論文の内容の要旨

論文題目　Rational Synthesis of Multipore Zeolites Using Simple Organic Structure-Directing Agents by Seed-Directed Method
（種結晶添加法によるシンプルな有機構造規定剤を用いたマルチポアゼオライトの合理的合成）

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During the last decades of porous material history, great efforts have been made to synthesize so-called “multipore” zeolites, which contain channels of different directions within the same crystalline structure. Their synthesis is a very attractive subject since the presence of differently sized pores would favor the preferential diffusion of reactants and products through different channels, allowing unique catalytic activities for specific reactions. However, the synthesis of multipore zeolites requires the usage of complex and expensive organic structure-directing agents (OSDAs), which hampers to manufacture these zeolites. Therefore, there is always a call to develop the rational synthesis of existing multipore zeolites.

The scope of this dissertation is to develop a rational synthesis route for multipore zeolites with medium and large pores solely using simple, inexpensive, and commercially available OSDAs in seed-directed method. The idea has been inspired from the review of Stacey Zones in which he points three methods to simplify the synthesis of zeolites. One of them was replacing much of OSDAs with less expensive pore fillers that is recently attracting increasing attentions. Moreover, composite building unit (CBU) hypothesis, by which structural similarities are considered to associate different zeolite architectures, is extended to select the appropriate simplified OSDAs and the synthesis conditions from a huge “zeolite synthesis library” for the synthesis of objective material. The concept applied in this research aims to suppress the formation of undesired products which might form due to the structure-directing effect of simple OSDAs,

and to promote the direct crystal growth of target multipore zeolites on the partially dissolved seed crystal surfaces. For doing this, the synthesis conditions were optimized by aging, modifying reaction composition and controlling the kinetics. These adjustments, combined with the advantageous of simple OSDA in seed-directed method, allow obtaining highly crystalline pure multipore zeolites with satisfying solid yields which could not be achieved in any other simplified synthesis paths, so far.

In Chapter 1, the general background and the rationalization of the objective and strategy of this dissertation are presented. In this dissertation, developing rational synthesis route for multipore zeolites with medium and large pores is described.

In Chapter 2, the synthesis of aluminosilicate MSE-type zeolites is investigated. Unlike previous reports stating that costly and bulky organic molecules are essential to form MSE-type zeolites, a simplified and efficient synthesis route to these multi-dimensional, large-pore zeolites by using tetraethylammonium hydroxide (TEAOH) as a simple OSDA is developed. Based upon CBU hypothesis, a clear relation was found among MSE, *BEA, and MOR framework types. According to this relation, TEAOH which is basically utilized for the industrial production of *BEA-type zeolite was determined to be used in a modified gel composition as an easily reachable and comparatively inexpensive OSDA. This novel approach allowed to obtain pure solid products with high yields ca. 54 wt.% by consecutively applying aging and hydrothermal synthesis steps. The series of characterizations revealed that the features of obtained products were similar to those of conventional MCM-68 with relatively better microporosity characteristics. Remarkably, the “second-generation” products can be synthesized via this novel route by optimizing the aging time. The overall results revealed that the method proposed here is the most simplified and efficient synthesis route for MSE-type zeolites.

In Chapter 3, the synthesis of zincoaluminosilicate MSE-type zeolites is studied. Simplified and efficient synthesis of MSE-type zeolites by using TEAOH is extended from aluminosilicate to zincoaluminosilicate by combining with co-precipitated gel technique. The direct crystallization of MSE-type zeolite could be realized from the synthesis gels containing co-precipitated gels in which homogenously dispersed zinc and aluminum species having a Zn/(Zn+Al) ratio up to 0.4. The overall characterizations revealed that most of the zinc species were incorporated as heteroatom, and created anionic charges in MSE framework. Based on the ion-exchange characteristics of those samples, it is found that the most of inserted zinc species exhibited two anionic charges per atom, which is expected to be suitable sites for divalent-cation exchange. Since the sample prepared by using Zn/(Zn+Al) ratio of 0.2 (MSE-TEA$_{Zn0.2}$) remained stable after thermal treatment, Ni^{2+} exchange was applied to that sample. The results revealed that MSE-TEA$_{Zn0.2}$ sample exhibited superior ion-exchange capacity to aluminosilicate MSE-TEA sample. Therefore, MSE-TEA$_{Zn0.2}$ sample can be purposed as a potential divalent-cation exchanger. Also, the comparison of XPS and ICP-AES analysis results implied that zincoaluminosilicate MSE-type zeolites were obtained in a core-shell structure, in which only shell was newly grown zincoaluminosilicate, while the core was partially dissolved aluminosilicate seed crystals. In this report, it is demonstrated that the simplified synthesis path is very effective alternative way to synthesize multipore zeolites containing medium and large pores in the frameworks with different heteroatoms.

In Chapter 4, synthesis of aluminoborosilicate CON-type zeolites is investigated. It is found that CON structure shares CBUs with *BEA and MFI, which are traditionally synthesized by using simple quaternary ammoniums such as TEAOH and tetrapropylammonium hydroxide (TPAOH) as OSDAs, respectively. Moreover, MFI can be fabricated from the synthesis gels containing TEAOH, hence, TEAOH is thought to be suitable simple and commercially available OSDA for crystal growth of CON-type zeolites. Regarding these results, it is found that rational synthesis is possible for CON structure which could not be synthesized other than conventional method, thus far. By using almost 2 μm borosilicate CIT-1 seed crystals, highly crystalline pure aluminoborosilicate CON-type zeolite with a maximum solid yield of 36 wt.% could be obtained from the gel containing TEAOH and binary alkali cations (Na^+ and K^+) system. Regarding SEM images, it can be said that CON-TEA sample exhibited different crystals compared to those of borosilicate CIT-1 seed crystals which confirms once again crystal growth occurring on the partially dissolved seed crystal surfaces. Based upon the physicochemical analysis, it can be said that the characteristics of obtained materials were comparable with those of aluminoborosilicate CIT-1 crystals, suggesting well-crystalline CON phase. Furthermore, the Raman spectra of CON-TEA sample revealed that almost 3 TEA^+ cations are occluded into CON structure to stabilize 12-R and intersections of the CON-TEA. These results revealed the validity of rational synthesis path for other multipore zeolites containing medium and large pores in their structure.

Finally, in Chapter 5, general conclusions and future perspectives of this doctoral dissertation is presented. Overall results revealed that the present research proposed a new synthesis path involving the usage of simple and commercially available quaternary ammonium as an OSDA and a certain amount of seed crystals. The selection of the simple OSDA has been done by considering common composite building units between target multipore zeolite and other zeolite which can be synthesized using the simple OSDA. In this regard, the rational synthesis of MSE and CON as multipore zeolites containing medium and large pores with reasonable solid yields has been achieved from the gels having binary alkali cations system and TEAOH as a simple OSDA. Moreover, the rational synthesis allowed the insertion of zinc species as a heteroatom in the aluminosilicate MSE-type zeolites which is the first direct synthesis of MSE or multipore zeolites with zinc in their framework. Also, this insertion bears the strong Lewis acidity features, and increased ion-exchange capacity of the conventional MSE structures.

As cited in this dissertation, the combination of seed-directed method and simple OSDAs, so-called rational synthesis, opened a new door for economical, high-yield synthesis of multipore zeolites containing medium and large pores. Besides these advantages, there are surely some key issues need to be deeply investigated. One of them is the exact role of Na^+ and K^+ alkali cations which are required to be used together for successful synthesis. The other one is the using an OSDA such as diethyldimethyl or dimethyldipropylammonium hydroxide which do not show structure-directing effect for any specific structure to understand the effectiveness of OSDAs. The last one is seeking the possibilities to design special gel compositions which can yield much higher product yields. After finding out these points, it is also expected that the applicability of rational synthesis can be expanded to other multipore zeolites containing various heteroatoms which generally require complex OSDAs in their production. This synthesis may enable us to reach more existing multipore structures under economic conditions, and help them to be industrialized. Moreover, it may merit to introduce different framework elements in those structures which can even open new application doors for new industries.

As a conclusion, it is shown in this dissertation that the rational synthesis is valid for the multipore zeolites containing medium and large pores by synthesizing of MSE and CON structures. Also, it is found that this method can be a way to improve the existing structures by allowance of the insertion different atoms in their frameworks which may open new windows to the zeolite world.