

論文の内容の要旨

Atomic-Resolution Electron Microscopic Imaging of Reaction Intermediates in Metal-Organic Framework Synthesis (金属有機構造体合成における反応中間体の原子分解能電子顕微鏡観察)

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Metal-organic frameworks (MOFs) are the compounds made by coordination bonding between metal ions and organic ligands. MOFs have attracted significant interests in the past two decades for their unique structures and properties. However, their formation mechanism, especially the nucleation, the initial stage of crystallization, is uncovered and limits their applications. That is mainly because there are no suitable methodologies to analyze their structures at the molecular level. In this thesis, I focused on detecting the nucleation mechanism of MOFs by determining structures of the prenucleation clusters (PNCs) of MOFs by high-resolution transmission electron microscopy.

Chapter 1 describes the general introduction of the nucleation process study of MOFs and the single-molecule atomic-resolution real-time electron microscopy (SMART-EM). The advantage and current achievement of SMART-EM are discussed.

Especially, SMART-EM imaging of PNCs of an organic crystal on a single molecule template is introduced as a key to experimental design of the current work.

Chapter 2 describes SMART-EM imaging the PNCs of MOF-2-DMF, a layer-packed two-dimensional MOF. The PNCs of MOF-2-DMF are demonstrated to be linear and square structures. The structure of a square PNC with a tetragonal node is determined. Its formation mechanism matches with two-step nucleation mechanism.

Chapter 3 describes SMART-EM imaging of PNCs of MOF-5, a three-dimensional MOF comprising the cubic unit structure. By using the SMART-EM technique, I successfully captured and identified cubic clusters with octahedral nodes as PNCs of MOF-5. By introducing iodine atoms, the structure of a cubic PNC comprising twelve ligands and 24 Zn atoms is precisely determined. The second step of two-step nucleation, the structure ordering step, is captured as SMART-EM videos.

Chapter 4 describes the formation mechanism investigation based on the time-course of dimension analysis of PNCs by SMART-EM. Like MOF-2-DMF case, the formation mechanism of MOF-5 is demonstrated to be a two-step nucleation mechanism. The MOF-5 crystal forms after reacting for 4 h and undergoes Ostwald ripening for tens of hours. The higher order PNCs are converted from lower order PNCs as the pH increases with the decomposition of DMF.

Chapter 5 describes a new method to analyze the motion blur of image sequences at molecular level quantitatively. Also, I created a new model that can provide a visual impression close to the corresponding TEM image. With the help of heavy atoms, quantitative analysis of the deviation between simulation and real TEM images can be done.

Finally, Chapter 6 summarizes present studies and does perspective to the future application of SMART-EM.