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Highlight Review

Hydrothermal Synthesis and Characterization of Zeolites

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Abstract

Zeolites have been widely utilized in industry and in household products, for example as adsorbents, ion-exchangers, and catalysts, and have attracted considerable attention as host materials for various nanotechnology applications. Recent developments in analytical methods have enabled detailed studies on the crystallization mechanism of zeolites. The purpose of this review is to give a survey of recent progress in hydrothermal synthesis and characterization of zeolites.

♦ Introduction

Zeolites are hydrated, crystalline tectoaluminosilicates that are constructed from TO_4 tetrahedra (T = tetrahedral atom, e.g. Si and Al).[1–4] They contain well-ordered, nanometer-sized void spaces (ca. 3–15 Å) in their structures. Figure 1 shows typical zeolite structures (zeolite A and faujasite). Synthesis of zeolites started in 1945. To date, 152 framework structures have been recognized for zeolites and related materials including tectosilicates and tectoaluminophosphates.[5] The resulting molecular sieving capabilities have enabled use of zeolites as adsorbents (e.g., zeolite A, zeolite Y, and zeolite X), ion-exchangers (e.g., zeolite A and zeolite P) and molecular-sieving membranes. Furthermore, their acidic properties are the basis of heterogeneous acid catalysis used in the petroleum and chemical industries.[6]

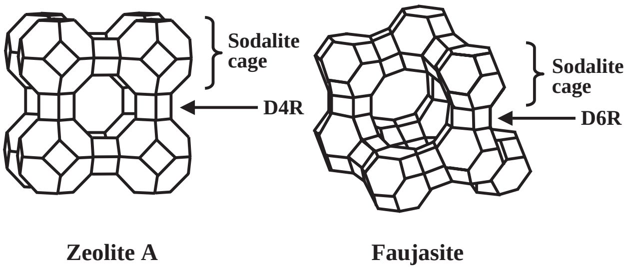

Figure 1. Typical framework structure of zeolites. Because isomorphous replacements are often found in zeolite syntheses, zeolites with different compositions (e.g., Si/Al ratios) of the same structures are produced. Therefore, in accordance with the recommendation of the IUPAC committee on chemical nomenclature of zeolites, each of the framework topologies is represented by "three capital letters".[1] For example, the frameworks of zeolite A and faujasite are described by the designations LTA and FAU, respectively.

In recent years, research into novel, i.e., optical and magnetic applications of zeolites[7–14] based on their unique and regular structures as host frameworks for molecules, ions, and clusters, has been reported. In addition to the internal structure, the external surface of zeolite can be a host for integration of nanoelements such as molecules and clusters, since the external surface provides nanometer-scale periodic structures.[15–21] Recently, some studies on the utilization of the external surface of zeolites for arraying molecules[15–17] and clusters,[18,19] and preparation of carbon nanotubes[20,21] have also been reported.

In summary, zeolites have been widely utilized in industry and in household products, for example as adsorbents, ion-exchangers, and catalysts, and have attracted considerable attention as host materials for various nanotechnology applications.

♦ Synthesis of Zeolites

Most zeolites have been synthesized under hydrothermal conditions. Before the 1960s, zeolites were synthesized using only inorganic reactants. After Si and Al sources and mineralizers such as NaOH or KOH are mixed in water, the hydrogels obtained are heated at prescribed temperatures and crystallized into zeolites. In general, the products obtained have a low Si/Al ratio framework ($Si/Al < 10$) and hydrophilic properties (since the structures contain a lot of anionic Al sites and charge compensation cations such as Na^+ or K^+). In the 1960s, however, a new synthesis method using organic compounds, particularly quaternary ammonium salts, was established.[22] These organic compounds are often called "structure-directing agents (SDAs)" since zeolite structures appear to form around them via hydrophobic interactions; therefore, zeolites with higher Si/Al ratios ($Si/Al > 10$) and hydrophobic frameworks are obtained, in contrast to the zeolites synthesized without SDAs, since there are few anionic Al sites.

Most of the zeolites are produced as "metastable phases" in a thermodynamic sense. For example, in the $Na_2O–Al_2O_3–SiO_2–H_2O$ system, albite, analcime, natrolite, nepheline, sodalite, and montmorillonite, which are so-called "dense phases," are often formed at 300–700 °C. At temperatures lower than 200 °C, however, different zeolites (e.g., zeolite A and faujasite) are formed as metastable phases.[1] Since there are many metastable phases under certain conditions, the products are sometimes obtained as a mixture. Therefore, from an industrial point of view, techniques for the synthesis of zeolite with a single-phase product are very important; the process for the large-scale synthesis of pure faujasite reported by Kasahara et al.[23] is one of

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such examples. In general, zeolite crystallization is readily affected by various experimental factors, e.g., starting composition, pH, temperature, mixing procedure, agitation, and synthesis time. Therefore, the crystallization mechanisms of zeolites are not well understood, and the elucidation is still one of the major topics in zeolite science.[24–48]

Crystallization Mechanism of Zeolites

Zeolite crystallization consists of two parts; nucleation and subsequent crystal growth. So far, two routes of zeolite crystallization have been proposed.[1,2] One is the direct transformation of amorphous intermediates into zeolite structures, and the other is a mediated route; that is, dissolution of amorphous intermediates into soluble species, followed by nucleation and crystal growth of zeolites by the soluble species.[1] In the latter process, nucleation often starts on the surface of amorphous matters present in the aluminosilicate solution; therefore, care needs to be taken so that the coexistence of zeolite with an amorphous phase may not be taken as evidence for the former process. In the former process, particle morphology and size do not generally show significant differences during crystallization, since the solid phase transformation proceeds only by thermal motion of atoms and/or precursors without significant mass transfer. Although experimental results supporting both mechanisms have been reported, the details have not been clarified yet.[49–59]

Figure 2 shows a typical crystallization curve of a zeolite and the corresponding analytical methods useful for its characterization. Typical photographs of a zeolite synthesis reactant and product are also attached to Figure 2. In general, when raw materials are mixed (Si source, Al source, water, mineralizers such as NaOH or KOH and structure directing agents (SDAs)), aluminosilicate species are formed in the solution (upper left of Figure 2). As the synthesis proceeds, condensed species are precipitated in the solution; therefore, amorphous aluminosilicate and dilute aluminosilicate solution phases are formed (upper middle of Figure 2). After the hydrothermal treatment, zeolites are formed and precipitated at the bottom of reaction vessels (upper right of Figure 2).

Recent developments in analytical methods have enabled detailed studies of the crystallization mechanism of zeolites. Several attempts have been made over the years, using various techniques including NMR,[28,60–64] conventional X-ray diffraction,[65–67] optical microscopy,[68,69] dynamic light scattering (DLS),[55,70–73] small-angle X-ray/neutron scattering,[74–80] transmission electron microscopy (TEM),[53,54,81,82] Raman spectroscopy,[83–88] and atomic force microscopy (AFM),[89–92] as shown in Figure 2. Agglomerated particles formed prior to and during the nucleation can be detected by small-angle X-ray scattering. Raman spectroscopy is useful to elucidate changes in the structure of aluminosilicate between the amorphous phase and zeolite. Crystal growth is often characterized by optical microscopy, DLS, and conventional X-ray diffraction, to elucidate the kinetics of crystallization and determine the activation energy of zeolite crystallization. Zeolites obtained are characterized by TEM (inner and terminal structures), SEM (morphology), AFM (surface structure), and NMR (branched units of silicates, Si/Al ratio).

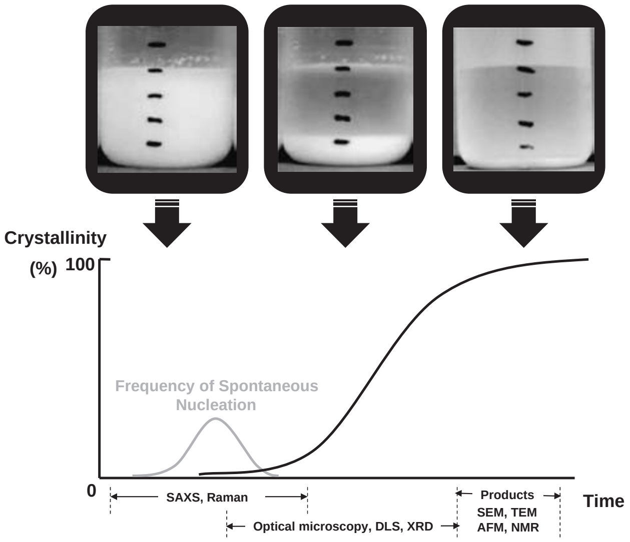


Figure 2. A typical crystallization curve of a zeolite and analytical methods useful for characterization.

Crystallization mechanisms of hydrophobic (synthesized using SDAs) and hydrophilic zeolites (synthesized without SDAs) have been explained independently. Crystallization mechanisms of hydrophobic and hydrophilic zeolites are summarized separately as follows;

Crystallization Mechanism of Hydrophobic Zeolite: The crystallization mechanism of silicalite-1, which is a pure silica with the same framework topology as ZSM-5, has been well studied, and its crystallization mechanism has been getting clearer.[64,75,76,80,93–101] De Moor et al.[75] investigated the whole mechanism of silicalite-1 crystallization by NMR and SAXS. It was revealed that hydrophobic silicates and SDAs are assembled by hydrophobic interactions, that primary units (ca. 2.8 nm) are formed in the solution prior to nucleation, and that nucleation occurs via aggregation of primary units. The primary units were also incorporated directly into the crystalline phase during crystal growth (see Figure 3). It is worth noting that the driving force for the self-assembly of silicate and SDA is the hydrophobic interaction in water. As a result, nucleation and subsequent crystal growth mechanisms are described by a cluster aggregation scheme.

Crystallization Mechanism of Hydrophilic Zeolite: The crystallization mechanisms of low Si/Al ratio zeolites synthesized without SDAs are more complicated, because the interactions among water, alkali cations, and aluminosilicate species are strong and are themselves interrelated. The most representative zeolites, zeolite A and faujasite, are focused on in this section. Several studies on the formation of faujasite and zeolite A, using various analytical methods, have been reported;

Dutta et al.[86] and Xiong et al.[87] investigated the crystallization of zeolite Y and zeolite X by using Raman spectroscopy (Note that faujasite with Si/Al ratios larger than 1.5 is called zeolite Y, and that with ratios smaller than 1.5, zeolite X). They reported that six-membered rings (6R) connected by four-membered rings (4R), and 4R connected by 6R, to form sodalite cages, are the mechanisms for nucleation of zeolite Y and zeolite X, respectively (see Figure 1). Dutta et al. also investigated the crystallization of zeolite A,[88] and concluded that the gel that transforms to zeolite A contains a well-defined structure consisting predominantly of 4R. Mintova et al.[53,54] proposed nucleation mechanisms of zeolite A and zeolite Y by using the results of

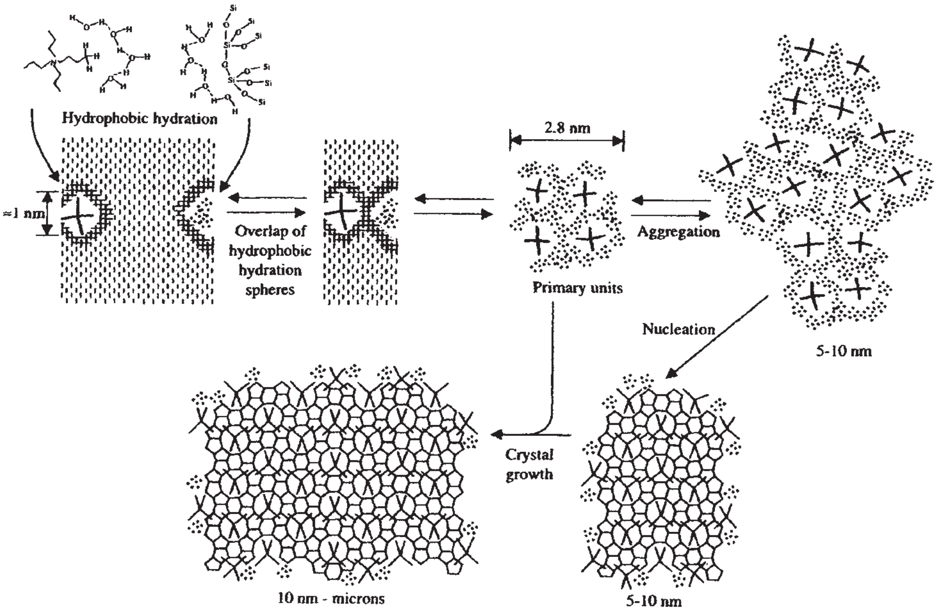


Figure 3. A scheme for the crystallization mechanism of silicalite-1. (Reproduced from Ref. 75)

TEM observations. In their study, a clear aluminosilicate solution containing less hydrophobic tetramethylammonium hydroxide as an SDA was used. It was shown that the nucleation occurred inside (zeolite A) and outside (zeolite Y) of amorphous particles (<80 nm) that were formed by the aggregation of aluminosilicate species (see Figure 4).

In order to understand the crystal growth behavior, Alfredsson et al.[82] and Anderson et al.[90] used TEM and AFM, respectively, to investigate ca. 1.43 nm-high steps on the top surface of zeolite Y. These steps correspond to the height of a unit cell repeat along the ⟨111⟩ direction. Agger et al.[91] examined ca. 1.23 nm-high steps on a zeolite A surface by AFM, and reported that crystal growth occurs via a process akin to a terrace-ledge-kink layer mechanism. On the other hand, Sugiyama et al.[92] investigated a zeolite A surface by AFM, and concluded that a double four-membered ring (D4R) is the key building unit for the crystal growth of zeolite A (see Figures 1 and 5). Recently, changes in the atomic-scale height at a set position have been investigated by the authors using AFM, and it was revealed that faujasite and zeolite A can grow in the same aluminosilicate solution, but that their crystal growth behaviors are different.[102] Corresponding aluminosilicate solutions for seeded growth were characterized by Raman spectroscopy. By combining the results of the surface characterization by AFM and the liquid characterization by Raman spectroscopy, key precursors of crystal growth for faujasite and zeolite A were proposed to be 6R and 4R, respectively. Moreover, detailed observations of the changes in atomic-scale height at a set position on faujasite were performed; showing that most of the top surface structure of faujasite is terminated with double six-membered rings (D6Rs), and that at least one of the precursors for faujasite crystal growth is equal to or smaller than 6R.[103]

Outlook and Future Directions

As mentioned in the previous section, the crystallization mechanism of zeolites is becoming clearer; however, there are limitations of the performances as far as recent modern analytical methods are concerned.

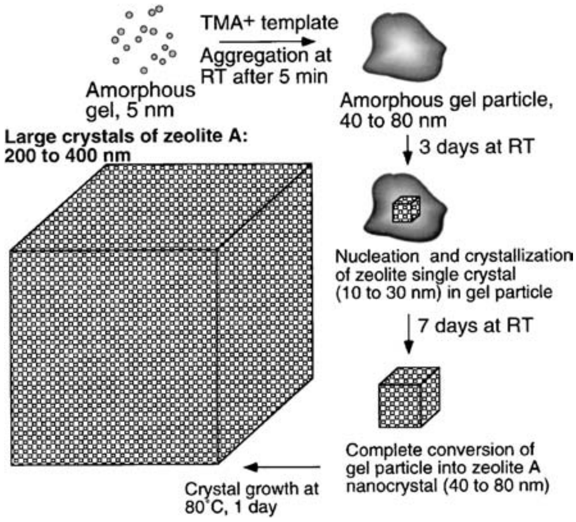
NMR has been widely utilized for the characterization of both amorphous and crystalline aluminosilicates, since it enables characterizations of the distribution of Al in the framework, some branched units of silicate, and Si/Al ratios of amorphous aluminosilicates and crystalline zeolites. The limitation of this technique is that it is difficult to determine the ring structures (for example 4-, 5-, or 6-membered rings) present in amorphous aluminosilicates.

Although conventional XRD studies provide detailed information on the kinetics of crystallization and the activation energy of zeolite crystallization, the initial stages of the crystallization, especially before nucleation, cannot be studied, since the target materials are amorphous.

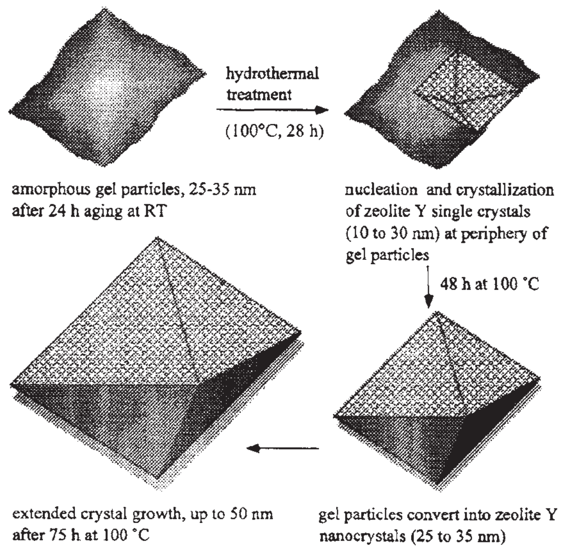
Dynamic light scattering and small-angle X-ray scattering can detect the shape and size of particles (>1 nm) formed prior to nucleation. It is possible to speculate on the nucleation and growth mechanisms of zeolites by using these techniques. However, limitations still remain, since it is difficult to determine the actual structures of the precursor species on a molecular scale.

Raman spectroscopy can provide information on the structures of amorphous aluminosilicates, such as ring structures, formed prior to nucleation. Several studies have addressed the mechanisms of zeolite crystallization. However, it is only possible to detect major ring species in the amorphous phase, and it is almost impossible to determine the ring distribution of amorphous aluminosilicates formed prior to nucleation.

AFM has contributed to the remarkable progress of surface science because the technique has made it possible to observe the surface of insulators with high resolution. It has also become possible to observe materials in liquids; therefore, in situ observation can be carried out. AFM images are, however, often affected by the shape of the tip, and the horizontal resolution is not as good as the vertical one (ca. 10 nm). Furthermore, it is very difficult to perform an in situ experiment to elucidate zeolite crystallization, as the tip of the AFM is soluble in a highly basic



Zeolite A



Zeolite Y

Figure 4. Nucleation and growth model of zeolite A and zeolite Y as represented by TEM. (Reproduced from Refs. 53 and 54)

aluminosilicate solution.

In summary, because of the limitations of the analytical methods available, only limited information on zeolite crystallization can be obtained at present. There still remain several target areas that have not been well clarified, which are shown in the following list;

- ➢ Structures of aluminosilicates formed prior to nucleation.
- ➢ Transformation process of aluminosilicate species to zeolites.
- ➢ Nucleation process.
- ➢ Size and shape of nuclei.

To acquire further knowledge on zeolite crystallization, various developments such as the introduction of new analytical methods and/or combined characterization using various analytical methods are inevitable. In our opinion, such knowledge might be obtained by use of the following three recently developed analytical methods; mass spectroscopy,[104] high-energy X-ray diffraction technique[105] (direct detection of aluminosilicate species present in an aluminosilicate solution) and noncontact AFM (direct observation of the atomic arrangement on a zeolite surface). Clarification of the basic understanding of zeolite crystallization should be a breakthrough towards the designed synthesis of highly functional zeolites; for example,

- ➢ Synthesis of zeolites with new framework structures.
- ➢ Synthesis of nanocrystalline zeolites.
- ➢ Synthesis of giant single crystals (centimeter order).
- ➢ Control of composition, defects and morphology.

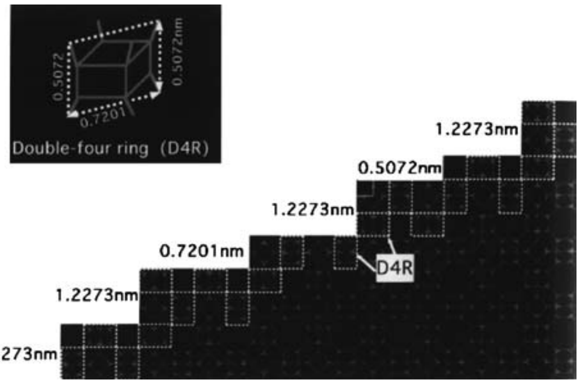


Figure 5. Crystal growth mechanism of zeolite A by D4R structure. (Reproduced from Ref. 92)

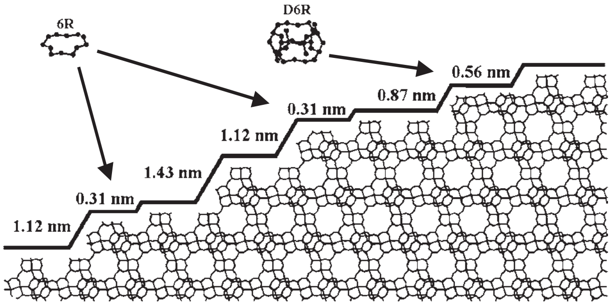


Figure 6. Crystal growth mechanism of faujasite by 6R and D6R structures (Reproduced from Ref. 103).

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