EXAFS Characterization for Immobilized Metal Ion-Containing Ionic Liquid

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Introduction

Design and preparation of a new class of immobilized single-reaction-site catalysts derived from structurally well-defined metal ion-containing ionic liquids may provide an opportunity to exploit new catalytic materials with good performance from fundamental interests as well as practical aspects of an environmental-friendly system. Ionic liquids or molten salts composed of entirely ions have received much attention as their versatile functionalities and can be regarded as new key precursor materials for catalysts. Imidazolium ions commonly used as cationic moiety are 1-ethyl-3-methylimidazolium (Emim) and 1-butyl-3-methylimidazolium (Bmim). We have synthesized a series of metal ion-containing Bmim salts for catalytic applications. We also synthesized a new ionic liquid molecule, 1-methyl-3-(trimethoxysilylpropyl)imidazolium chloride that allows us to prepare immobilized metal ion-containing ionic liquids [1].

The aim of the present study is to characterize the newly prepared immobilized Cu²⁺ ion containing ionic liquid (Imm-Cu²⁺-IL) by EXAFS in comparison with the measurement for BmimCuCl₄ for which X-ray single crystal structure analysis was already performed in order to find the local structure around Cu ion.

Experimental

The preparation of Imm-Cu²⁺-IL on silica support (Aerosil 300) is described in the reference [1]. Cu-K edge EXAFS spectra were measured at BL-10B station of KEK-IMSS-PF. The energy and current of electrons in the storage ring were 2.5 GeV and 250 - 400 mA, respectively. Ionization chambers filled with pure N₂ and Ar/N₂ (50:50) mixed gas were used to monitor the incident and transmitted X-rays, respectively. The EXAFS spectra were analyzed with the UWXAFS package. The curve-fitting analysis was carried out using the FEFFIT program in the R-space. The fitting parameters were coordination numbers (CN), interatomic distances (R), Debye-Waller factors (σ²), and a correction-of-edge energy (ΔEₑ). The phase shifts and backscattering amplitudes were calculated by the FEFF8 code.

Results and Discussion

Fig. 1 shows the k³-weighted Cu K-edge EXAFS Fourier transforms and curve fitting results for Imm-Cu²⁺-IL, where the single Cu-Cl shell appears. EXAFS measurements were also performed for BmimCuCl₄, in which Cu is coordinated by four Cl atoms with the distance of 0.226 nm in a distorted Td symmetry as found by XRD analysis. Therefore, fitting was performed with the coordination number fixed at 4 and S₀² was fitted to be 0.83 ± 0.03. This value was used to fit the data for Imm-Cu²⁺-IL as summarized in Table 1.

The analyses led us to conclude that Cu atom in Imm-Cu²⁺-IL has the same local structure as that for crystalline BmimCuCl₄.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN</th>
<th>Distance / 10⁻¹ nm</th>
<th>DW / 10⁻⁵ nm²</th>
<th>Rf(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Bmim]₂CuCl₄</td>
<td>4.0 (fix)</td>
<td>2.256±0.002</td>
<td>5.56±0.3</td>
<td>0.25</td>
</tr>
<tr>
<td>Imm-Cu²⁺-IL</td>
<td>3.9±0.6</td>
<td>2.25±0.01</td>
<td>10.4±2</td>
<td>3.36</td>
</tr>
</tbody>
</table>

a  k=3.0 - 12.0 Å⁻¹, R=1.0 - 3.0 Å, ΔEₑ=-0.1 ±0.4 eV. S₀² was fitted to be 0.83 ± 0.03.
b  k=3.0 - 11.0Å⁻¹, R=1.0 - 3.0 Å, ΔEₑ=-3 ±2 eV. S₀² was fixed at 0.83.

References

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