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Development of time-resolved XPS system and its application to the observation of transient adsorption states of ethylene on Rh(111) surfaces

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Introduction

Direct observations of adsorbates in transient states during adsorption or reaction processes are important to elucidate their mechanisms. Recently, x-ray photoelectron spectroscopy (XPS) measurements from monolayer adsorbates at a time scale of several seconds have been made possible [1]. Though they have been successfully applied to studies of macroscopic kinetics, further improvement of the time resolution is necessary for the direct observation of reaction intermediates or transient adsorption states. We developed a time-resolved XPS (TRXPS) method by applying the pump-probe technique to repeatable phenomena. To test the performance of our experimental setup, we applied it to the observation of the transient adsorption states of ethylene on Rh(111) surfaces.

Experimental

The experiments were carried out at BL-7A with an UHV system. To conduct a time resolved measurement, we used a pulsed supersonic molecular beam and a chopped x-ray. The x-ray is chopped by a mechanical beam shutter driven by a solenoid. Fig. 1 shows the time structures of the molecular beam, chopped x-ray and the MCP detector of the electron-energy analyzer. The surface is irradiated with the x-ray after the arrival of the molecular beam at the surface with a delay time of Δt. A series of spectra are obtained with systematic variation of the delay time. The time resolution of the whole system is limited by that of the beam shutter; the highest time resolution was 1 ms.

Saturated overlayers of ethylene (C_2H_4) were prepared at 120 K. Ethylidyne (C_2H_3) overlayers were prepared by annealing the ethylene overlayers at 230 K. TRXPS measurements were done under ethylene molecular-beam irradiation. The time resolution was 10 ms, and the repetition frequency was 1 Hz.

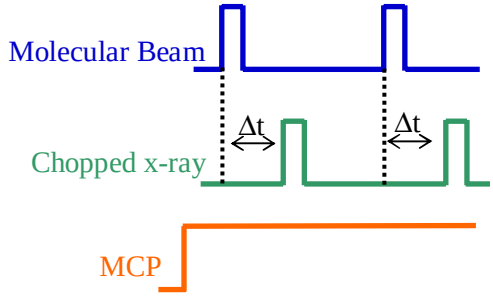

Fig. 1. Time structures of the molecular beam, x-ray, and MCP for TRXPS.

Results and discussion

Fig. 2. shows TRXP spectra before (Δt=-40ms) and at (Δt=0ms) the arrival of the molecular beam on the ethylene- and ethylidyne-covered surfaces at 120 K. The ethylene coverages are readily enhanced under molecular beam irradiation (Δt=0ms) on both surfaces. Difference spectra clearly show new peaks at higher binding energy than the main peaks. When the surface was kept at 150 K, no changes were observed by molecular-beam irradiation. These results indicate that ethylene molecules are transiently adsorbed on ethylene- and ethylidyne- covered Rh(111) surfaces under molecular beam irradiation at a low temperature. Transient adsorption of ethylene is also observed on other metal surfaces [2]. Ethylene chemisorption on the Rh(111) surface takes place in a di-σ-bonded configuration. The higher binding energy of the transiently adsorbed species indicates that ethylene is more weakly bound to the surfaces than the chemisorption state. Two adsorption states are proposed as weaker ones than the di-σ-bonded state: π-bonded or physisorption states. It can not be determined from our data which one is responsible for the observed transient adsorption state, but it is more easily formed on the ethylene monolayer than on the ethylidyne monolayer.

Reference

[1] A. Baraldi et al., Surf. Sci. Rep. 49, 169 (2003)
[2] L. Vattuone et al., Phys. Rev. B 66, 085403 (2002), *etc.*

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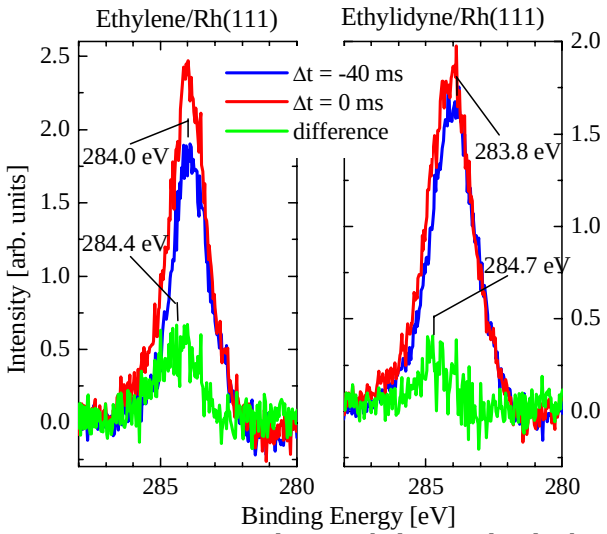

Fig.2 TRXP spectra during ethylene molecular-beam irradiation on ethylene- and ethylidyne-covered Rh(111) surfaces at 120 K.