

Kinetics of water formation reaction on Pt(111) studied by dispersive NEXAFS

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Introduction

The catalytic formation of water on platinum has been extensively studied by exposing (2×2) O-covered Pt(111) surfaces to gaseous H₂ under UHV conditions. However, this mechanism is not fully understood because it is complicated as evidenced by the presence of an induction period and a long-lived reaction intermediate (OH) below the desorption temperature of H₂O (T_{des} : 170 K). Recently, Sachs et al. [1] revealed that OH domains propagate on the O-covered Pt(111) surface by producing H₂O in backward areas below T_{des} from the mesoscopic-scale observation of STM, and proposed a reaction mechanism that a cycle of two elementary reaction processes, OH + H → H₂O and O + 2 H₂O → 3 OH + H, causes such a propagation of the OH domains. However, the STM observations provide only information for a limited area, while the OH domains rapidly propagate with a mesoscopic scale over the whole surface. It is necessary to measure the kinetics for the whole surface and to examine whether the observed kinetics can be explained by the proposed microscopic mechanism. Then we measured the kinetics of the surface species (O, OH, and H₂O) below T_{des} by using dispersive NEXAFS [2], and investigated the reaction mechanism with two kinds of simulation: kinetic Monte Carlo method and Reaction Diffusion method.

Experimental

The experiments were performed at BL-7A under UHV condition (2.0×10^{-10} Torr). Dispersive NEXAFS is a newly developed method to measure a NEXAFS spectrum in several tens seconds and is useful for the study of the surface reaction.

The (2×2) O-covered Pt(111) surface was prepared by exposing to 30 L gaseous O₂ at 120 K, followed by annealing at 240 K. For the water formation reaction, the surface was exposed to gaseous H₂ (5.0×10^{-9} Torr) at a constant surface temperature (120 K – 140 K). Each O K-edge NEXAFS spectrum was taken in 35 s during H₂ exposure to monitor the real-time change of O, OH, and H₂O coverages.

Results and Discussion

The time evolution of the dispersive NEXAFS spectra shows that the peak due to O (530.3 eV) disappears and the broad structure associated with OH and H₂O (541.0 eV) increases with exposure. These spectra were fitted by a superposition of the standard spectra from O, OH, and H₂O adsorbed on Pt(111). Although the OH spectrum resembles the H₂O one, the difference is large enough to distinguish these two contributions. Figure 1 shows the

changes of O, OH, and H₂O coverages at different temperatures obtained from the curve fitting analyses. It is clearly recognized that the reaction has three characteristic steps; an induction period (I), fast increase of OH and H₂O with consuming O (II), and slow conversion of OH to H₂O (III). It was also found that the maximum OH coverage becomes smaller at a higher temperature.

To interpret these results and understand the reaction mechanism, we performed two kinds of simulations. As a result, the kinetic Monte Carlo simulation has reproduced the three reaction steps; the adsorbed H₂O molecules from the residual gas create the OH nuclei, whose density is smaller at a higher temperature (I), OH domains propagate until they contact each other (II), and the merged OH domains slowly convert to H₂O (III). The Reaction Diffusion simulations successfully explained the temperature dependence of the maximum OH coverage.

References

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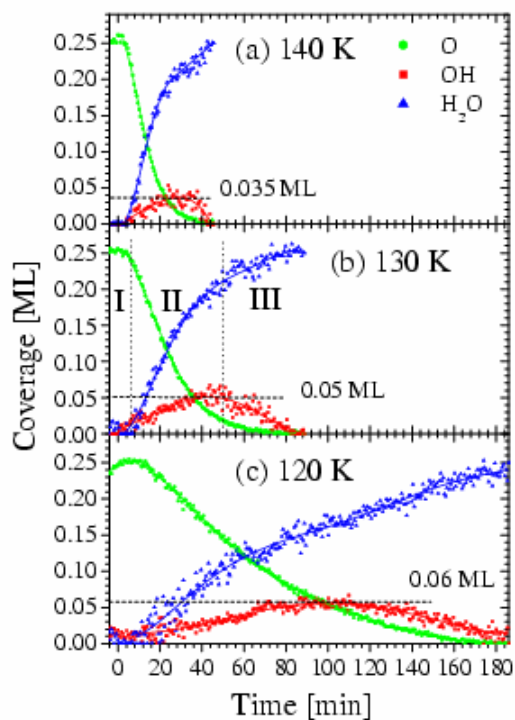


FIG. 1. Coverages of O, OH, and H₂O as a function of time at different temperatures.