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研究課題名(和文) 特異的ヘテロ原子サイトを有する革新的ゼオライトの計算機支援合成

研究課題名(英文) Computer-aided synthesis of innovative zeolites with heteroatoms in specific locations

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研究成果の概要(和文)：ゼオライトは結晶性多孔質アルミノケイ酸塩であり、その高い比表面積、水熱安定性、固体酸性などの特性から、触媒、吸着剤、イオン交換剤として広く用いられている。骨格構造中における、AlやZnなどのヘテロ原子の位置は、ゼオライトの物理化学的特性の根幹であり、その制御はゼオライト合成の究極の目標の一つと言える。本研究では、計算機化学により設計した有機構造規定剤を用いることで、Al原子を有するゼオライトの結晶化経路をエンジニアし、Al原子位置の制御されたゼオライトを合成した。また、Alだけでなく、新規ジンコシリケートゼオライトの合成にも成功した。

研究成果の概要(英文)：Zeolites are crystalline microporous aluminosilicates. Owing to their unique properties such as high surface area, hydrothermal stability, and solid acidity, they have been widely used as catalysts, adsorbents, and ion-exchangers. The locations of heteroatoms such as Al and Zn in the framework structures of zeolites are one of the fundamental descriptors determining the physicochemical properties of zeolites. With the aid of computational calculations, in this research, zeolites with controlled locations of Al were synthesized by using designed organic-structure directing agents to engineer the crystallization pathway of zeolite formation. In addition to aluminosilicates, a new zincosilicate zeolite was successfully synthesized.

研究分野：材料化学、化学工学

キーワード：ゼオライト 多孔性材料 有機構造規定剤 ナノ空間材料 触媒 計算機化学

1. 研究開始当初の背景

Zeolites are microporous crystalline silicates, aluminosilicates, and other metallosilicates constructed from corner-sharing, tetrahedrally-coordinated $TO_{4/2}$ primary units (where T is a tetrahedral atom such as Si, Al, B, Ga, Zn, and so on). Their framework structures possess well-defined pores and channels of molecular dimensions, making them become one of the most important key materials in chemical industries, utilized for ion exchange, adsorption, membrane separation, and catalysis.

Isomorphous substitution of B(III), Al(III), Ga(III), or Zn(II) for Si(IV) in the tetrahedral site (T-site) of the zeolite framework generates negative charges that constitute Brønsted acid sites when they are counter-balanced by protons. In addition to protons, the counter-ions can be metal ion species, having various structures and coordination, exhibiting extraordinary redox behaviors. It is well known that the location of heteroatoms such as Al can have dramatic influences on the properties of zeolites. For example, in catalysis the stability of reactants and transition intermediates and subsequent reaction rates can be altered depending on the spatial constraints of reactants and intermediates located near Al (and protons). Therefore, it is of great scientific and technological interest to develop synthetic methods allowing for the placement of heteroatoms into the specific crystallographic T-sites within the zeolite frameworks.

Because of such significant influences, there are many attempts to develop characterization techniques to quantify the distribution of heteroatoms and to establish synthetic methods for controlling the location of heteroatoms. Thus far, however, it is impossible to explicitly attribute the differences in the locations of heteroatoms to the respective synthetic conditions. The rational design of synthetic parameters to selectively place heteroatoms into the desired site remains elusive.

2. 研究の目的

In this work, Al and Zn are selected as model heteroatoms. The computational tools are used to integrate the structural chemistry of heteroatoms with the synthetic chemistry of zeolites to direct the crystallization of zeolites with heteroatoms substituted at specific crystallographic

T-sites with a particular focus on the design of organic structure-direct agents (OSDAs) to engineer the crystallization pathway of zeolites.

3. 研究の方法

In this work, the central strategy to control the location of Al is to engineer the crystallization pathways of zeolites by energetic means. To do so, OSDAs are selected among many other possible synthetic parameters. OSDAs are generally bulky, water-soluble organic cations used to guide the crystallization of specific zeolite frameworks since their molecular structures are commensurate with zeolite cavities. In addition to their ability to direct the crystallization of specific crystalline phases, OSDAs can control the chemical composition of zeolites by charge compensation, implying that the positive charges of OSDAs strongly interact with negative charges induced by Al. This work begins with the study to understand the location of OSDAs inside the cavities of zeolites and its effects on the physicochemical properties of zeolites. Then, OSDAs are designed to minimize the energy of OSDA–Aluminosilicate zeolite composites, with the aim of localizing Al at the specific T-site providing the energetic minima. In addition, the work is extended to Zn. A new Zn-containing zeolite (zincosilicate zeolite) is synthesized by particularly focusing on the procedures to pretreat the raw materials for zeolite synthesis.

4. 研究成果

(1) Understanding of the locations of organic structure-directing agents and their effects on the zeolite properties

The hierarchically organized MFI zeolite with a complex and unusual morphology can be achieved by control of intergrowth sequentially using a simple diquatery ammonium OSDA (Pr_6 -diquat-5) (Fig. 1a). The obtained zeolites possessed three classes of porosity in one body: the intrinsic microporosity of zeolite together with mesoporosity existing within the zeolite plates and macroporosity stemming from the complex intergrown structure. The number of carbon atoms between two charged nitrogens in the OSDAs was found to significantly affect the intergrowth and morphology of MFI zeolites formed. Computational modeling and advanced characterization techniques including polarized stimulated Raman

scattering (SRS) microscopy suggested that Pr₆-diquat-5 is occluded along, but imperfectly fitted to, the *b*-axis of MFI zeolite (Fig. 1b). Pr₆-diquat-5 has to adapt their intramolecular N–N distance to be occluded intact within the MFI zeolite framework, generating structural constraints or stresses that can yield more strain and subsequently framework distortion (Fig. 1c), thereby enhancing the defects. These defects can then act as connectors for sequential intergrowths.

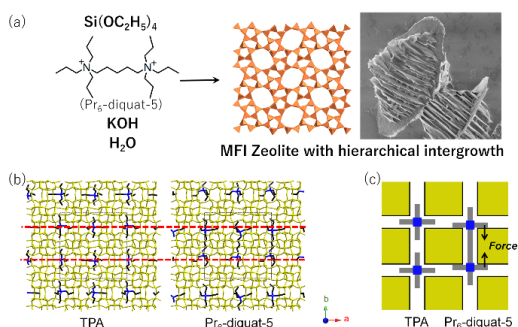


Fig. 1 (a) Schematic of the synthesis of hierarchically intergrown MFI zeolite. (b) Comparison of locations of TPA, a typical OSDA for the MFI zeolite, and Pr₆-diquat-5 siting along the *b*-axis of the MFI zeolite. (c) Schematic of the unusual fitting of Pr₆-diquat-5.

These results suggested that the structural matching between OSDAs and zeolite frameworks does not allow for the free movement and rotation of OSDAs, yielding the zeolites with unique properties. It can be further postulated that the appropriate structural matching can provide a chance of OSDAs to control the Al locations at specific sites in zeolite frameworks.

(2) Control of the locations of Al atoms in the zeolite frameworks

The most siliceous FAU zeolite (zeolite Y) can be achieved via a one-step organic-free route. Computational modeling revealed that this highly siliceous FAU is thermodynamically feasible. The amounts and distributions of Al in the double-six-ring (*d6r*), a composite building unit of FAU, in zeolite models were analyzed. In the models replicating the synthesized FAU, it seemed that Al speciation in the FAU product is more discriminate than random since *d6r* configurations with 3 Al atoms are more pronounced, while units with 0, 1, 5, and 6 Al are not observed.

To further explain such unusually biased configurations, structure optimization was performed. The results

suggested that the synthesized FAU with unique Al configurations exhibits lower relative framework energy than FAU counterparts with identical Si/Al but random Al distribution, suggesting that, under particular synthesis conditions, zeolites can be formed with specific Al locations to yield (on average) more energetically favorable configurations. It, therefore, can imply that zeolites with specific Al locations can be achieved as an “equilibrium” product by controlling the energetic pathways of zeolite formation, which is the motivation to rationally design the locations of Al in zeolites by controlling the energy difference.

As a proof-of-concept, IFR zeolite was selected. Three different OSDAs were used to synthesize IFR zeolite under an identical synthesis condition (Fig. 2a). The one-dimensional pore of IFR zeolite is composed of the sequence of cavities that tightly accommodate OSDAs on a one-by-one fashion (Fig. 2b).

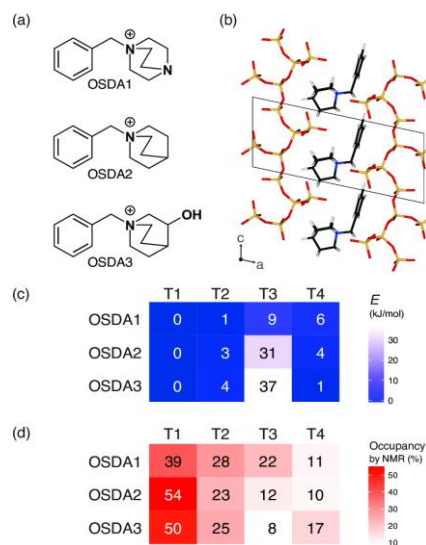


Fig. 2 (a) OSDAs used in zeolite synthesis. (b) Structural match between IFR zeolite and OSDAs. (c) Heatmap of relative energies of aluminosilicate IFR having Al in different T sites with three OSDAs. (d) Heatmap of the occupancy of Al in IFR synthesized with different OSDAs estimated from results of ²⁷Al MAS NMR.

The computational calculations suggested that OSDAs used for the synthesis of IFR zeolite are able to alter the energetically favorable T sites for Al atoms (Fig. 2c). The IFR zeolite products were characterized by ²⁷Al solid-state NMR spectroscopy with the aid of DFT calculations. The results indicated that the fractions of Al atoms at different

crystallographic T sites can be tuned in accordance with the energies derived from the zeolite-OSDA complexes (Fig. 2c and 2d). These results suggested again that Al siting in the zeolite framework is yielded at (on average) lower energetic configurations. This combined computational and experimental investigation thus provides evidence for the ability of OSDAs to direct Al atoms into more energetically favorable T sites of the zeolite framework, thereby offering rationally synthetic guidelines for the selective placement of Al atoms into specific crystallographic sites.

(3) Synthesis of new Zn-substituted zeolites

There is growing interest to develop zeolites that can effectively stabilize divalent cations such as Cu^{2+} , Fe^{2+} , and Ni^{2+} for catalytic applications. Zincosilicate zeolites have been considered as a promising platform for stabilization of divalent cations because isomorphous substitution of Zn(II) for Si(IV) in the zeolite framework can generate two anionic charges per Zn atom. The synthesis of a new microporous zincosilicate zeolite with CHA topology was achieved for the first time.

One of the obstacles in the synthesis of Zn-containing zeolites is the precipitation of zinc oxides or hydroxides under basic conditions of zeolite synthesis. To prevent this, the mixing procedures of the raw materials prior to hydrothermal synthesis of CHA zeolites were paid particular attention as the initial state of Zn species in a basic solution seems to be very crucial for the successful synthesis. The obtained zincosilicate CHA showed remarkably higher ion-exchange ability for divalent cations compared to that of aluminosilicate and zincoaluminosilicate analogs.

5. 主な発表論文等

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6. 研究組織

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