

Proton transfer between water and hydroxyl on a Pt(111) surface observed by micro-scale x-ray photoelectron spectroscopy

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Introduction

Proton transfer in hydrogen-bonding systems is a fundamental process in nature and has a significant role in many physical, chemical, and biological processes. Although the investigation of the time scale of the proton transfer is essential to understand the process, the experimental rate determination has been so far quite limited

During water formation on a Pt(111) surface, the mixed phase of OH and H₂O is produced. Our kinetic Monte Carlo simulations suggested that the proton transfer plays a significant role for supplying H₂O to the reaction front [1]. However, it has not been clear how fast the two-dimensional (2D) proton transfer in the mixed OH+H₂O overlayer occurs. In this work, the time scale of the 2D proton transfer was studied by combining laser desorption and micro-scale x-ray photoelectron spectroscopy (micro-XPS) techniques.

Experimental

The experiments were performed at BL-7A under ultrahigh vacuum condition (below 1.0×10^{-10} Torr). First, the mixed OH+H₂O overlayer was prepared on Pt(111) by exposing an oxygen atom covered surface to 5 L H₂O at 130 K, and subsequent annealing to 175 K. To obtain the one dimensional (1D) adsorbate pattern, OH+H₂O/H₂O/OH+H₂O, a laser pulse was focused on 400 μm scale spot over the mixed OH+H₂O overlayer to remove the adsorbates. A Q-switched Nd-doped YAG laser was used with a pulse width of 5 ns at 532 nm (7 mJ/pulse). Then, the laser-desorbed surface was exposed to 2 L H₂O at 130 K for filling the vacant area, and annealed at 160 K.

The surface distribution change of OH and H₂O was measured by micro-XPS with a spatial resolution of 16.5 μm by using a position sensitive electron energy analyzer (SCIENTA SES-2002). During the proton transfer, spatially-resolved XPS spectra were successively measured at 140 K with the time interval of 36 minutes.

Results and Discussion

Figure 1(a) shows the coverages of the patterned structure OH+H₂O/H₂O/OH+H₂O obtained by fitting the XPS spectra with the standard spectra of OH and H₂O. After several hours, we confirmed that the OH coverage in the center region increases, while the H₂O coverage decreases. Scanning tunneling microscopy revealed that OH does not diffuse at 140 K [2]. Therefore, the increase

of OH is caused by the proton transfer between H₂O and OH.

In order to determine the change of OH coverage quantitatively, the integrated OH coverage in the central region marked by vertical lines (Fig. 1(a)) is plotted as a function of time (Fig. 1b). From the analysis of the OH coverage plot by a random walk theory, we found that the proton transfer occurs every 23 ± 5 ns. The diffusion coefficient D was found to be $(6.8 \pm 1.5) \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. Comparison of the diffusion coefficient with those in the other systems reveals that the proton transfer in the 2D network is rather slow due to suppression of the degree of freedom of oxygen atoms bound to the Pt(111) surface.

References

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[2] C. Sachs et al., Science 293, 1635 (2001).

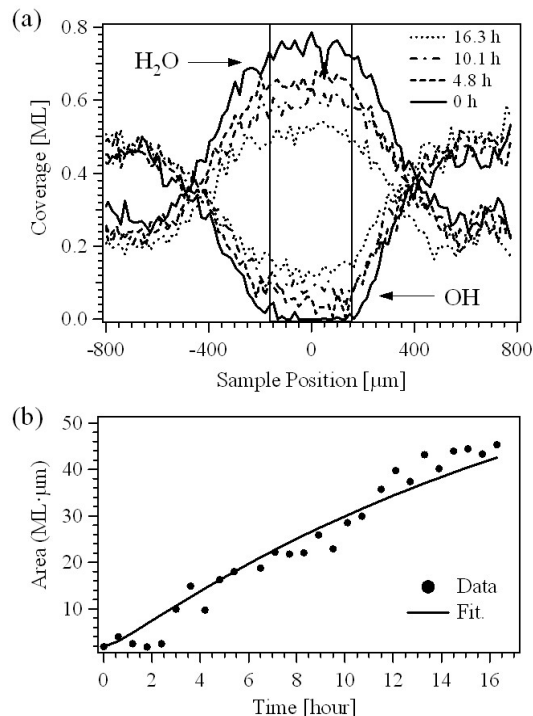


FIG. 1. (a) The coverage distribution of OH and H₂O as a function of time. (b) The intensity of OH area in the box of (a) as a function of time.

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