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Non-situ XAFS study of the alkali on the noble metal surface

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Introduction

The simulation of the electrochemical interface under UHV condition is one of the useful methods to investigate the electrochemical reaction, especially to reveal the role of water molecules. The simulated interface can be made of water molecules coadsorbed with suitable chemical species like halogen and alkali metal. The halogen is used for reproducing the anodic interface, while the alkali metal is used for the cathodic one. In the real electrochemical interface, however, the alkali metal is thought to be adsorbed with hydration shell, since the reduction potential of alkali cation is lower than that of hydrogen in the normal aqueous electrolytes. Thus, if the modelled interface reproduces the real interface precisely, the alkali metal coadsorbed with water molecules on the surface should exist in the hydrated forms, in other words, the water molecules should sever the alkali-substrate bond to make the hydrated alkali cation on the surface. We have traced whether this is true or not by potassium K-edge XAFS coadsorbed with water molecules on the Cu(111) surface.

Experimental

The Cu(111) surface was prepared by the normal surface science methods. Potassium was introduced from the SAES Getter’s source, and water was dosed through variable leak valve at about 120 K. Potassium K-XAFS measurements were performed at BL-11B in the fluorescence detection mode at 120 K.

Results and Discussion

Fig. 1 shows the NEXAFS spectra of K K-edge on the Cu(111) surface with (solid line) and without (dotted line) water. The spectra were collected with the grazing incidence geometry so that the electric vector of the incident x-ray is almost perpendicular to the surface. There is a shoulder at the absorption edge in the spectrum of K without water. This feature is assigned to K 1s - 4p transition and is reduced when water molecule is coadsorbed as can be seen in the spectrum of K with water. The reduction of the shoulder is caused by either the direct coordination of water molecules on the potassium or the indirect electronic effect through the substrate. Fig.2 shows the Fourier transferred EXAFS spectra of K/Cu(111). The dotted line represents the spectrum of K without water and the solid line that of K with water. The first prominent peak comes from the K-Cu first shell for both the spectra. This means that K-Cu bond still exists when water molecules are coadsorbed with potassium as opposed to the predicts described in Introduction. The position of the peak shifts to a shorter distance with water molecules and the peak height becomes larger. From the curve fitting analysis, the K-Cu bond lengths without and with water molecules are determined to be 0.294 nm and 0.284 nm, respectively. The coordination numbers are 3.4 for both samples, which associates atop adsorption. The difference of the peak height comes from the difference of Debye-Waller factor, which is quite small when water molecules are coadsorbed. The small Debye-Waller factor may be caused by the shorter bond distance and/or long range ordering of K with hydrogen bond network of water. The K-Cu bond persistence with water molecules will be discussed with further studies of K on other metal.

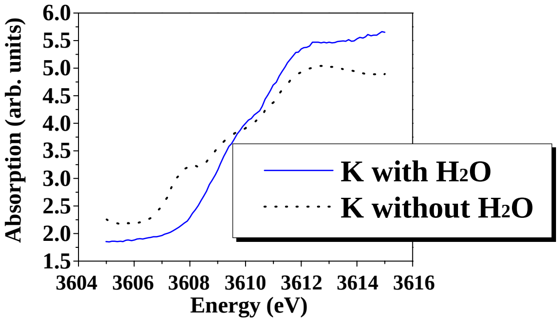

Fig.1. NEXAFS spectra of K K-edge on the Cu(111) surface collected with grazing incidence geometry.

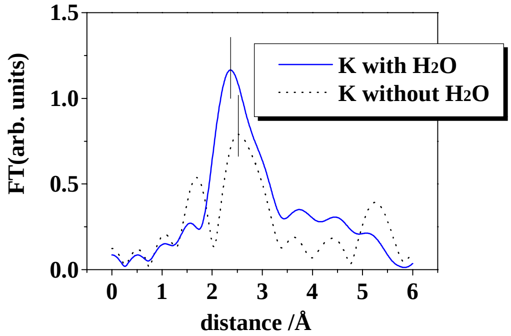

Fig.2. EXAFS FT spectra of K K-edge on the Cu(111) surface collected with grazing incidence geometry.