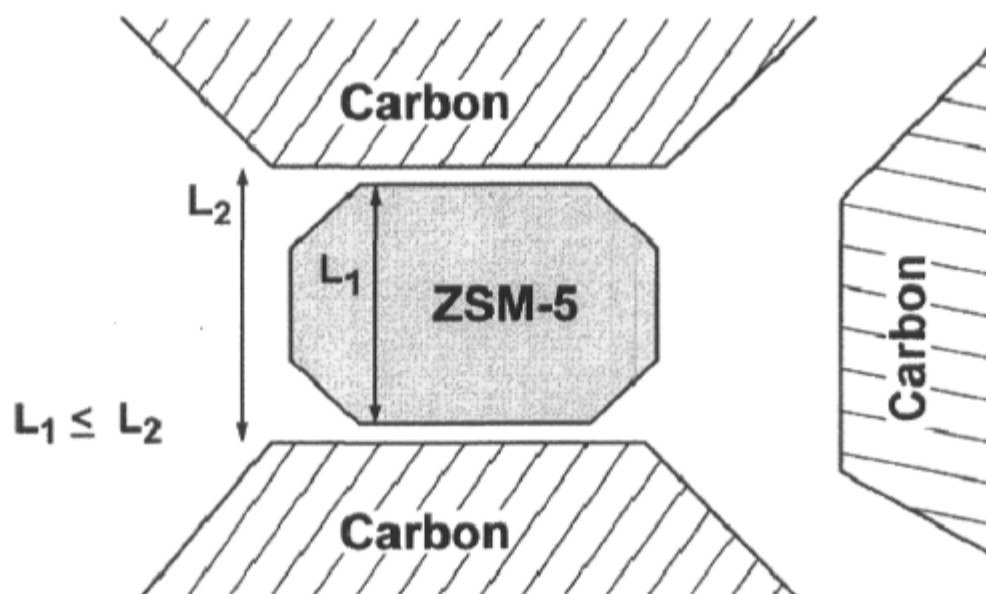


Figure 2.9. Schematic illustration of confined space synthesis [18]

This method has also been applied to the synthesis of beta, X and A zeolites [18,19]. Two carbon black matrixes were used with a pore diameter of 31.6 and 45.6 nm, respectively. Generally, the crystal size distributions of the zeolites obtained were governed by the pore size of the carbon black matrix and were typically in the range 30-45 nm. Crucial factors in the synthesis are (i) restriction of the crystallization of the zeolite gel within the pore system of the matrix, which was achieved by the incipient wetness impregnation method employed to load the mesopores with a synthesis gel, and (ii) prevention of diffusion of the zeolite gel species from the mesopores, which was ensured by avoiding direct contact between the impregnated carbon black matrix and the water at the bottom of the autoclave [33]. Jacobsen et al. [20] later reported that the failure in controlling these two factors could lead to the formation of mesoporous zeolites rather than nanozeolites. Although the confined space synthesis by these authors eliminates the

problem of recovering nanocrystals from solution, it has its own drawback. For example the carbon matrix must have a uniform distribution of mesopores to ensure the size distribution of the product. Careful procedures were needed to impregnate the synthesis solution just inside not outside. And finally, the zeolite particles are aggregated and not discrete.

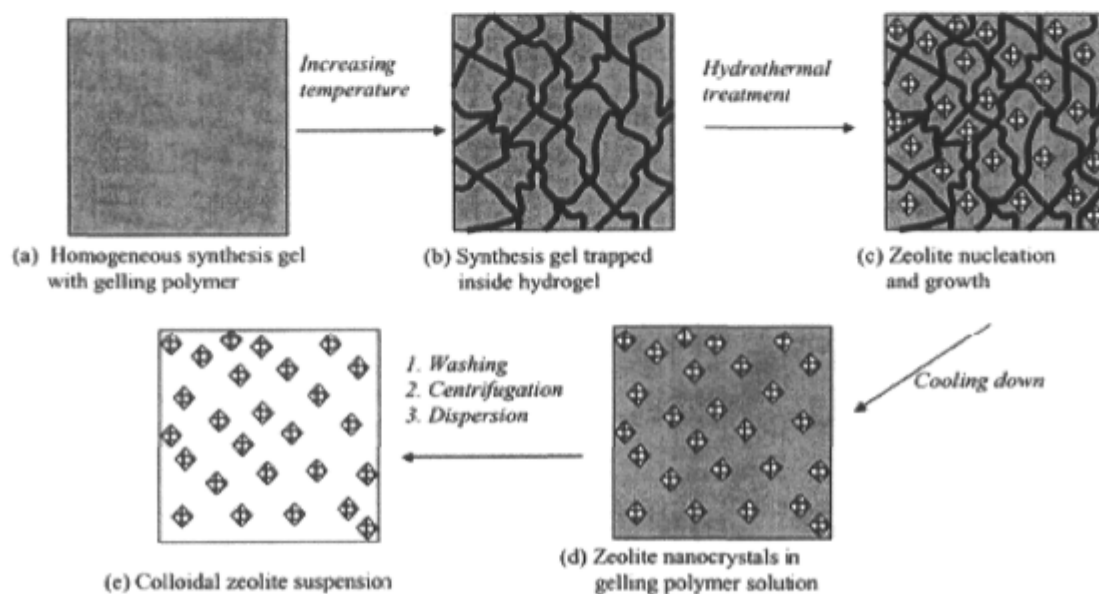


Figure 2.10. Schematic representation of synthesis of template-free zeolite nanocrystals by using in situ thermoreversible polymer hydrogels [21].

Another type of confined space synthesis has been developed by Wang et al. [21]. The technique works on the thermoreversibility of gelling polymers. These polymer gels are hydrogels with three-dimensional networks of polymer chains that are cross-linked via either physical or chemical bonds, and they can entrap a large volume of water. The interesting gelation behavior of thermoreversible polymer hydrogels is that it is reversibly responsive to temperature. In particular, the polymers gel at elevated temperatures and turn back to solution at room temperature. This feature is attractive because the temperature profile of their solution-gel transition can very nicely fit that of hydrothermal synthesis of zeolite. The three-dimensional pores of polymer hydrogels can potentially serve as microreactors or nanoreactors for controlling zeolite growth. The general synthesis

procedure is illustrated in Figure 2.10 [21]. A (20 – 180 nm) and X (10 – 100 nm) zeolites were prepared using this technique, however, the size distributions were broad. In addition, this method encounters the following difficulties: (i) Gelation of methyl cellulose is complicated. The thermoreversibility depends strongly on the heating and cooling rates. Any variation in these rates can lead to different gel properties [109]. (ii) It is difficult for the gelation of methyl cellulose to occur in the presence of zeolite synthesis gel since the highly basic content of the gel facilitates the solubility of methyl cellulose [110]. (iii) The authors applied slight hydrothermal conditions to prepare A and X zeolites, i.e. at 80°C for 2 – 3 h. However, for the synthesis of other zeolite structures, the conditions generally involve the temperature higher or equal to 100°C and crystallization time of several days. It is likely that the gel structure of methyl cellulose would not be able to be maintained under these hard conditions.

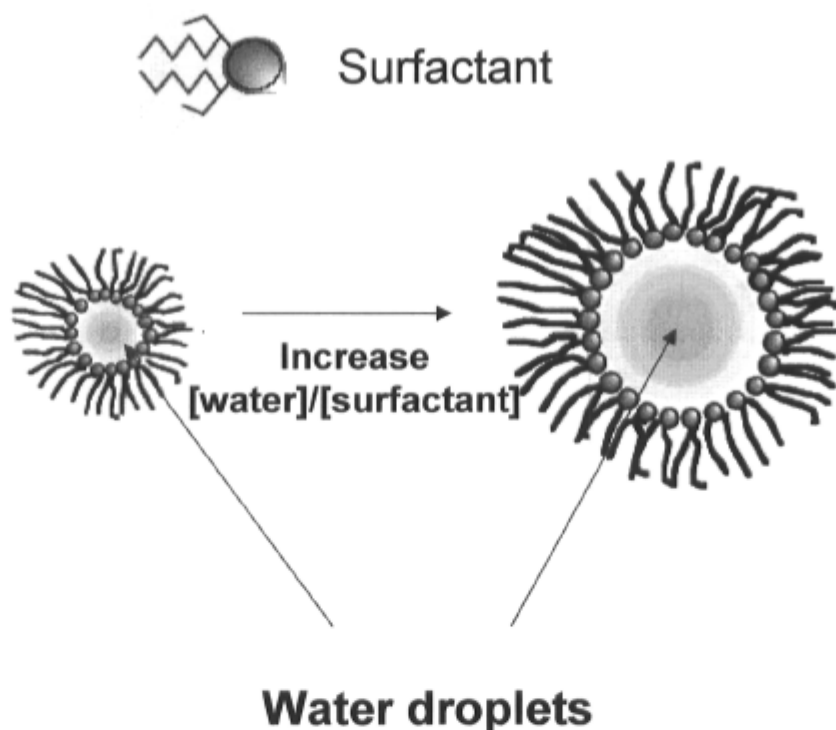


Figure 2.11. Schematic representation of reversed microemulsion [111]

Finally, it would be worth mentioning the synthesis of nanozeolites using microemulsion. Microemulsions are colloidal ‘nano-dispersions’ of water in oil (or oil in

water) stabilized by surfactants [111]. These thermodynamically stable dispersions can be considered as true nanoreactors which can be used to carry out chemical reactions and, in particular, to synthesize nanomaterials. The main idea behind this technique is that by appropriate control of the synthesis parameters one can use these nanoreactors to produce tailor-made products down to a nanoscale level with new and special properties (Figure 2.11). Reversed microemulsions have been widely used to prepare inorganic nanoparticles [111,112]. Thus, the application of this technique in the synthesis of nanozeolites is of interest. The first attempt of using microemulsion to prepare zeolites can be credited to Dutta et al. [113,114]. The authors reported the synthesis of 1 – 2 μm A-type zeolite and 0.6 μm zeolite-type zincophosphate. Nevertheless, the preparation of zeolites is somewhat different from that of inorganic particles. The technique has the following difficulties:

(i) The crystallization of zeolites often involves heating at high temperature. Under these conditions the microemulsion becomes unstable, the nanoreactor effect is not attained. Manna et al. [115] reported the synthesis of silicalite-1 in a microemulsion of tetraethylenepentamine–sodium bis(2-ethylhexyl) sulfosuccinate (AOT)–water system containing fluoride ions. At the crystallization temperature of 170 $^{\circ}\text{C}$, the microemulsion system was destroyed and turned into bicontinuous emulsion. Hence the resulting silicalite-1 crystals were twinned and have large diameter of 4 μm .

(ii) The interaction between surfactant and aluminosilicate species is complicated and can affect the stability of microemulsions and the morphology of zeolites. Shantz et al. [116-118] found that, initially, the microemulsion acts as a confined space, effectively inhibiting zeolite growth in the early stages of synthesis as compared to bulk syntheses. However, once the particles reach a critical size, approximately 100 nm, the effect of surfactant adsorption at the aluminosilicate surface becomes so important that the small particles formed in the microemulsions aggregate to form large particles.

Recently, Chen et al. [119] reported the successful synthesis of 40-80 nm A-type nanozeolite. To overcome the above problems, the microemulsion system containing the synthesis gel was crystallized at a low temperature of 75 $^{\circ}\text{C}$ for very short duration less

than 60 min. To facilitate the crystallization, microwave heating was applied instead of conventional heating. In spite of that, the size distribution is still broad (Figure 2.12).

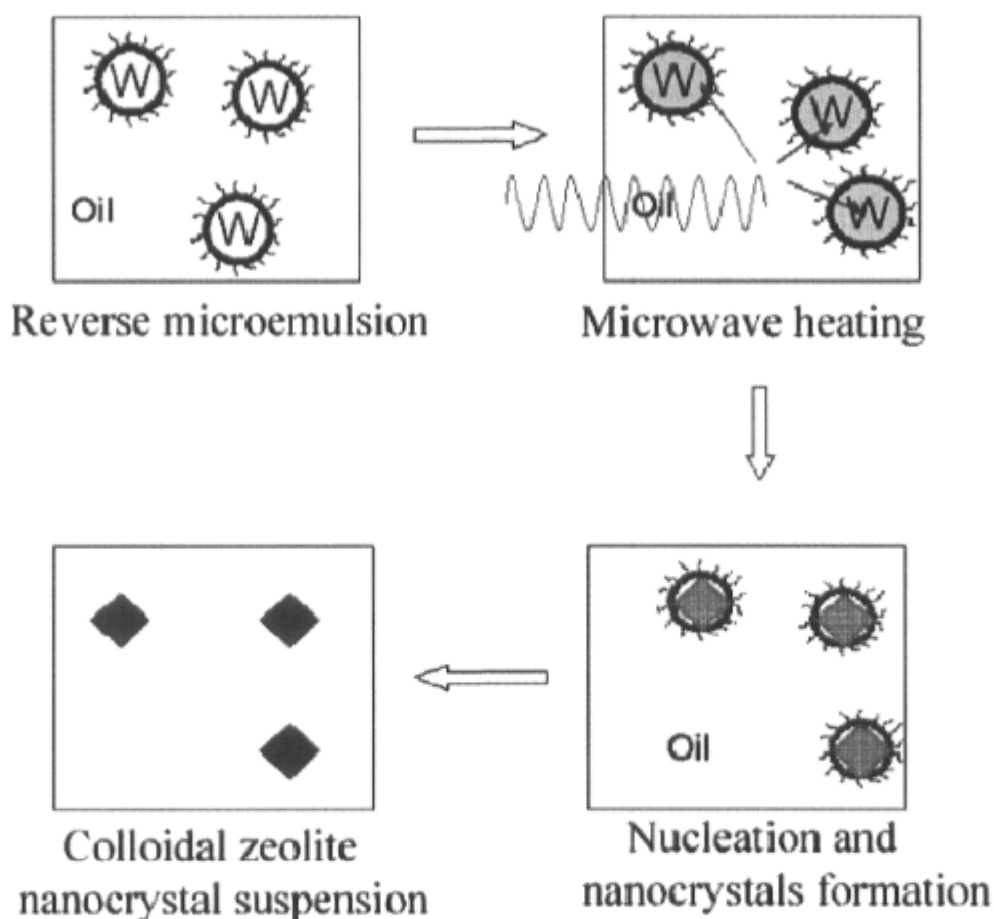


Figure 2.12. Schematic representation of microemulsion-microwave synthetic method [119]

In conclusion, several synthetic routes have been reported for the preparation of nanocrystalline zeolites. However, none of these attempts has produced an easy means of controlling the small size. Furthermore, the external surface of nanocrystalline zeolites is hydrophilic and thereby has significantly silanol groups that limit catalytic reactivity to the internal pore surface [33]. Herein, we demonstrate new approaches for the synthesis of highly uniform nanozeolites with the hydrophobic external surface and controlled crystal

size. An organic solvent is used as a medium for the crystallization instead of water. The zeolite precursors are functionalized with organic silane groups thus become hydrophobic and able to highly disperse in the organic solvent. Because the crystallization occurs in the organic phase and the zeolite precursors are protected by functional groups, the aggregation can be avoided hence resulting in small and uniform nanozeolites with the hydrophobic external surface.