



非晶質配位高分子の配位構造の同定

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1. 背景と研究目的

Coordination polymers (CPs) is an organic-inorganic hybrid material that self-assembles from metal ions and crosslinkable organic ligands. Until now, CPs have been utilized in various field of applications, such as gas adsorption / separation, ion conduction and many more by the virtue of their structural design. We succeeded in synthesizing bulky cyanide ligand (mL1) containing Ag(I) CP (Ag-mL1), which melts at 170 °C. In addition, degas crystalline Ag(I) CP (Ag-mL1-degas) can be transformed into glassy Ag(I) CP by gentle grinding. We performed hard X-ray XAFS to understand the local geometry and structural features of Ag(I) in the crystalline and glass CPs.

2. 実験内容

The crystalline (Ag-mL1-degas) and glass (Ag-mL1-d_Glass) compounds are moisture sensitive, so the sample preparation was carried out in Ar filled glovebox. The as-synthesized CP (Ag-mL1) was measured as a standard sample, as the composition of the Ag-mL1 was similar with the degas crystalline (Ag-mL1-degas) and glass (Ag-mL1-d_Glass) samples. The hard X-ray was sufficient to excite the electron from the core K-shell for all these Ag(I) CPs to understand the electronic structure and local geometry.

3. 結果および考察

The Ag K-edge XANES spectra for all the three Ag(I) CPs was performed and analysed. It was confirmed that the oxidation state (electronic structure) retained in +1 for all three CPs (Fig.1a). The sharp transition around 25520 eV is due to the electronic transition from core 1s (K) shell to the higher shell. On the other hand, EXAFS analysis was performed to evaluate the coordination number around the Ag(I). The coordination environments were all nearly identical to Ag-mL1-d, Ag-mL1-d_Glass, Ag-mL1 (Fig.1b).

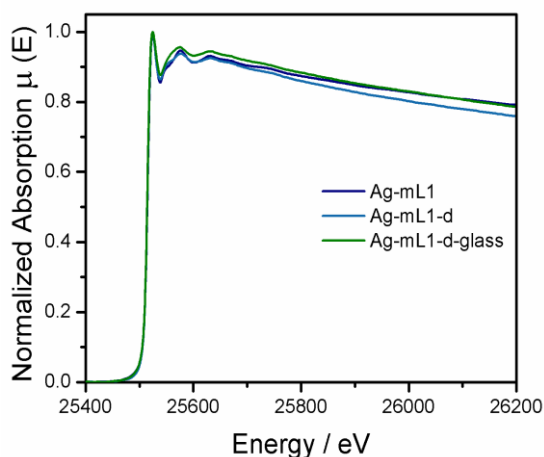


Fig.1a XANES for Ag(I) CPs

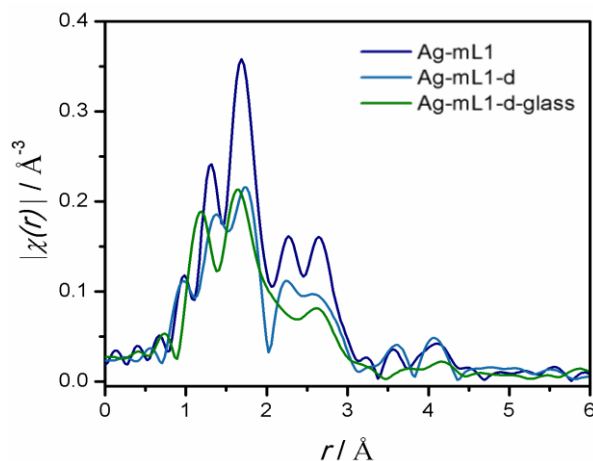


Fig.1b EXAFS for Ag(I) CPs