

## II-C Surface Chemical Reactions Studied by NEXAFS Spectroscopy

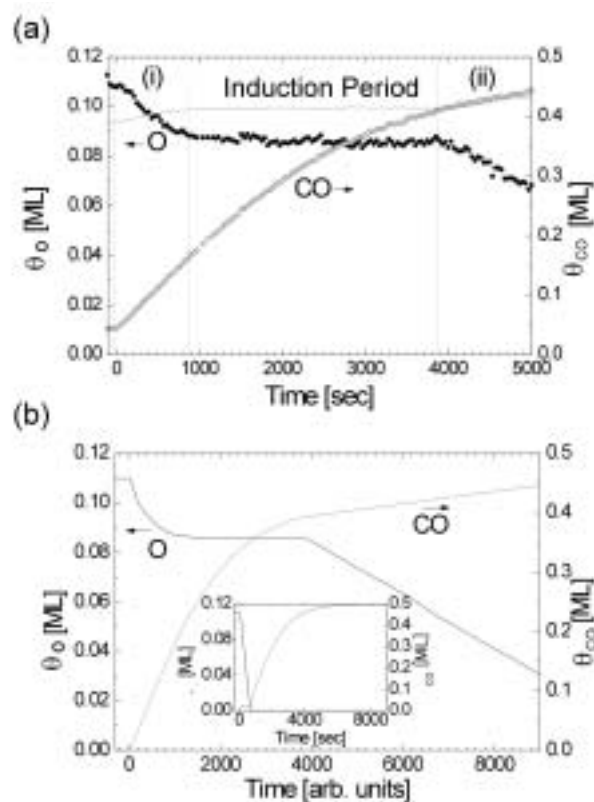
Recently, we have developed an energy dispersive NEXAFS (Near Edge X-ray Absorption Sine Structure) method, which is a technique to measure a NEXAFS spectrum in a certain range simultaneously. This method shortens the measuring time by 1/100 compared with the conventional energy scanning method and enables us to apply the NEXAFS spectroscopy to surface chemical reactions related to fundamental catalytic reactions. Since the time scale is comparable with STM measurement, combined information of NEXAFS and STM as well as dynamic Monte-Carlo simulations provides deep insight to fundamental chemical reactions which have not been clarified yet. So far, we have applied it to the reactions of water formation reaction/Pt(111) and ammonia formation on Rh(111).

### II-C-1 Reaction-Path Switching Induced by Spatial-Distribution Change of Reactants: CO Oxidation on Pt(111)

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CO oxidation on Pt(111) surfaces is one of the most prototypical catalytic reactions. We studied the mechanism of CO oxidation on O-covered Pt(111) surfaces during CO exposure by means of time-resolved NEXAFS spectroscopy. Recent STM study proposed that the oxidation reaction takes place exclusively at island peripheries after an "induction period" where the reaction does not proceed. However, we found that the whole reaction process is composed of two distinct processes; (1) a reaction of isolated oxygen atoms with adsorbed CO, and (2) a reaction of island-periphery oxygen atoms after the CO saturation. If CO pressure is lowered, these two processes are separated by an induction period, in which CO saturates the O-covered surface. A drastic switching of reaction path in CO oxidation reaction is caused by the CO adsorption induced 2D condensation of the O atoms. These results demonstrate that the effects of long-range interactions and consequent dynamic spatial-distribution changes of the reactants are of fundamental importance for understanding the kinetics in the reaction systems deviated from the conventional Langmuir-Hinshelwood kinetics.



**Figure 1.** (a) Time evolution of  $\theta_{\text{O}}$  and  $\theta_{\text{CO}}$  under a low pressure of CO ( $5 \times 10^{-10}$  Torr). The annealing temperature and the reaction temperature were 260 K and 252 K, respectively. The gray line shows the saturation coverage of CO. The areas (i) and (ii) correspond to the former and latter processes, respectively.

(b) Variation of  $\theta_{\text{O}}$  and  $\theta_{\text{CO}}$  from Monte Carlo simulation under the same condition as for the experiment shown in (a). The solid and dashed lines represent  $\theta_{\text{O}}$  and  $\theta_{\text{CO}}$ , respectively. Inset: Simulated curves without taking account of CO adsorption-induced condensation of O atoms.