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EXAFS Analysis for Immobilized Metal Ion-containing Ionic Liquids

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Introduction

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 [1]. 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 [2,3].

The aim of the present study is to characterize the newly prepared immobilized metal ion-containing ionic liquid (Imm-M^{2+}-IL) by EXAFS in comparison with the measurement for $[Bmim]_2[MCl_4]$ for which X-ray single crystal structure analysis was already performed in order to find the local structure around M ion. The examined metal ions were Pd^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+} and Co^{2+}.

Experimental

The preparation of Imm-M^{2+}-IL on silica support (Aerosil 300) is described in the reference [3]. Measurements of extended X-ray absorption fine structure (K-edge EXAFS of each element) were carried out at the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF). The measurements were made in a transmission mode. 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 (σ), amplitude factor (S_0^2), and a correction-of-edge energy (ΔE_0). The phase shifts and backscattering amplitudes were calculated by the FEFF8 code.

Results and Discussion

Fig. 1 shows the k^3-weighted Ni K-edge EXAFS Fourier transforms and curve fitting results for Imm-Ni^{2+}-IL, where the single Ni-Cl shell appears. EXAFS measurements were also performed for $[Bmim]_2[NiCl_4]$, in which Ni is coordinated by four Cl atoms with the distance of 0.227 nm in a distorted *Td* symmetry as found by XRD analysis. Therefore, fitting was performed with the coordination number fixed at 4 and

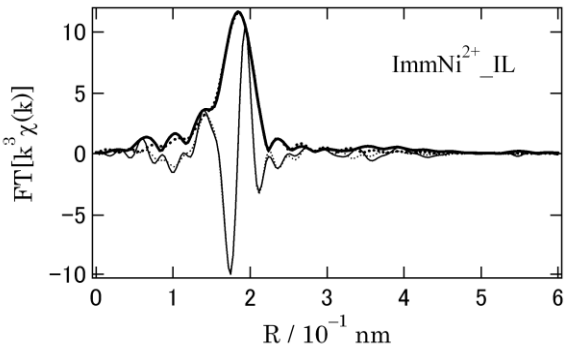

Fig. 1 k^3-weighted Ni K-edge EXAFS Fourier transforms and curve fitting results for Imm-Ni^{2+}-IL. Two solid curves and dotted curves represent the absolute values (thick) and imaginary parts (thin) of the observed data (solid) and the fitted spectra (dotted), respectively.

Table 1 Curve-Fitting results of the Fourier-transformed EXAFS data (M-Cl shell) for $[Bmim]_2[MCl_4]$ and Imm-M^{2+}-IL measured at room temperature

Sample	CN	M-Cl Distance / 10^{-1} nm	DW/ 10^{-5} nm^2	R_f(%)
Imm-Pd^{2+}-IL	4.3±0.3	2.31±0.002	2.7±0.4	1.45
Imm-Cu^{2+}-IL	3.9±0.6	2.25±0.01	10±2	3.36
Imm-Ni^{2+}-IL	3.6±0.2	2.27±0.003	6.1±0.4	0.65
Imm-Mn^{2+}-IL	3.8±0.4	2.36±0.008	7±1	0.77
Imm-Zn^{2+}-IL	3.6±0.2	2.28±0.004	6.1±0.5	1.03
Imm-Co^{2+}-IL	3.7±0.3	2.28±0.006	4.7±0.9	0.47

S_0^2 was fitted to be 0.83 ± 0.04. This value was used to fit the data for Imm-Ni^{2+}-IL as included in Table 1. As for other metal ions, the corresponding method was adopted, where the value of the amplitude factor was obtained by the measurement and analysis on $[Bmim]_2[MCl_4]$ and the analysis for Imm-M^{2+}-IL was achieved based on the obtained S_0^2. These results (Table 1) led us to conclude that metal atom in Imm-M^{2+}-IL has the same local structure as that for crystalline $[Bmim]_2[MCl_4]$. Catalytic performances of Imm-M^{2+}-IL with reusability have been reported elsewhere [2,3].

References

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