7C, 9C, NW10A/2007G151

# EXAFS Analysis for Immobilized Metal Ion-containing Ionic Liquids on Porous Alumina Disc

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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 on silica surfaces [2,3].

In the present study we adopted a porous alumina disc as a support for immobilizaion of ionic liquid molecules, since a porous alumina disc has a wide surface area and it can be handled as a solid pellete, therefore, if it is used in a liquid phase catalytic reactions, we can expect a more convenient recycle process of catalysts as compared to immobilization on powder supports. In this study, we prepared several kinds of metal chlorides containing ionic liquids immobilized on a porous alumina disc and EXAFS analyses were achieved.

## Experimental

The preparation of Imm-$M^{2+}$-IL on a porous alumina disc (Whatman Anodisc 13) was performed in the same way as Ref. [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 fluorescence detection mode using a Lytle detector with Kr gas. 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 ($\sigma$), amplitude factor ($S_0^2$), and a correction-of-edge energy ($\Delta E_0$). The phase shifts and backscattering amplitudes were calculated by the FEFF8 code.

## Results and Discussion

Fig. 1 shows the $k^3$-weighted Cu K-edge EXAFS Fourier transforms and curve fitting results for Imm-$Cu^{2+}$-IL, where the single Cu-Cl shell appears. In the fitting process of EXAFS functions, the value of the amplitude factor $S_0^2$ was fixed at 0.83 according to Ref. [3].

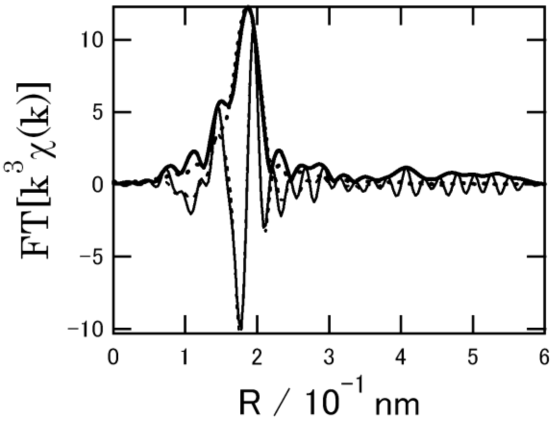

Fig. 1 $k^3$-weighted Cu K-edge EXAFS Fourier transforms and curve fitting results for Imm-$Cu^{2+}$-IL on porous alumina disc. Two solid curves and dotted curves represent the absolute values (thick) and imaginary parts (thin) of the observed data (solid) and the fitted spectra (dotted), respectively.

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

| Sample | CN | Cu-Cl Distance / $10^{-1}$ nm | DW/ $10^{-5}$ $nm^2$ | $R_f$(%) |
|---|---|---|---|---|
| Imm-$Cu^{2+}$-IL on $Al_2O_3$ | 3.3±0.4 | 2.26±0.008 | 4.6±0.9 | 3.44 |
| Imm-$Cu^{2+}$ -IL on silica | 3.9±0.6 | 2.25±0.01 | 10±2 | 3.36 |

The results of curve-fitting is summarized in Table 1 in comparison with the result for immobilization on silica [3]. It is clearly seen that immobilization on Alumina disc resulted in the similar values for silica, indicating that immobilization of ionic liquid layer and introduction of Cu chlorides proceeded successfully. The same results were obtained for Pd K-edge EXAFS for Imm-$Pd^{2+}$-IL on a porous alumina disc. These metal ion-containing immobilized ionic liquid layer on alumina discs are examined for catalytic reactions.

## References

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