KINETIC STUDIES OF STRUCTURAL PHASE TRANSITONS AND CATALYTIC ACTIVITIES VIA IN SITU SURFACE X-RAY SCATTERING

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Kinetics of electrochemical processes is often influenced by structural phase transitions at the electrode surface. In situ surface x-ray scattering technique can provide time-resolved structural information while the reaction current is simultaneously measured.

For high resolution, a low resistance drop cell was used, in which the counter and reference electrodes were placed closely and in contact with the electrolyte drop held between them and the single crystal working electrode. The results of kinetic study of Bi UPD on Au(111) will be presented to demonstrate the structural evidence for nucleation-growth processes on msec and sec time scales.

The catalytic activity studies will be illustrated with the results on the correlation between CO adsorption and its inhibition effect on H_2 and methanol oxidations. Brief summaries of the major results are given below.

Phase transition kinetics of Bi on Au(111):

As shown in Fig.1 and 2, The low-coverage disordered ↔ commensurate (2 × 2)-Bi phase transitions occur on a millisecond time scale, which is three orders of magnitude more rapid than the (2 × 2) ↔ high-coverage incommensurate (p × √3)-2Bi phase transition. The nucleation-growth processes have been found for both the formation and loss of the (2 × 2) phase in positive potential steps. This can be rationalized by the preference of stripping to occur more rapidly at the edges of the Bi islands where the bonding with the neighboring adatoms is weaker. In contrast, the reversed phase transitions are dominated by Langmuir adsorption processes.

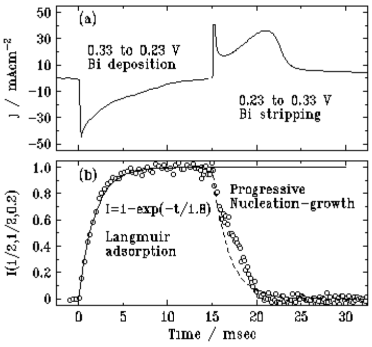

Fig. 1. Current and intensity transients for the disordered ↔ (2×2) phase transition on Au(111) in 1M $HClO_4$ with 5mM Bi^{3+}.

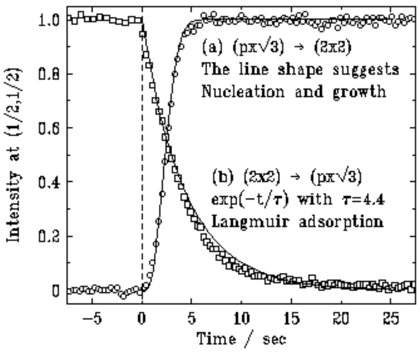

Fig. 2. X-ray intensity transients for the (2 × 2)-Bi ↔ (p × √3) phase transition upon potential steps between 0.17 and 0.27 V.

CO Adsorption and its inhibition for H_2 and CH_3OH oxidation on Pt(111):

The (1/2,1/2) in-plane diffraction intensity, as shown in Fig. 3, starts to rise after some time, signaling a formation of the (2×2)-3CO phase. Coincidently the hydrogen oxidation current decreases. When the current drops to zero, the x-ray intensity stabilizes at the maximum value. Switching back to pure hydrogen results in an 80% decrease of the diffraction intensity. These facts show that the formation of the (2×2)-3CO phase requires a certain concentration of CO in the solution, and that H2 oxidation on Pt(111) is completely blocked by the ordered adlayer with 0.75 monolayer coverage. Some irreversibly adsorbed CO molecules, albeit at a lower coverage, inhibit a recovery of the oxidation current.

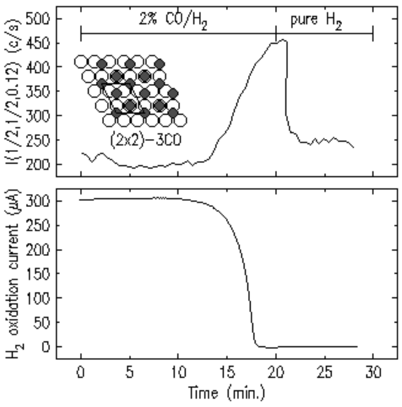

Fig. 3 Time-dependent x-ray intensity from the (2×2)-3CO adlayer and the hydrogen oxidation current on Pt(111) in 0.5M H_2SO_4. The potential was held at 0.2 V versus RHE.

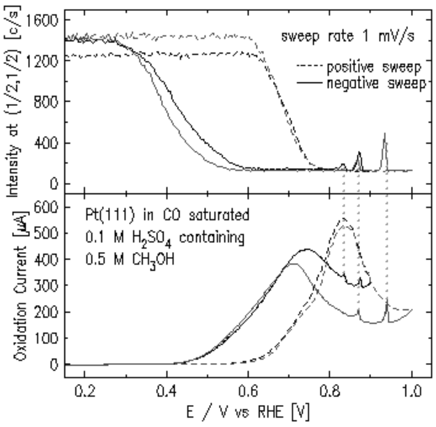

Fig. 4. Potential dependent x-ray diffraction intensity and current measured with different positive potential limits.

The major effect of the coexistence of CH_3OH with CO on the phase behavior of CO adsorption and the observed current is the oscillatory behavior in negative potential sweeps. As shown in Fig. 4, sharp peaks appear coincidently in both the (1/2,1/2) diffraction intensity and the current curves, although the peak potentials and heights vary with the positive potential limit. These data indicate a strong correlation between the current spike and the temporal formation of the (2×2)-3CO phase. The competition for adsorption sites among CO, OH, and CH_3OH and the interdependence of multiple surface reaction steps, coupled with the slow recovery of the surface morphology, may lead to the oscillatory current peaks and the coincident temporal formation of the (2×2)-3CO phase.