

博士論文（要約）

**Critical Factors for Regulating Nucleation
and Crystal Growth of Zeolites**

（ゼオライトの核生成と結晶成長を制御する因子に関する研究）

Chen, Ching-Tien

陳 靖天

Department of Chemical System Engineering
The University of Tokyo

Chapter 1. General Introduction

Zeolites, a group of crystalline aluminosilicates with well-defined micropores, have been widely applied in the field of adsorption, ion-exchange, and catalysis owing to their unique framework characteristics. To fulfill the industrial demand of zeolites, it is crucially important to control their crystallization kinetics for efficient production. However, the crystallization of zeolites has not been well-understood yet because of the complexity of the synthesis system. The typical synthesis medium of zeolites is an alkaline mixture comprising silicate and aluminate species, inorganic and/or organic cations, and water, while reactions between these reactants are initiated upon mixing. Depending on the species formed in the system, the reactant mixture of zeolites can be roughly categorized into the “clear-sol” and “hydrogel” systems. The former is a suspension of nanosized aluminosilicate species, whereas the latter contains larger particles that are visible to human naked eyes.

After the preparation of reactant mixtures, hydrothermal treatment is usually employed for the crystallization of zeolites, where the synthesis temperature can range from room temperature to over 200°C. Rapid condensation between the active species initially creates diverse and complicated aluminosilicate structures without long-range order, namely the amorphous matter. Thus, the crystallization of zeolites represents a disorder-to-order transformation of the aluminosilicate structure through continuous reorganization. Currently, it is still a difficult task to resolve the nucleation of zeolites during this process, especially for the study on dense hydrogel systems because of the presence of large and highly nonuniform aluminosilicate particles. However, dense hydrogel systems exhibit great importance in the industry as most types of zeolites are synthesized from these systems. Therefore, it is essential to understand the crystallization behavior of zeolites in such systems and learn how to control the crystallization kinetics.

This dissertation aims to gain insights into the crystallization of zeolites in dense hydrogel systems, in which three unique synthesis methods that could alter the crystallization kinetics of zeolites are demonstrated, and time-resolved analyses are conducted to understand the evolution of aluminosilicate species during the synthesis. The particle size of the crystalline-end products and the crystallization rate are the main references to evaluate the nucleation and crystal growth of zeolites, assuming that each crystal will grow at a constant growth rate regardless of its size. In this dissertation, although the exact structure of the zeolite nucleus remains elusive, it is defined as a relatively stable structure that will eventually evolve to a crystal without being decomposed. Consequently, the system that produces smaller crystals should contain more nuclei when the solid yield maintains constant.

Chapter 2. Zeolite Crystallization Triggered by Intermediate Stirring

The crystallization of zeolites from dense hydrogel systems usually requires a long synthesis period, and the solid phase often forms a large bulk during the synthesis, which produces polycrystalline aggregates with a broad particle size distribution. In this chapter, the crystallization behavior of mordenite (**MOR**) in a dense hydrogel ($0.275\text{Na}_2\text{O}-0.025\text{Al}_2\text{O}_3-1\text{SiO}_2-25\text{H}_2\text{O}$) was investigated. In addition, an “intermediate stirring” method was designed to break the sedimented bulk solid into fragments: quenching the reactor halfway during the synthesis and stirring the substances for 1 min by hand using a spatula. It was found that the intermediate stirring accelerated the crystallization of mordenite, while the particle size of the crystalline-end products decreased with the stirring timing. This phenomenon implied that the number of mordenite nuclei gradually increased during the synthesis, and the growth of these nuclei was triggered by the intermediate stirring.

Two types of amorphous aluminosilicate particles were observed in this system: the worm-like particles (WLPs) and the large condensed aggregates (CAs) due to the aggregation and fusion of WLPs. It was found that the number of CAs gradually increased during the synthesis, indicating that the WLP-to-CA transformation is a continuous process. It was further discovered that mordenite nuclei already exist in the WLPs, and the formation of CAs is not necessary for the crystallization of mordenite. Accordingly, it is considered that although the number of mordenite nuclei increases with synthesis time, the growth of these nuclei is largely hindered as the formation of CAs and the increasing packing density of the bulk solid reduce the chance for these nuclei to contact with the liquid phase. Consequently, the function of intermediate stirring is to enhance the exchange of species between the solid phase and liquid phase by breaking the bulk solid into fragments, which promotes the dissolution of amorphous particles and activates the growth of embedded nuclei.

Chapter 3. Crystallization Behavior of Zeolite Under Ultrasonication

For the preparation of zeolites, ultrasonication is an efficient pretreatment that homogenizes the reactant mixture before the hydrothermal synthesis. However, very few studies directly employ ultrasonication during the hydrothermal synthesis, and the effect of ultrasonication on zeolite crystallization has not been fully understood yet. In this chapter, ZSM-5 (**MFI**) was, for the first time, synthesized from a dense hydrogel ($0.25\text{Na}_2\text{O}-0.01\text{Al}_2\text{O}_3-0.2\text{TPAOH}-3\text{SiO}_2-50\text{H}_2\text{O}$) under continuous ultrasonic irradiation. A homemade ultrasonic device was designed, which allows the adjustment of ultrasonication power while maintaining the temperature during synthesis.

It was found that the crystallization of ZSM-5 was accelerated when the ultrasonication power increased. Crystals formed under 97 W irradiation possessed a mean particle size similar to the ones in the nonultrasonic system; thus, it was considered that low-power ultrasonication primarily enhanced the crystal growth rate of ZSM-5. In contrast, syntheses under 194 and 323 W irradiation resulted in the formation of smaller ZSM-5 with narrow particle size distributions, which indicated that under a sufficiently strong ultrasonic irradiation power, the nucleation of ZSM-5 could be promoted. However, it was discovered that applying 323 W irradiation for less than 45 h did not help reduce the particle size (ca. 600 nm) of the crystalline-end products. Instead, only when the system received at least 70 h of ultrasonication could a reduced crystal size (ca. 200 nm) be observed, indicating that massive nucleation of ZSM-5 occurred during 45–70 h.

Further investigation revealed that the formation of inorganic-organic composites (IOCs) during the induction period was enhanced under 323 W irradiation. Besides, the fusion behavior of aluminosilicate particles at the early stage of crystal growth was found to be affected by ultrasonication. In the nonultrasonic system, the 30 nm nanoparticles apparently fused to form large crystals (300–600 nm), while in the ultrasonic system, small crystals (100–200 nm) were formed. Therefore, it is reasonable to suggest that ultrasonication directs uniform evolution of the IOCs during the disorder-to-order transformation so that relatively ordered structures can appear at a similar timing and be well distributed within the solid phase. Consequently, the fusion of particles occurs everywhere in the solid phase, producing an abundance of tiny ZSM-5 crystals. Finally, it was shown by Fourier transform-infrared spectroscopy (FT-IR) that the enhanced crystal growth rate under ultrasonication was due to the increased amount of silanol groups on the crystal surface, which facilitated the condensation between aluminosilicate species. In conclusion, the discoveries in this study hint alternative ways for promoting the nucleation and crystal growth of zeolites in an organic cation-containing system. Developing effective methods to direct the formation of IOCs and surface silanol groups should benefit the control of zeolite crystallization kinetics.

Chapter 4. Effect of Precursor Structures on Zeolite Crystallization

Structure of the aluminosilicate species generated during the preparation of reactant mixture or hydrothermal synthesis would largely influence the subsequent crystallization kinetics of zeolites. In this chapter, zeolite X (FAU) was synthesized from a dense hydrogel ($1\text{Na}_2\text{O}-0.2\text{Al}_2\text{O}_3-1\text{SiO}_2-50\text{H}_2\text{O}$) at 80°C through different reactant mixture preparation methods. For the Cab–O–Sil system, the reactant

mixture was prepared by adding Cab–O–Sil (fumed silica) to the Al-containing solution; for the dissolved Cab–O–Sil system, Cab–O–Sil was first dissolved in NaOH_(aq), followed by the addition of Al-containing solution.

It was found that crystallization of zeolite X in the Cab–O–Sil system was much faster than that in the dissolved Cab–O–Sil system, while the former system produced much smaller crystals (ca. 1.2 μm) than the later system (ca. 15 μm). This result indicated that the rapid crystallization in Cab–O–Sil system was due to the intense nucleation event. Raman spectroscopy revealed that the amorphous aluminosilicates in both systems comprised a large portion of 4-membered rings (4R). It is noteworthy that these 4R bands were significantly intensified during the crystal growth period, meaning an increase in their abundance. This phenomenon indicated that double 6-membered ring (D6R) was formed through the combination of two 6Rs, hence six additional 4Rs were generated during this process. Pair distribution function (PDF) derived from synchrotron X-ray total scattering showed that Si-rich 6Rs and Al-rich 4Rs were formed in the Cab–O–Sil system after 1 h of synthesis, and heating to 3 h resulted in the incorporation of Al atoms into Si-rich 6Rs. Solid-state nuclear magnetic resonance (NMR) spectroscopy further pointed out that the chemical environment of these Al atoms remained unchanged during the induction period. Given these observations, a possible crystallization scheme of zeolite X in the Cab–O–Sil system was considered as follow: (1) insertion of Al-rich 4Rs into the Si-rich 6Rs, (2) formation of β -cage and D6R, and (3) formation of zeolite X framework.

In contrast, it was revealed that the dissolved Cab–O–Sil system produced distorted aluminosilicate structure immediately upon mixing, and heating at 80°C could further increase their degree of distortion. As a result, the reorganization of these aluminosilicates to produce ordered structures is not easily promoted and requires relatively long synthesis time. It is worth mentioning that aging the reactant mixture at room temperature (RT) for 24 h reduced the degree of distortion of the aluminosilicates, which shortened the subsequent synthesis time at 80°C and increased the nucleation frequency of zeolite X. This result suggested that the distorted aluminosilicate structures would be stabilized at high temperatures, and only the low-temperature synthesis enabled their transformation toward a facilitated nucleation of zeolite X. To conclude, it is essential to consider the formation of aluminosilicate species from a thermodynamic point of view, as increasing the synthesis temperature would not always promote the crystallization kinetics.

Chapter 5. General Conclusions and Future Perspectives

The crystallization of zeolites in dense hydrogel systems holds great importance from both scientific and industrial points of view. It can be concluded that the nucleation of zeolites depends on the ease of the formation of structural building units, while the growth of zeolites is related to the rate of the condensation reaction. The knowledge obtained in this work should be applicable to other types of zeolites beside **MOR**, **MFI**, and **FAU** as in most situations there exist no clear boundaries between each reaction system. It is demonstrated that the rational design of control experiments followed by a detailed analysis of the system's evolution could shed light on the crystallization behavior of zeolites. Therefore, this work is expected to improve the currently developed synthesis systems and inspire the design of new synthesis methods toward better control of the production of functional materials and deeper understandings on their formation mechanisms.