

# 博士論文(要約)

Synthesis of Zeolites Using Diquaternary Ammonium

Organic Structure-Directing Agents

(ジ四級アンモニウム有機構造規定剤を用いたゼオライトの合成)

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## 論文の内容の要約

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In this dissertation, utilization of diquaternary ammonium cations as the organic structure-directing agents (OSDAs) in the synthesis of zeolites is described. OSDAs play important roles in the synthesis of zeolites. For example, they can influence crystallization rates and product phase selectivity. Diquaternary ammonium cations can control the morphology of zeolites, lead to zeolites with hierarchical structure, and direct the formation of several novel zeolites structures. Owing to the advantages of diquaternary ammonium cations, this dissertation investigates the effects of different substituted groups and/or lengths of methylene groups between two charged nitrogen atoms of diquaternary ammonium OSDAs on the synthesis of zeolites. Background and objectives of this dissertation are summarized in Chapter 1. Utilization of alkylamine-derived OSDAs for the synthesis of zeolites is demonstrated in Chapters 2 and 3. On the other hand, Chapters 4 and 5 involve the usage of cyclic amine-derived OSDAs for the synthesis of zeolites. Finally, Chapter 6 describes general conclusions and future perspectives

In Chapter 1, brief introduction and objectives of this dissertation are described. Zeolites are crystalline microporous aluminosilicates with well-defined micropores, high surface area, large pore volume, and high hydrothermal stability. As a result, zeolites have been widely used as catalysts, ion-exchangers, and adsorbents. In the synthesis of zeolites, the crystal structures of the resultant zeolites depend on starting gel compositions, types of inorganic and organic cations, hydrothermal conditions, and so on. Monoquaternary ammonium cations have

been typically utilized as the OSDAs in the synthesis of zeolites. However, diquatery ammonium cations with methylene groups in between two charged nitrogen atoms can also be employed as the OSDAs in the synthesis of zeolites. In Chapters 2–4, the design of diquatery ammonium OSDAs is based on the connection of two conventional monoquatery ammonium OSDAs with methylene groups. This approach can reduce the degree of freedom of the monoquatery ammonium end-groups from free rotation. Meanwhile, the presence of methylene groups in between two charged nitrogen atoms provides the flexibility to the diquatery ammonium OSDAs. The lengths of methylene groups connecting two monoquatery ammonium cations are decided based on the  $C/N^+$  ratio of the OSDAs. Generally, intermediate hydrophobicity of the OSDAs with the  $C/N^+ = 10\text{--}16$  is preferable. In Chapter 5, a smaller diquatery ammonium OSDA without methylene chains is also studied.

In Chapter 2, synthesis of hierarchical **MFI** zeolite using propyl-substituted diquatery ammonium OSDAs is investigated. The sole presence of micropores in zeolites encounters molecular mass transport limitation. This problem becomes more significant when zeolites are used to catalyze reactions involving bulky molecules. One of the strategies to solve this problem is to fabricate hierarchical zeolites with different levels of porosity. Here, the effects of the synthesis conditions on the formation of hierarchically and sequentially intergrown **MFI** zeolite were systematically investigated using *N,N,N,N',N',N'*-hexapropylpentanediammonium cations ( $\text{Pr}_6\text{-diquat-5}$ ) as the OSDA. Meanwhile, OSDAs with different substituted groups and/or lengths of methylene groups were employed in zeolite synthesis. It was found that the synthesis condition is somewhat narrow with the optimum gel compositions of 1  $\text{SiO}_2$ : 0.2  $\text{Pr}_6\text{-diquat-5}$ : 0.375–0.500 KOH: 200  $\text{H}_2\text{O}$ : 4 ethanol. In addition, the morphology of the obtained zeolites highly depends on the structures of OSDAs. However, only  $\text{Pr}_6\text{-diquat-5}$  directed the formation of hierarchically and sequentially intergrown **MFI** zeolite. This was explained in terms of its molecular dimension and stabilization energy, resulting in the unusual fitting of  $\text{Pr}_6\text{-diquat-5}$  inside the pore channels of **MFI** zeolite. This unusual fitting may cause the internal framework stresses. As a consequence, the intergrowth should be generated to relax the framework stresses or distortions caused by  $\text{Pr}_6\text{-diquat-5}$  somehow in a sequential fashion, resulting in the unique hierarchical **MFI** zeolite.

In Chapter 3, fabrication of mesoporous **MFI** and **MEL** zeolites is investigated by a two-stage crystallization method with *N,N,N,N',N',N'*-hexabutylheptanediammonium cations as the OSDA. The two-stage crystallization method was employed with the intention to promote the formation of zeolite precursors during the first stage (low temperature) and subsequent crystallization in the second stage (high temperature). Mesoporous **MFI** and **MEL** zeolites with

microsphere morphology were synthesized at different alkaline conditions. The gas physisorption experiments suggest that mesopores of both zeolites are ink-bottle type pores. The formation of zeolite precursors can be strongly influenced by the synthesis conditions, for instance, the synthesis time of the first stage. In order to control the crystal sizes of the mesoporous **MFI** and **MEL** zeolites, synthesis time in the first stage was varied. The results revealed that as the synthesis time in the first stage was prolonged, the obtained crystals became smaller. This observation suggests that prolonged synthesis time in the first stage can enhance the formation of zeolite precursors and spontaneous nucleation, resulting in smaller crystals.

In Chapter 4, synthesis of small-pore zeolites using piperidine-derived diquatery ammonium OSDAs is studied in the presence of sodium or potassium cations in the synthesis gels. Some small-pore zeolites consisting of 8-membered-ring openings with large cavities in their framework structures have been demonstrated as the efficient catalysts for methanol-to-olefins and selective catalytic reduction of  $\text{NO}_x$ . With the intention to synthesize zeolites with larger cavities, bigger diquatery ammonium cations were designed and employed in the synthesis of zeolites. Here, the workability of bigger diquatery ammonium 1,5-bis(*N*-methyl-2,6-dimethylpiperidinium)pentane (Pip<sub>2</sub>-diquat-5) as the OSDA in the synthesis of zeolites with larger cavities was investigated. When sodium cation was included in the synthesis gel, **MOR**, **ANA**, **GIS** and **AFX** zeolites were formed, depending on the synthesis conditions. On the other hand, in the presence of potassium cation, the formation of **LTL** and **ERI** zeolites was observed. The formation of **AFX** and **ERI** zeolites using Pip<sub>2</sub>-diquat-5 as the OSDA was considered to relate to the sizes of the OSDA and the cages of the zeolites. Bigger diquatery ammonium cations can be fitted in the larger cages and subsequently stabilize the cages of **AFX** and **ERI** zeolites. As the phase selectivity of **AFX** and **ERI** zeolites depends on inorganic cations, it can surmise that the sodium cation stabilizes the *gme* unit in the **AFX** zeolite, while potassium cation stabilizes the *can* unit in the **ERI** zeolite. Up to date, the Pip<sub>2</sub>-diquat-5 is the new OSDA to direct the formation of both **AFX** and **ERI** zeolites.

In Chapter 5, synthesis of **ERI** zeolite using smaller size of diquatery ammonium cations is studied. The synthesis was performed using 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane cations (dimethyl-DABCO) as the OSDA and **FAU** zeolite (Si/Al = 5.5) as the aluminium source. The obtained **ERI** zeolite has elliptical morphology, which is different from the needle-like morphology of the **ERI** zeolite synthesized in Chapter 4. This result suggests that the aluminium source (**FAU** zeolite or  $\text{Al}(\text{NO}_3)_3$ ) and synthesis conditions may influence the morphology of the **ERI** zeolite formed. Based on thermogravimetry analysis, approximately 1.5–2.0 molecules of dimethyl-DABCO per cage

were occluded in the **ERI** product. This suggests that smaller diquatery ammonium cations such as dimethyl-DABCO may also direct the formation of zeolite with large cages, in addition to the larger diquatery ammonium OSDA demonstrated in Chapter 4.

In conclusion, the substituted groups and/or the methylene groups of the diquatery ammonium OSDAs strongly influence the morphology and phase selectivity of the zeolites. Particularly, morphology control of the medium-pore, channel-type zeolites (**MFI** and **MEL** zeolites) is achieved by using alkylamine-derived OSDAs. When the charged nitrogen atoms of the diquatery ammonium OSDAs are located at or close to the channel intersections of the medium-pore zeolites, the morphology of the as-synthesized zeolites is affected by the lengths of methylene groups in between two charged nitrogen atoms of the diquatery ammonium OSDAs. In addition, phase selectivity of small-pore and cage-type zeolites is observed by using cyclic amine-derived OSDAs, which tend to be fitted in the larger cages in small-pore zeolites (**AFX** and **ERI** zeolites). This dissertation demonstrates that the morphology control and phase selectivity of zeolites have been achieved by careful selection of diquatery ammonium OSDAs with different substituted groups and/or lengths of methylene groups in between two charged nitrogen atoms.

The applications of zeolites have a close relationship to their pore architecture and chemical compositions. Therefore, continuous efforts have been made to discover novel frameworks of zeolites as well as new applications. The design of the diquatery ammonium OSDAs in this dissertation is based on the connection of two monoquatery ammonium cations (original OSDAs in the synthesis of zeolites) with methylene groups. This consideration merits the future investigation in the design of new OSDAs for the control of the zeolite morphology and/or the synthesis of new zeolites.