X-ray Photoemission Spectroscopy and Scanning Tunneling Microscopy of Model Catalysts at Elevated Pressure Conditions

David E. Starr[1] and Hendrik Bluhm[2]
[1]*Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973*
[2]*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720*

Scientific Thrust Area

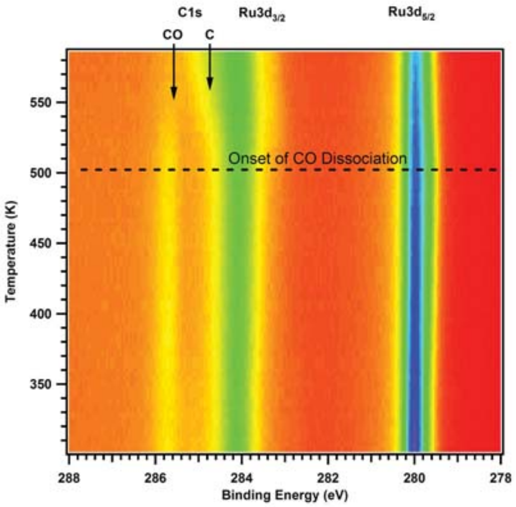
This work has been performed through the *Interface Science and Catalysis* research theme of the Center for Functional Nanomaterials at Brookhaven National Laboratory in collaboration with staff in the Chemical Sciences Division of Lawrence Berkeley National Laboratory.

Research Achievement

Ultra-high vacuum surface science techniques using single crystals have a long history of providing detailed molecular level information about the structure of model catalyst systems and the chemical state of adsorbates on their surfaces. However, such studies have two major limitations that hinder their direct application for the development of more effective catalysts. These are the materials gap and pressure gap. The materials gap arises from the inability of single crystal surfaces to fully capture the structural complexity of real catalysts. In addition, due to the approximately thirteen orders of magnitude pressure difference between ultra-high vacuum measurements and typical catalyst operating conditions, ultra-high vacuum experiments may not capture the chemical nature of the catalytically active phases. This is known as the pressure gap. Modern catalyst development continues to be largely via trial and error due to these pressure and materials gaps. Combining the use of more complex model systems and recently developed surface sensitive elevated pressure experimental techniques, this research aims to bridge the pressure and materials gaps to facilitate a more cognitive approach to catalyst design.

As a first step we have used ambient pressure photoemission spectroscopy to investigate the adsorption of carbon monoxide onto two model catalyst surfaces, Ru(0001) single crystal surfaces and PtRu/Ru(0001) near surface alloys, at pressures up to 1 Torr. CO adsorption on Ru(0001) is a model system for the Fischer-Tropsch synthesis of fuels which involves catalytically reacting CO and hydrogen (syn-gas) to form long chain hydrocarbons. A crucial step in the mechanism of fuel production on Ru is the dissociation of CO. PtRu alloys are currently used as the anode catalyst in proton exchange membrane fuel cells. Pure Pt catalysts are particularly susceptible to poisoning by CO when the concentration of CO in the hydrogen fuel stream approaches tens of ppm. Alloying Pt with Ru increases the CO tolerance of these catalysts. Despite this known property of the alloy simple questions such as the quantity and chemical nature of CO adsorbed on both Pt and Ru sites in the catalyst under realistic CO partial pressures are unknown. In this work we have addressed both the nature of CO adsorption and the onset of CO dissociation on Ru(0001) at pressures up to 1 Torr as well as the amount of CO adsorbed on Pt and Ru sites in model alloy catalyst surfaces at pressures corresponding to real CO partial pressures in PEMFC hydrogen fuel streams.

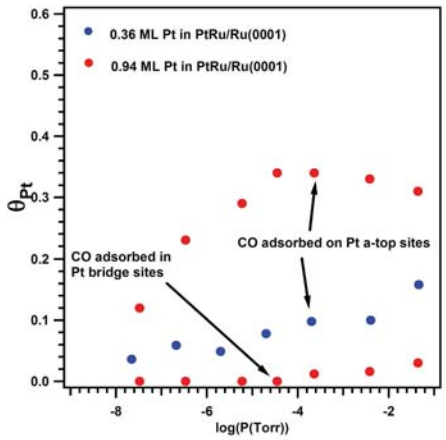
UHV studies of CO adsorption/desorption on Ru(0001) indicate that CO desorbs from the surface by ~ 500 K. This has led to the conclusion that the active sites for CO dissociation on Ru surfaces are under-coordinated Ru atoms such as those found at step sites. We have found that at room temperature the quantity of CO on the Ru(0001) surface at 1 Torr CO pressure is higher by ~ 1/3 than previously observed using UHV studies. The additional CO is adsorbed in a site on



Temperature dependence of the C1s and Ru3d photoemission peaks during heating of a Ru(0001) single crystal in 0.04 torr CO

the Ru surface previously not observed under UHV conditions. Comparison of the O1s binding energy to those found for CO adsorption on other metal surfaces indicates that this site is most likely a bridge site between two Ru atoms. Upon heating the Ru(0001) single crystal in the presence of 0.04 Torr of CO, we have observed the dissociation of CO and formation of C on the surface beginning at ~ 500K. The amount of C on the surface far exceeds what would be expected for simple dissociation and formation of immobile species at step edges. This implies that either the flat Ru(0001) terraces are active for dissociation (counter to what has been previously thought) or more likely that the carbon species formed by CO dissociation at the steps are mobile on the surface at 500 K.

CO adsorption onto PtRu/Ru(0001) near surface alloy systems at pressures up to 0.04 Torr provide model studies of fuel cell catalysts under realistic partial pressures of CO in the hydrogen fuel stream. Using high pressure photoemission spectroscopy we have been able to quantify the amount of CO adsorbed on Pt sites and Ru sites at 300 K. UHV studies have indicated that Pt sites should be largely free of CO at this temperature. Our results not only show that under realistic partial pressures a certain fraction of Pt sites are covered by CO, but that this fraction depends on the relative concentrations of Pt and Ru in the surface. This may indicate that an optimum Pt:Ru ratio exists for these catalysts that provides both sufficient activity and CO tolerance and also lends support to the idea that the alloys increased CO tolerance is due to a decrease in the local binding strength of CO to Pt upon alloy formation.



Fraction of Pt covered by CO as a function of CO pressure for PtRu near surface alloys with Pt concentrations of 0.94 (red) and 0.36 (blue).

Future Work

In the future we plan to more directly correlate the chemical nature of adsorbates on complex model catalysts with catalyst structure under elevated pressure conditions. Model catalysts produced by the growth of thin oxide films on single crystal metal surfaces (providing a model support) followed by vapor deposition of the catalytically active metal onto the oxide film will be studied using scanning tunneling microscopy at elevated pressures. We expect such studies to provide direct evidence for catalyst restructuring under near operating conditions. Correlating such restructuring with the chemical information from ambient pressure photoemission spectroscopy, as discussed above, will provide a detailed molecular level understanding of model catalysts near operating conditions.