

Local Structure of Zr(IV) in Nitric Acid Solutions

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1. Introduction

Zirconium has been used in the cladding material of nuclear fuel. On the nuclear fuel reprocessing, uranium is separated by solvent extraction mixing with organic solution containing extractants and aqueous solution containing nuclear fuel elements dissolved into nitric acid. It is important to study chemical behavior of Zr ion in those solutions to increase the extractability and selectivity of uranium. It has been reported the coordination structure of Zr(IV) depends on the concentration of H⁺ as well as that of Zr(IV). Takasaki recently reported that Zr-Zr coordination number decreased with increasing the hydrogen chloride concentration, but did not change in case of perchloric acid [1]. This indicates that counter anion also plays an important role for the coordination of zirconium. On the other hand, the first coordination sphere of Zr(IV) and oxygen in aqueous acidic solution is not clear because of the similar Zr-O bond distance in the hydrolysis and zirconyl species. In the present study, local structure of Zr in various concentration of nitric acid was analyzed.

2. Experimental

ZrO(NO₃)₂ and ZrCl₄ were dissolved in various concentration of HNO₃ from 0.1 to 10 M. Zr(IV) concentration was 0.05 M. ZrCl₄ was treated in glove box, where oxygen and moisture are controlled less than 1ppm, to avoid its oxidation. Zr K-edge XAFS measurements were performed at the beamline BL-27B of the Photon Factory. A suite of principle component analysis, PCA, including target transformation and iterative target transformation was performed both on the acquired EXAFS spectra using the program code ITFA developed by Rossberg [2].

3. Results

Our group has reported the ligand exchange of hydroxide and halides to Au(III) ion occurred in aqueous solution by PCA of EXAFS spectra[3,4]. These analytical methods were applied into the present Zr system. In the measurement of XANES spectra, there are little differences in each HNO₃ concentration. In the data of EXAFS spectra, there are slightly change in oscillation pattern depending on the HNO₃ concentration as shown in Figure 1 (a). It was suggested that these spectra are consisted of one or two components based on the PCA results. Fitted spectrum was shown in dotted line of

Figure 1 (a). The calculated component fraction was plotted as a function of HNO₃ concentration as shown in Figure 1 (b). It was found that fraction of component 1, which was mainly observed at 10 M HNO₃ of ZrCl₄, increased with HNO₃ concentration increasing whereas the fraction of component 2 was main species at lower HNO₃ concentration. The results of Fourier transformations suggested that Zr-O bond distance slightly increased with increasing HNO₃ concentration due to different Zr-O coordinations such as Zr=O, Zr-OH, and Zr-OH₂.

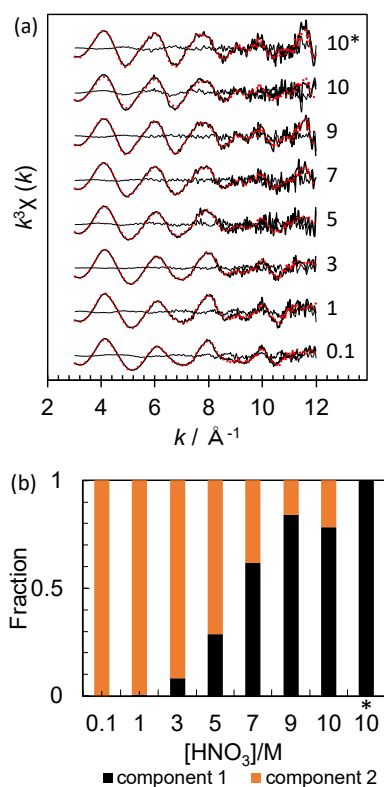


Figure 1. (a) Fitted EXAFS response of ZrO(NO₃)₃ dissolved into various concentration of HNO₃. Sample * was prepared using ZrCl₄ and 10 M HNO₃. (b) Fraction of two components calculated by PCA.

References

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