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Development of time-resolved XPS system and its application to the observation of transient adsorption states of NO on Pt(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. X-ray photoelectron spectroscopy (XPS) measurements from monolayer adsorbates at a time scale of several seconds have been made possible. 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 surface repeatable phenomena. To obtain photoemission signals in a short period, we have used chopped x-ray generated by a mechanical chopper, and have achieved a time resolution of several milliseconds [1]. In order to improve the time resolution further and to stabilize the incident x-rays, new detection method was applied where the photoemission signal is detected with a gated CCD camera under continuous x-ray irradiation. We applied the new method to the observation of the transient adsorption states of NO on Pt(111) surfaces, which is important as a fundamental model for the NO_x reduction catalyst.

Experimental

The experiments were carried out at BL-2C with an UHV system. The photoelectron spectra are obtained with a gated CCD camera for a short period 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 the width of the molecular beam: the highest time resolution was 500 μs. The time distribution of the molecular beam was measured with a time-of-flight mass spectrometer (TOF-MS) placed on the line.

A saturated overlayer of NO was prepared at 290 K. TRXPS measurements were done under NO molecular-beam irradiation. The photon energy for the N 1s XPS measurement was 530 eV. The time resolution was 2 ms, and the repetition frequency was 0.2 Hz.

Results and discussion

Figure 1 shows N 1s TRXP spectra with (Δt=0ms) and without the irradiation of the NO molecular beam on the NO saturated surface at 290 K. It is evident that the coverage of NO is increased by the molecular-beam irradiation. The increase in coverage is plotted in Fig. 2 as a function of the delay time Δt with the profile of the molecular beam measured with the TOF-MS. The coverage of the molecular-beam induced NO adsorbates jumps up at the same time as the molecular beam arrives at the surface (Δt=0) and decreases in coincidence with the decrease of the flux of the molecular beam. These results indicate that transient adsorption of NO is induced by the NO molecular beam.

On Pt(111) at 290 K, NO occupies the fcc-hollow site (0.25 ML) [Ref. 2]. Unfortunately, no chemical shift is observed for the molecular-beam induced species and it is difficult to determine its adsorption sites from the XP spectrum. It was previously revealed that NO occupies also the atop site at 240 K, which exhibits no N 1s chemical shift [2]. We tentatively attribute the molecular-beam induced species to the NO molecules transiently occupying the empty atop site. It decreases with almost the same time profile as seen for the molecular beam (Fig. 2), which indicates that the lifetime of the transiently adsorbed NO is shorter than the time resolution of the beam width, 3.5 ms.

References

[1] I. Nakai *et al.*, PF Activity Report 21, 46 (2003).
[2] P. Zhu *et al.*, Surf. Sci. 565, 232 (2004).

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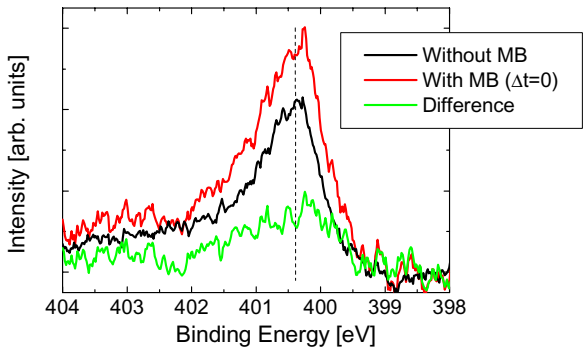

Fig.1 N 1s TRXP spectra with (Δt=0) and without NO molecular-beam irradiation.

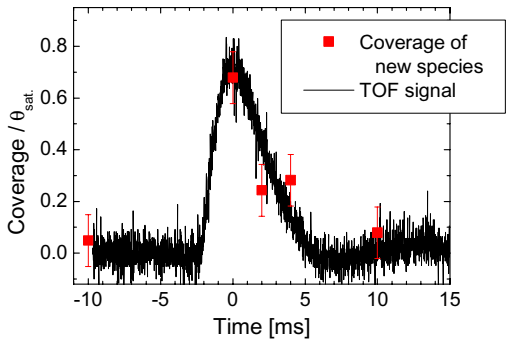

Fig.2 coverage of molecular-beam induced NO adsorption as a function of the delay time and the profile of the molecular beam measured with TOF.