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XAFS study on rhodium-tin complexes in hydrochloric acid solutions

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Introduction

The properties of Rh-Sn complexes in HCl solutions are attracting much attention in the field of hydrometallurgy [1], since the addition of $SnCl_2$ to Rh in HCl solution markedly accelerates the Rh extraction from the aqueous to organic phases. Rh(III) complexes in HCl solutions are reduced to Rh(I) by the oxidation of Sn(II) to Sn(IV). However, detailed structural parameters in this system have not been obtained yet. This work investigated the change of valences and local structures of Rh with an increase in the Sn content.

Experimental

Sample solutions were prepared by adding $SnCl_2$ to Rh in 1M HCl solutions ([Rh]:[Sn]=1:1-12; [Rh]=0.1M) and then allowing to stand for 2d at room temperature. They were sealed in a polyethylene bag with a Teflon spacer. All of XAFS spectra were measured in transmission mode at the BL-10B station in the KEK-PF. The experimental data were analyzed by WinXAS Ver. 2.3 [2] and fit using theoretical phase and amplitudes calculated from the program FEFF 8 [3].

Results and Discussion

Figure 1 shows the dependencies of the XANES spectra on the Rh:Sn mole ratio. The XANES spectrum of the solution in the absence of Sn (i.e., Rh(III)) has one broad peak. When the Sn concentration increases, this broad peak decreases and then two peaks arise. In the 1:12 [Rh]:[Sn] solution, the spectrum shows that the Rh is probably monovalent [4]. The Fourier transforms of the EXAFS data (the phase shifts are not corrected) are shown in Fig. 2. A broad peak appears in the absence of Sn, which corresponds to Rh-O/-Cl correlations. A new peak occurs at larger *R* and the peak for Rh-O/-Cl correlations decreases with an increase in the content of Sn, suggesting that the Sn coordinates to the Rh. Therefore, the inner coordination sphere of the Rh in the 1:12 [Rh]:[Sn] solution consists of Sn. Structural parameters of the Rh-Sn correlation in this solution are determined from curve fitting. The results are as follows: coordination number N=5.3; bond length r=2.54Å; Debye-Waller factor σ^2=0.0041Å^2; the shift in threshold energy ΔE=2.3eV; amplitude reduction factor S_0^2=0.9. The obtained coordination number agrees with the ^{119}Sn NMR result, N=5 [5]. The Rh-Sn bond length is similar to the averaged value in the five coordinated Rh(I) crystal complex, 2.52Å [6].

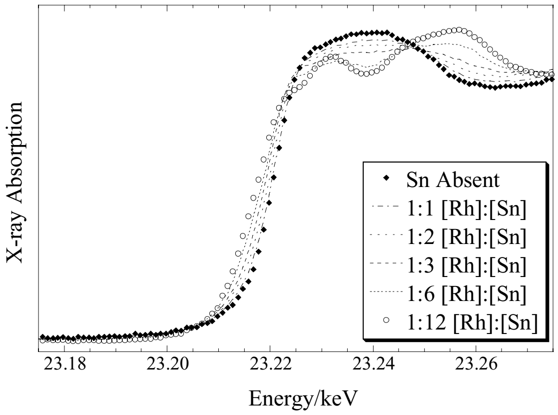

Fig.1 Rh K-edge XANES spectra of Rh-Sn complexes in 1M HCl solutions.

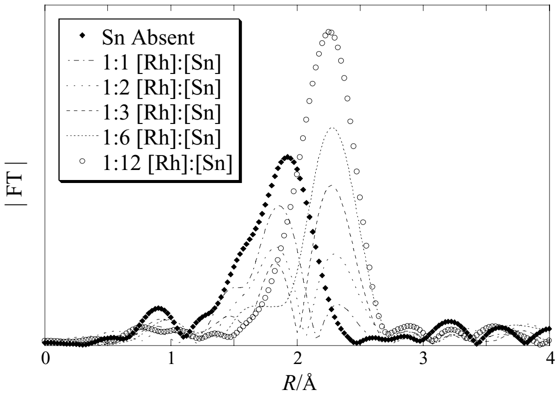

Fig.2 Fourier transforms of Rh K-edge EXAFS spectra of Rh-Sn complexes in 1M HCl solutions.

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