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# Molecular Studies of Surfaces under Reaction Conditions; Sum Frequency Generation Vibrational Spectroscopy, Scanning Tunneling Microscopy and Ambient Pressure X-Ray Photoelectron Spectroscopy

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**Abstract:** Instruments developed in our laboratory permit the atomic and molecular level study of NPs under reaction conditions (SFG, ambient pressure XPS and high pressure STM). These studies indicate continuous restructuring of the metal substrate and the adsorbate molecules, changes of oxidation states with NP size and surface composition variations of bimetallic NPs with changes of reactant molecules.

The studies of surfaces during the last forty years became an atomic scale and molecular level science<sup>1</sup>. Using model surfaces, single crystals at first, the evolution of electron, ion and molecular scattering techniques provided information on atomic and molecular structures, composition and oxidation states and energy transfer, adsorption, desorption and scattering of molecules from surfaces. Since the instruments used for these techniques required high vacuum and clean surfaces, surface science at low pressures developed first. However, applications of surfaces in technologies required studies at high pressures and at buried interfaces, solid-gas, solid-liquid, solid-solid and liquid-liquid. These applications included nanomaterial technologies, catalysis, biointerfaces, tribology, electrochemistry, coatings, corrosion, integrated circuitry and sensors; just to mention a few pervasive technologies that we use in our life. Since life on this planet does not operate in high vacuum, the techniques that probed buried interfaces opened up molecular level investigations of many applications of interfaces. Many of the surface scientists trained in our laboratories pursue research in these fields. Our research, at present, focuses on catalysis at surfaces by transition metals and studies of biointerfaces as the human body which may be viewed as a polymer-water interface with a layer of proteins. To this end we developed four techniques in Berkeley that

operate under reaction conditions. These are ambient pressure X-ray photoelectron spectroscopy<sup>2</sup>, sum frequency generation vibrational spectroscopy<sup>3</sup>, high pressure scanning tunneling microscopy<sup>4</sup>, and the metal-semiconductor nanodiode<sup>5</sup>.

## Surface Composition and Oxidation States Under Reaction Condition Revealed by High Pressure XPS

The ambient pressure X-ray photoelectron spectroscopy instrument can be operated at total reactant pressure of up to 10 Torr. The key component that makes this technique different from the conventional XPS is the differentially pumped electrostatic lens system that refocuses the photoelectrons from the sample surface into the object plane of a standard electron energy analyzer working under high vacuum. The kinetic energy of the photoelectrons can be tuned by varying the energy of the X-ray source for which we use the Advanced Light Source synchrotron in Berkeley. By tuning the kinetic energy of the photoelectrons to an appropriate value, the electron mean free paths can be minimized for a given sample surface so that the oxidation state and the composition of the surface layer with the thickness of about 1 nm can be determined. HPXPS has been applied to study the oxidation states of rhodium nanoparticles with size in the range of 2-11 nm under CO oxidation reactions<sup>6</sup>. Recent HPXPS

studies of the surface composition of bimetallic nanoparticles of rhodium-palladium and palladium-platinum demonstrated that the surface composition of nanoparticles is extremely sensitive to their ambient chemical environment <sup>7</sup>. The surface composition changes under oxidizing atmospheres and becomes very different under reducing mixtures of carbon monoxide or hydrogen.

### **Sum Frequency Generation (SFG) Vibrational Spectroscopy**

The SFG vibrational spectroscopy is a non-linear spectroscopy technique, in which two high energy pulsed laser beams are overlapping spatially and temporally on an interface of interest. Due to properties of the non-linear susceptibility tensor media with inversion symmetry such as isotropic gases or bulk metal crystals cannot generate an SFG signal. Thus the entire signal is generated at the interface. The infrared visible SFG process can be thought of as infrared and visible excitations followed by an anti-stoke Raman relaxation emission, the result of which is emitted radiation at the sum of the two incoming frequencies. This technique has been applied in our laboratory to many catalytic reactions over single crystal and nanoparticle model surfaces <sup>8,9</sup>. The technique helps us to determine the major reaction intermediates on the catalyst surfaces and understand the competition between intermediates for active sites. Many catalytic reactions and interfaces were studied by SFG. This technique is equally good at determining reaction intermediates on single crystals as well as on metal nanoparticles.

### **High Pressure Scanning Tunneling Microscopy (HPSTM)**

HPSTM applied at high pressures and temperatures offers promising ways to monitor the structure of surfaces and adsorbates on the molecular level during surface reactions. Our findings in studies of

platinum single crystal surfaces indicates that at high ambient pressures of carbon monoxide, oxygen and other gases the metal restructures and becomes cluster-like <sup>10</sup>. The roughening and clustering of the surface is reversible as the high-pressure gas is pumped out. Adsorbate mobility is another important phenomenon observed in the HPSTM studies <sup>11</sup>. Under catalytic reaction conditions no distinguishable feature of the surface can be resolved by STM, but the featureless STM image implies that the adsorbates move at a speed much higher than that of the STM tip. After poisoning the reaction by a small amount of carbon monoxide the reaction turnover stops and ordered structures emerge on the surface since the coadsorption of the CO limits the mobility of the hydrocarbon adsorbates.

### **Catalytic Metal Semiconductor Nanodiode**

The metal semiconductor nanodiode is capable of detecting the flow of electrons transported from the metal surface to the semiconductor. Electrons excited during catalytic reactions may travel ballistically through a metal film with thickness less than the mean-free path of the electron, about 5 nm for platinum. The ballistic electrons with kinetic energy higher than the Schottky barrier height can enter into the semiconductor. These electrons return to the metal thin film through an ammeter connecting the semiconductor and the metal film. In this way a continuous electric current, called chemicurrent, can be generated during a catalytic reaction on a metal surface. So far, the chemicurrent has been detected for several catalytic reactions including carbon monoxide oxidation and hydrogen oxidation <sup>12,13</sup>. The chemicurrents are correlated very well with the turnover rates for these exothermic reactions. The fact that the activation energies for the turnover rate and the chemicurrent are very close to each other indicates that the electron transport is induced by the catalytic reactions over the metal surface. Manipulations of the catalytic reaction rate by changing the

electron flow in the direction forward or reverse as compared to the hot electron flow from the catalytic reaction can change the turnover. It should be noted that photon adsorption in the semiconductor of the metal-oxide Schottky barrier can also be used to generate additional photocurrent and thereby changing the turnover rate of the catalytic reaction.

### Conclusion

New spectroscopic and microscopic techniques that has been developed in our laboratory and elsewhere that operate under reaction conditions and detect the molecular scale working of the buried interfaces revealed a dynamic change of molecular structure of catalysts and adsorbed molecules as the reactions proceed with changes in reaction intermediates, catalyst composition and oxidation states. SFG vibrational spectroscopy detects amino acids, peptides and proteins adsorbed at hydrophobic and hydrophilic interfaces and monitors the change of surfaces structures and interactions with coadsorbed water<sup>14,15</sup>. Exothermic reactions and photons generate hot electrons in metal nanoparticles that may be utilized for chemical energy conversion.

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