

## 論文の内容の要旨

論文題目 New synthesis routes of zeolites based on control of precursors  
(前駆体の制御に基づくゼオライトの新規合成ルートに関する研究)

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In this dissertation, three new synthesis routes of zeolites based on control of the crystallization precursor are described. In this study, “precursor” means the one state of aluminosilicate species, and is not limited as specific clusters for crystallization. Zeolite is formed as metastable phase, and, in addition to chemical compositions, operation of crystallization and the preparation of the reactant mixture decide the crystallization path. Thus, the preparation of specific reactant aluminosilicate precursors and the control of crystallization processes can potentially determine the final products. In this dissertation, three new approaches controlling the preparation method of precursor are proposed, and new zeolites were synthesized by conventional synthesis method.

In the Chapter 1, the background, and the aim of this research are described. Zeolite is a crystalline microporous materials consisted of  $TO_{4/2}$  units and has been used in wide industrial fields as catalyst, ion-exchanger, adsorbent, molecular sieve, and so on. Its unique chemical properties and functions have interested many researchers, and the design of its pore structure has been a big challenge. Although hydrothermal reaction has been a conventional method to synthesize zeolite, the reaction process has still remained as a black-box because the reaction progresses under high temperature, high pressure, and high pH condition. Thus, repeated try-and-error trials have been required for the synthesis of new zeolitic materials although new techniques have been developed such as computer simulation for the prediction and design of zeolite framework. For now, one of the most promising approaches for the synthesis of new zeolites is the use of new structure-directing agent (SDA), which has enabled us to synthesize various new zeolitic materials. However, organic SDAs (OSDA) have become more complicated and high-cost recently, which make it difficult to apply them in an industrial field. The alternative approach that has a potential to synthesize new zeolite with conventional cheap SDAs has been desired.

In the Chapter 2, crystalline layered silicate is prepared as the precursor of zeolite and converted to zeolite by non-hydrothermal reaction. Without using the conventional black-box reaction, the well-ordered precursors are build-up by solid-state reaction. Novel pure-silica sodalite with plate-like morphology is prepared by topotactic conversion of layered silicate RUB-15, and the details of the conversion are also reported in this chapter. Most of zeolites are recognized as repeated structure of small units, and the different stacking or connection of the same unit produces the different final structure, such as sodalite cages seen in SOD, LTA, FAU, and EMT-type zeolite. Whereas all the attempts to synthesize zeolite from such a cluster unit under hydrothermal reaction have been failed, building-up of layered silicate into zeolite under solid-state reaction, called “Topotactic conversion”, has been succeeded. In this chapter, the synthesis of novel pure-silica plate-like sodalite is synthesized by the topotactic conversion of layered silicate RUB-15. This is the eighth example of the conversion of layered silicate into zeolitic material. It was figured out that acidic pretreatment of layered silicate is the key for the successful conversion, and the carboxylic acid showed the best performance. As topotactic conversion is achieved by the dehydration-condensation of surface silanol groups of the layered silicate, adjustment of interlayer distance or surface state of layers and stability against the reaction condition is critical for the synthesis. The treatment with 6 M of propionic acid was best method to prepare the acid-treated intermediate state. Moreover, obtained sodalite had characteristic features. Conventional pure-silica sodalite was synthesized by solvothermal method and organic templates were occluded in the cage structure. Cages and very small windows of the sodalite have not been used effectively, because it was difficult to remove the occluded organics without collapsing of sodalite structure. On the other hand, pure-silica sodalite synthesized from topotactic conversion achieved the hollow-cage structure for the first time. This is because the topotactic conversion does not require the template for the synthesis.

In the Chapter 3 and 4, silicate and aluminosilicate networks of reactant mixtures are considered as zeolite precursor. In the conventional synthesis of zeolite, it has been difficult to define the “precursor” because of insufficient understanding of crystallization mechanism, although previous works have revealed the presence of specific aluminosilicate network or formation of particulate matter before nucleation. Thus it would be possible to recognize the whole gel network as one precursor.

In the chapter 3, the crystallization path is controlled indirectly by the preparation of the gel and the chemical composition, and surfactant molecule is tried to use as OSDA by devising the gel composition and the crystallization process. In the synthesis of zeolite, one OSDA molecule usually works as one structure template, whereas micelle of surfactant molecules works as structure template of mesoporous silica. The template mechanisms are

completely different, thus introduction of both conventional OSDA and surfactant into the reactant gel had generated physical mixture of zeolite and mesoporous silica in one batch. Because of their partial charge distribution, surfactant molecules have never been successfully used as OSDA of zeolite. Based on the present knowledge about the crystallization mechanism of pure-silica zeolite and formation mechanism of mesoporous silica, the difference would be the interaction between molecules, and molecule and silicate framework. In the case of surfactant molecule, chemical potential would be lower in the case that organics and silicate are aggregated separately than the formation of composite. If the micelle formation of surfactant molecules during the hydrothermal reaction was hindered, it could be possible to use surfactant as OSDA. To fulfill the requirement, dry-gel conversion method of dense gel was applied. In this approach, crystallization proceeds under the presence of water steam, and rearrangement of surfactant molecules through water phase does not occur. The representative surfactant molecule, cetyltrimethylammonium cation, was successfully used as OSDA for the first time, and pure-silica MFI-type zeolite was obtained. From the structural point of view, its 1-dimensional structure of 10-membered ring structure could be template by the surfactant molecule. The obtained zeolite surely contained organic molecules and the framework was maintained after removal of the organics by calcination.

In the Chapter 4, the crystallization path is controlled by the preparation of aluminosilicate precursor combined with aging process. An aging process, which is the process in that the precursor gel is placed at lower temperature ( $\sim 100$  °C) for specific period of time without inducing crystallization, has been used in the synthesis of several zeolites to obtain the well crystalline product, to avoid the contamination of other phase, and to control the crystal size. In this chapter, synthesis route is controlled by new aging process, known as “Charge density mismatch” method developed by UOP group. In this method, two types of SDAs, one is an OSDA used for the aging of the reactant gel and the other is SDAs to induce the crystallization, are added to the reactant gel step-by-step at the proper stage. Especially, I focused on the UZM-4 zeolite, which is synthesized from tetraethylammonium, tetramethylammonium, and lithium cations. Although all SDAs used in this approach are well-known conventional ones, it has been succeeded to obtain new zeolite only by controlling the aging process. The detailed characterization of aging process revealed that the aging process is critical for the preparation of precursor for the UZM-4, which is small silicate and aluminosilicate species stabilized by OSDAs in liquid-phase. Moreover, based on the knowledge obtained through the study, the seed-assisted synthesis of UZM-4 without aging process was expected. The trial was successful and obtained UZM-4 showed higher Si/Al ratio than seed crystal. This success also indicated that the aging process of UZM-4 is critical only for the nucleation stage. Moreover, it showed the possibility to prepare a new zeolite

without using high cost OSDAs.

Finally, the general conclusions and future perspectives are summarized in the Chapter 5. Practically, 1) Layered silicate was used as a crystalline precursor of zeolite by acidic pretreatment, 2) Surfactant molecule was successfully applied in the synthesis of zeolite by tuning the crystallization condition, and 3) Controlled aging process combined with step-by-step addition of SDAs was used for the synthesis of new zeolite and its seed-assisted synthesis was achieved. The results and understandings of this research would help not only synthesizing new zeolites but also synthesizing previous zeolite with lower cost. Every approach shown in each chapter would have a potential to synthesize new zeolitic materials.

In this dissertation, new synthesis routes of zeolite were investigated based on control of the precursor. All approaches were free from the use of complicated and expensive OSDAs. Zeolites with new properties were obtained from these approaches. This dissertation showed the importance of precursor preparation and its handling in the synthesis of zeolite as well as the starting gel compositions and its crystallization condition.