X-ray Reflectivity Investigation of Physically Adsorbed Noble Metal Complexes on Oxide Surfaces in Aqueous Solutions

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Introduction

The revised physical adsorption (RPA) model [1] predicts the adsorption behavior of metal complexes at oxide surfaces without an adjustment of parameter (i.e., the "chemical" free energy term). A key concept that is predicted by RPA theory is that the adsorption phenomena of metal complexes at oxide surfaces (the potential of which is better described in terms of a "non-Nernstian" model) are usually physical (electrostatic) rather than chemical in nature. The molecular understanding of noble metal catalyst impregnation [2] is largely based on this RPA model. Recently, the coordination chemistry of adsorbed species on alumina surfaces has been studied for hexachloro-platinate [3], in which the adsorbed species behave as if they were in the liquid phase, as the RPA model presumes.

High-resolution specular x-ray reflectivity has been measured to directly probe the structure of electrostatically adsorbed metal complexes. In particular, we studied adsorption of tetraamonium-platinate (TAP) complexes on a quartz (100) surface at pH 10 in a 200-ppm concentration of Pt. A large difference in the x-ray reflectivity was observed between the quartz-water interface and the quartz-TAP solution interface. The results reveal that the electrostatic adsorption of metal complexes on a solid surface in an aqueous solution strongly affects the solid-liquid interfacial structure, causing distinct layers to form within the aqueous-quartz interfacial region.

Methods and Materials

The oxide surface employed in this study was identical to that used in the previous study: a quartz (100)-water interfacial structure [4], in which a naturally grown "Herkimer diamond" (Herkimer County, New York) showing optically clear surfaces was used. Before the x-ray reflectivity measurements were made, the sample used for the quartz (100) surface was kept in deionized water for a day after it had been ultrasonically cleaned for 1 hour.

X-ray reflectivity measurements were performed at BESSRC beamline 12-BM at the APS. The incident energy was tuned at 19.5 keV by using a double-crystal Si(111) monochromator. The beam was focused vertically and horizontally by using a toroidal mirror. Details on the measurement techniques and the procedure for data analysis are essentially the same as those given in Ref. 5.

The x-ray reflectivity of the quartz-deionized water interface is used as a point of comparison for changes associated with TAP adsorption. These data reveal a typical crystal truncation rod profile, with weak reflectivity between Bragg peaks (Fig. 1) and with subsequent reflectivity minima becoming progressively smaller at a larger momentum transfer Q. The electron density profile derived from these data is essentially the same as that derived in a previous study of the quartz (100)-water interfacial structure [4].

When the surface was exposed to a 200-ppm TAP solution at pH 10, large changes were observed in the reflectivity data (Fig. 1). Care was taken to ensure that the deionized water was fully exchanged with the TAP solution by several flushes and that the surface was fully equilibrated with the TAP solution. The reversibility of TAP adsorption was directly proved when the cell was flushed with deionized water. The reflectivity after desorption quickly recovered to the original values
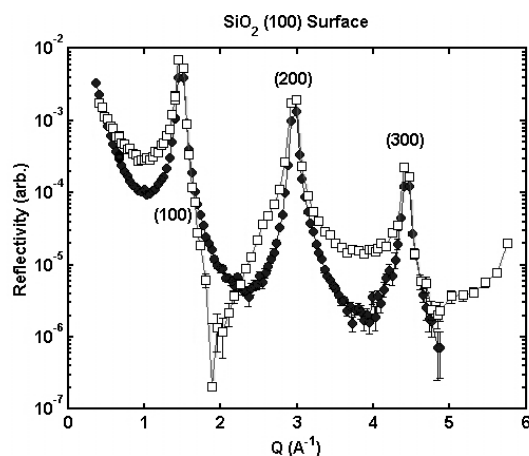

FIG. 1. X-ray reflectivity data (arbitrary units) are plotted as a function of momentum transfer $Q = (4\pi/\lambda)\sin(\theta)$, where θ is the angle of incidence, for the SiO_2(100)-water interface (solid circles), and after the surface was exposed to a 200-ppm solution of TAP at a pH of 10 (open squares). The lines are guides to the eye.

measured for the quartz-water interface. This supports the concept that adsorption of the TAP complexes is physically (i.e., electrostatically) controlled.

Results and Discussion

A comparison between the x-ray reflectivity of a quartz (100)-water interface and that of a quartz (100)-TAP solution interface is given in Fig. 1. A clear characteristic of the TAP reflectivity profile is that the reflected intensity is modulated about the values observed for the quartz-water interface. This immediately implies that a new Fourier component is introduced to the total structure factor by TAP adsorption. X-ray reflectivity is sensitive to the total electron density. Since the surface coverage of TAP is expected to be small and controlled by the size of the aqueous species, these data do not provide a unique measurement of the TAP (i.e., Pt). Electron density profiles derived through detailed analysis of these data, however, show that the major change in the profile is due to the addition of discrete layers with respect to the existing quartz (100)-deionized water interfacial profile [4, and present results]. The electron density corresponding to the additional layers is increased by ~30% relative to that of water, if we assume an average bulk water, which corresponds to adding ~0.1 Pt-equivalent monolayer (ML; here, 1 ML = 1 atom per 26.6 Å^2) to the existing water density profile. In contrast, no significant changes are observed in the first peak in the electron density above the quartz surface, previously determined to be due to the completion of the Si coordination shell by an oxygen-containing species (e.g., OH) [4].

The results indicate that the physical (electrostatic) adsorption of these relatively large charged aqueous species induces significant changes to the structure of the quartz-water interface structure. However, additional measurements will be needed to uniquely constrain the location of the TAP complex. An element-specific technique, like resonant anomalous x-ray scattering, would be required for this purpose.

Acknowledgments

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