学 位 論 文 審 査 の 要 旨

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Synthesis, Structure and Property of Polyoxometalate-based Novel Microporous Crystalline Oxides.
（ポリオキソメタレートアセンブリによる新規結晶性ミクロポーラス酸化物の合成・構造・機能）

Polyoxometalates (POMs) are molecular metal oxides with numerous structures and chemical compositions. Recently, an increasing number of researches focus on POM and relative materials based on POM, because POM has interesting properties, which would result in the applications of POM and POM-based material in many fields, including catalysis, adsorption, separation, photocatalysis, electrochemistry, magnetism, and medicine. Both structure and chemical composition of POM can be easily modified, and thus variety of POM-based materials can be synthesized, which offer advantages of not only POM but also other structure building blocks of the materials. Therefore, synthesis of novel POM and POM-based material are interesting and important.
This thesis mainly focuses on the ordered crystalline novel POM-based materials. First, synthesis of novel crystalline POM-based materials and preparation of large well-crystallized materials for structural analysis were conducted. Second, structural characterization of the obtained novel materials by using either single crystal X-ray analysis or powder diffraction method was performed. Third, property and application of the materials, including adsorption, ion-exchange, and catalysis, were investigated.
In chapter 2, a new well-crystallized material based on Mo, V, and Bi was prepared, and single crystal X-ray analysis showed that the material was constructed by assembly of ε-Keggin POM, [ε-VMo9.4V2.6O40], with linking Bi ions. There were cages and channels being found in the framework of material, and cages were surrounded by ten ε-Keggin POMs. The cage was connected with channels tetrahedrally to form a 3D pore system of the material. After removal of the guest molecules in the material, the basic structure was stable, and opened micropores appeared in the material. The material showed zeolite-like property. Small molecules, such as nitrogen, carbon dioxide, methane, and ethane, could be adsorbed in the material.
In chapter 3, the author demonstrated that the ε-Keggin POM-based complex metal oxides display high chemical composition diversity. Chemical composition of ε-Keggin POM, linker metal ions, and counter-cations were able to be varied. Different kinds of transition metal ions, including Zn, Mn, Fe, and Co, were incorporated in the ε-Keggin POM-based 3D framework. Several complex metal oxides based on polyoxomolybdate could be synthesized. The structures of the new materials were determined by powder diffraction data combined elemental analysis and valence analysis. Structural analysis showed that the materials were iso-structural materials of Mo—V—Bi oxide. The existing guest molecules were partly or mostly removed by heat treatment, which was indicated by TPD-MS measurement.
In chapter 4, the author reported the detailed investigation of the conditions for synthesis of Mo—V—Bi oxide. Synthesis temperature, synthesis time, pH of the precursor, concentration of the precursor, and starting materials were studied. Solubility of the starting materials was found to have significant influence on the size of the resulting material. Nanometer-sized single crystal of Mo—V—Bi oxide was prepared by using all soluble starting materials. Properties of the material, such as adsorption, was altered by changing the size of the material. Formation mechanism of Mo—V—Bi oxide was studied with Raman spectroscopy, indicating that ε-Keggin POM of [ε-VMo9.4V2.6O40] and a ball-shaped polyoxovanadomolybdate formed in precursor solution assembled to Mo—V—Bi oxide and orthorhombic Mo—V oxide, respectively.
Adsorption properties of ε-Keggin POM-based 3D framework were presented in chapter 5. The ε-Keggin POM-based 3D framework, Mo—Zn oxide, could selectively adsorption of carbon dioxide and methane. The material showed high adsorption entropy of carbon dioxide than that of methane. The material strongly interacted with carbon dioxide but weakly with methane. Counter-cation of the material affected the adsorption of carbon dioxide. Sodium ions improved the interaction with carbon dioxide while the interaction with methane was kept constant. Na—Mo—Zn oxide was successfully applied to gas chromatographically separation of methane and carbon dioxide.
In chapter 6, ion-exchange property of the materials of Mo—V—Bi oxide, Na—Mo—Zn oxide, and NH4—Mo—Mn oxide was studied. It was found that the original counter-cation in materials could be replaced by other alkaline metal ions, as zeolite did. Large cations, such as Cs+ and Rb+, showed high ion-exchange ability, while small cation showed low ion-exchange ability. For the K-exchanged Mo—V—Bi oxide, the position of K+ in the material of Mo—V—Bi oxide was determined with single crystal X-ray analysis, which indicated that the cation was mostly in channel site of the material.

In chapter 7, the first transition metal oxide molecular wire was successfully synthesized, the structure of which was firstly determined with powder diffraction data. Then it was confirmed with single crystal X-ray analysis. The material was constructed with a molecular wire in a hexagonal fashion. The molecular wire could be separated from the crystal easily.
In chapter 8, the author showed general conclusion. This thesis showed the first example on the synthesis of a series of all-inorganic microporous POM-based crystalline oxides as a new class of mixed oxide material. Compared with the traditional porous materials such as zeolite, the porous POM material can show outstanding properties such as redox property which zeolites do not have. The thesis showed that different metal elements are easily incorporated into the framework, which can allow us fine tuning of its property, and the material shows zeolite-like properties including molecule adsorption and ion-exchange. Thus, the thesis opens a new door for developing new porous materials based on POM. The author also synthesized the first transition metal oxide molecular wire as a new class of inorganic molecular wire. Potentially, different metal elements can be incorporated into the molecular wire, which can be applied to many fields including sensor, semiconductor, and transistor.
Considering these research achievements, we conclude that the author is eligible to have a Doctor degree of engineering.