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NEXAFS study of CO-Cs coadsorption on Pt(111)

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Introduction

The coadsorption of CO and alkali-metal on transition metal surfaces is of considerable interest because of the technological importance in heterogeneous catalysis and also because of the importance of a fundamental understanding of the strong effects of alkali-metals on the properties of coadsorbed CO [1]. In this work, the CO structures adsorbed on Cs-saturated Pt(111) were studied by using near-edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS).

Experimental

The experiments were performed in ultrahigh vacuum (UHV) chamber (the base pressure of less than 2 $\times$ 10^{-10} Torr) which equipped with a hemispherical analyzer. All the measurements were carried out at the soft X-ray beamline BL-7A. A Pt(111) surface was cleaned by repeated cycles of Ar ion sputtering and annealing. Residual carbon species were removed by O_2 treatment. The Cs was deposited at 250 K from a well-outgassed SAES getter source and annealed at 300 K to obtain Cs monolayer-covered surface. CO exposure was done by back filling the chamber to a pressure in the 10^{-7} Torr range. Coadsorption was always done by exposing the Cs-precovered surface to CO. All the C-K NEXAFS and XPS measurements were performed at 300 K. The C-K NEXAFS spectra were recorded in the partial electron yield mode with a retarding vltage of -200 V.

Results and discussion

Fig.1 shows C-K NEXAFS spectra for various CO exposures, 25, 100, 400 L (1 L = 1 $\times$ 10^{-6} Torr s) respectively. Below 290 eV, two resonance peaks are observed at all the CO exposures. Considering the polarization dependence, the lower energy resonance peak consists of at least two components. Therefore, these resonance peaks were fitted by three components. These fitted peaks were found at 287.4, 288.3 and 290.0 eV. No energy shifts are observed for various CO exposures. (Fig. 1). Former two peaks correspond to the position expected for π^* resonances arising from photoexcitation from C 1s to the unoccupied orbital of CO. These indicate that two kinds of CO species exist on this surface. The latter one corresponds to the position expected for π^* resonance arising from photoexcitation from C 1s to the unoccupied orbital of CO_3^{2-}. Analysis of the angular dependence of the CO π^* intensity yields a tilt angle of $0 \pm 10°$ and $30 \pm 10°$ with respect to the surface normal for all the coverages. On the other hand, the molecular plane of CO_3^{2-} is tilted from the surface normal by $10 \pm 10°$, $25 \pm 10°$ and $35 \pm 10°$ for the CO exposure of 25, 100 and 400 L, respectively. Fig.2 shows C 1s photoelectron spectra for various CO exposures. These spectra also indicate the production of CO_3^{2-}. The formation of the CO_3^{2-} species results from CO oxidation by oxygen atoms that are inevitably adsorbed from the residual gas to the Cs layer. The tilted CO species is tentatively attributed to those adsorbed at domain boundaries of the Cs+CO coadsorption phase.

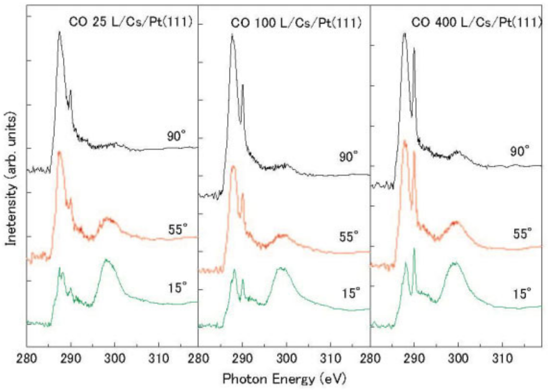

Fig. 1 C-K NEXAFS spectra for CO+Cs/Pt(111) measured at 300 K. The CO exposure on Cs pre-covered surfaces are 50 L (right), 100 L (center) and 400 L (right).

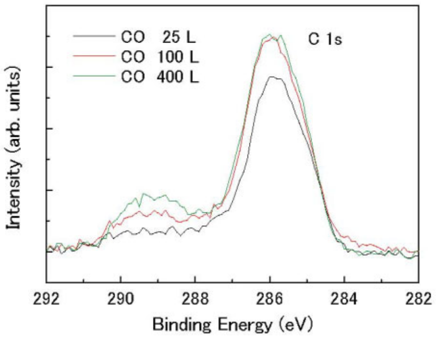

Fig.2 C 1s photoelectron spectra for CO+Cs/Pt(111).

Reference

[1] H. P. Bonzel, Surf. Sci. Rep. 8, 43 (1987).

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