

Surface Structure and Relaxation During the Oxidation of Carbon Monoxide on Pt-Pd Bimetallic Surfaces

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Thin transition metal films supported on single crystal metal surfaces have been studied in great detail in order to establish a link between the physical properties of a surface and its chemical reactivity. These results are particularly relevant to the field of electrocatalysis where changes in catalytic activity can be attributed to ensemble effects (or morphological effects), structure effects due to changes in local bond geometry and electronic (or ligand) effects where a metal's reactivity is modified directly. The experimental work has been supported and motivated by theoretical calculations in which, for example, a strong correlation was found between molecular chemisorption energies and the location of the d-band center of the surface metal atoms [1]. The experimental, ultra-high-vacuum (UHV) work has also stimulated progress in the field of surface electrochemistry, where similar bimetallic systems can be studied in an aqueous environment under electrostatic potential control. These systems have the advantage that they can be studied under conditions of chemical equilibrium and that catalytic reactions can be monitored by traditional voltammetric methods. By using techniques which can probe the surface structure *in-situ*, such as surface x-ray scattering (SXS) and scanning tunneling microscopy (STM), catalytic reactions can also be probed on the atomic level. Furthermore, recent work on platinum electrode surfaces has shown that effects such as surface relaxation induced by the adsorption of hydrogen and CO [2] are in remarkable agreement with theoretical calculations of the ideal adsorption system [3], *i.e.* a 2% outward relaxation induced by the adsorption of a monolayer of hydrogen.

The adsorption and oxidation of carbon monoxide on transition metal single crystal surfaces has been a prototypical system with which to study molecular adsorption and catalytic reactions. In a recent series of publications [2], we have shown that CO forms a densely packed p(2x2) structure on the Pt(111) surface that undergoes an order-disorder transition induced by partial oxidation of the CO adlayer that is in a 'weakly-bonded' adsorption state. In the presence of the p(2x2) structure the Pt(111) surface was expanded by ~4 % of the bulk atomic spacing, presumably as a result of the charge transfer in the back-bonding mechanism. It was possible to follow the CO oxidation reaction indirectly by

monitoring the Pt surface expansion as a function of the applied electrode potential. In this paper we will present data which extend these results to a bimetallic system, namely a monolayer of Pd on the Pt(111) electrode surface. Given that Pt and Pd are neighboring elements in the periodic table and that their lattice constants differ by <1 %, a monolayer of Pd on Pt(111) represents a catalytic system in which only a 'pure' electronic effect is expected. By utilizing SXS, in combination with voltammetric experiments to provide adsorption isotherms, it is possible to build up a detailed picture of the surface atomic geometry during the CO-oxidation process.

Data will also be presented for multilayer Pd films deposited onto Pt electrodes. Previous interpretation of cyclic voltammetry data has assumed that Pd grows layer-by-layer on Pt due to the small lattice mismatch. The x-ray data, however, are not consistent with this interpretation and indicate an island growth mode. The adsorption of CO on the multilayer Pd films appears to enhance the absorption of hydrogen at cathodic electrode potentials.

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