

Study on Fine Structure of Hydroxyapatite-bound Rare Earth Metal Complex Catalysts for Carbon-Carbon Bond-Forming Reactions

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1. Introduction Apatites and related compounds, most notably hydroxyapatite (HAP), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, and fluoroapatite (FAP), $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, are of considerable interest in many areas owing to their multiple functionalities. Our strategy for the design of nanostructured heterogeneous catalysts focuses on the ability of the HAP, which can be considered as a rigid macroligand for catalytically active centers.¹ We found that La species could be introduced on the HAP surface (LaHAP) to afford an efficient heterogeneous catalyst for the Michael reaction. Moreover, a FAP-bound La catalyst modified with (*R,R*)-tartaric acid (TA-LaFAP) provided the Michael adduct quantitatively in up to 60 % *ee*.² The catalytically active La species of the LaHAP and TA-LaFAP were elucidated by La K-edge XAFS spectroscopy.

2. Experimental The LaHAP was obtained by treating the CaHAP with an aqueous solution of $\text{La}(\text{OTf})_3$ at room temperature. La K-edge X-ray absorption spectra were recorded at room temperature using a transmission mode at the beam line 01B1 station attached with Si(311) monochromator. The procedure of data treatment was described elsewhere.³

3. Results and Discussion Formation of a trivalent La species was indicated by the edge position of the La K-edge XANES spectrum of the LaHAP, which was identical to that of La_2O_3 . The FT of k^2 -weighted EXAFS data are depicted in Figure 1. There were no peaks suggestive of contiguous La–O–La bonds in the LaHAP (A), detectable in that of La_2O_3 (D) at around 3.7 Å. The inverse FT of the main peaks of the LaHAP was well fitted using five short (2.52 Å) and three longer (2.59 Å) La–O bonds. We therefore propose a monomeric La^{III} complex surrounded by hydroxyl, phosphate, and weakly coordinated aqua ligands on the HAP surface, as

illustrated in Figure 2. In the case of the LaFAP prepared by the same method with the FAP in place of the HAP, the shape and edge position of the XANES spectra resembled those of the LaHAP. Additionally, comparing analogous FT-EXAFS spectra of the LaFAP with the LaHAP (B and A in Figure 1) shows that the La species are supported on the FAP in a monomeric form having +3 oxidation state and that the local structure around the La species is quite similar to that of the LaHAP.

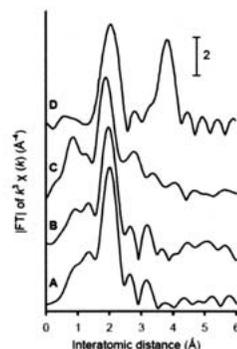


Figure 1. Fourier-transforms of k^2 -weighted La K-edge EXAFS experimental data for (A) LaHAP, (B) LaFAP, (C) TA-LaFAP, and (D) La_2O_3 .

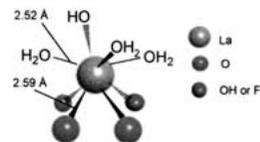


Figure 2 A proposed surface structure of the LaHAP

References

- [1] For examples, see: Kaneda, K. *et al. Chem. Commun.* **2005**, 3331; *J. Am. Chem. Soc.* **2003**, *125*, 11460; *ibid.* **2002**, *124*, 11572; *ibid.* **2000**, *122*, 7144.
- [2] Kaneda, K. *et al. Tetrahedron Lett.* **2005**, *46*, 4283.
- [3] Tanaka, T. *et al. J. Chem. Soc., Farad. Trans.* **1998**, *84*, 2987.

in-situ XANES observation of cerium electrochemical reaction from various molten chloride baths

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Introduction

To contribute on the development of pyrochemical reprocessing of nuclear fuels, one of the most key issues for separation of transuranium elements is how to control the condition at electro-winning process. There exists special concern with electrochemical behaviour of rare earths, however, it is very difficult to evaluate since experimental condition is too severe to explore electrochemical phenomena during such transient state. Thus in order to develop one of the *in-situ* evaluation techniques for electrode reactions, we have tried to utilize XAFS technique. We have focused on the behaviour of Ce electro-deposition reaction at molybdenum cathode from various molten alkali chlorides, since we need to find out another candidate melt bath for actinide extraction.

Experimental

The mixtures of alkalis and cerium chlorides were prepared in glassy carbon crucibles under dried argon atmosphere. These chemicals were installed in the specially designed quartz cell for *in-situ* electrochemical XAFS measurements (see 2005A0697-RI-np). The electric furnace used was equipped to make electrochemical condition at

high temperature. During these six shifts of beamtime, we have carried out *in-situ* XAFS measurement on molten NaCl-RbCl-CeCl₃, LiCl-KCl-CeCl₃ ($x_{\text{CeCl}_3} = 0.1$ and 0.01) during electrochemical reaction using Ce-K X-ray absorption edge (40.449keV).

Results and discussion

Figure 1 and 2 shows XAS and extracted $\chi(k)$ of molten LiCl-KCl-CeCl₃ before and after electrolysis near molybdenum cathode area. These features are drastically changed after electrolysis. We have also carried out XAFS measurements of CeCl₃ in various molten salts to obtain structural parameters, and the local structural difference around cerium depending on various melts bath would be highly related to electrochemical behaviour. XANES variation at electrode regions can give valuable information when we will optimize the condition at electrodeposition process. These results indicate the applicability of XAFS to one of the speciation techniques of electrochemical reaction. Still further modification on the cell and electrodes should be needed, however, quick scan technique developed at BL01B1 would be promising to apply such as electrochemical transient condition.

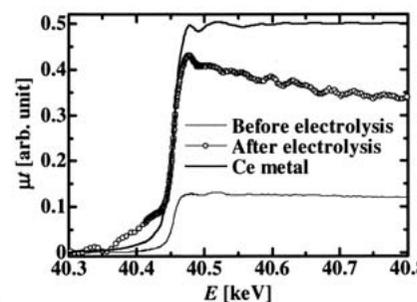


Fig. 1 XAS of molten LiCl-KCl-1mol% CeCl₃.

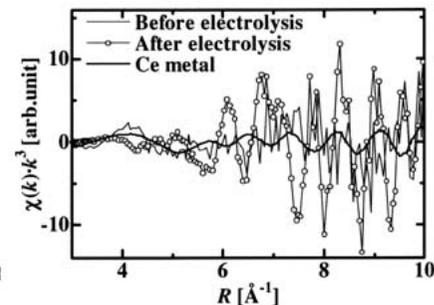


Fig. 2 $\chi(k)$ of molten LiCl-KCl-1mol% CeCl₃.