

Structure and Spectroscopy under ambient conditions of Pressure and Temperature: Novel techniques for fundamental studies in catalysis

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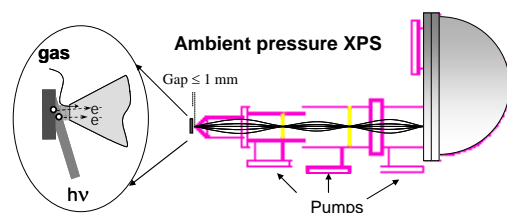
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Introduction

The nature of the sites where catalytic reactions take place on surfaces is a matter of fundamental and continuous inquiry in the scientific and engineering community. Of particular relevance are studies that approach the conditions of pressure, temperature and catalyst structure operating in industrial reactions. Common characteristics of surfaces under these conditions are: a) the surfaces are crowded with adsorbates, which means that the chemistry is strongly influenced by the dynamics of vacancies; b) they are complex surfaces, often small particles, whose structure is not well known during the reaction. We have developed techniques that allow us to approach some of these conditions. These include Scanning Probe Microscopies and several X-ray Photoelectron Spectroscopies. With them we have unraveled the structure and composition of model catalyst surfaces that are in equilibrium with reactants at or near atmospheric pressures and ambient temperatures. These include Pd, Pt and Ru single crystals, and Co, Au and Rh-Pd nanoparticles. I will show results that provide new insights into the nature of H₂ dissociation sites on Pd, Ru and Pt. I will also show how Co, Au and PdRh nanoparticles can be characterized in situ and the influence of particle size in their electronic and chemical properties.

Materials and Methods

The techniques used in this work have been all developed in my laboratory, and include Scanning Probe Microscopies (STM), ambient pressure X-ray Photoelectron Spectroscopy (APPES) [1] and X-ray absorption Spectroscopy (XAS) (Figure 1). The firsts are



stand alone instruments working in the laboratory. The second were implemented in the ALS, the Berkeley Synchrotron. The gas pressures can reach up to a few Torr (APPES) and also to 1 or more atmospheres (STM, XAS).

Results and Discussion

The dissociative adsorption of H₂ on Pd(111) and Ru(0001) was studied in ultra-high vacuum when the coverage of H atoms is near saturation (1H per metal atom). Under these conditions the chemisorption is determined by vacancies, their concentration and aggregation state. We discovered that in all cases the dissociation took place only when aggregates of 3 or more vacancies were formed [2]. Theoretical analysis revealed that only

then metal atoms not bound to any H atom are present and that these atoms provided the active site for dissociation [3]. Similar results were found for Pt in the reaction of H₂+D₂ = 2HD. The generality of this finding was demonstrated in the Fischer-Tropsch reaction CO+3H₂ = CH₄ + H₂O on Co nanoparticles, where H₂ adsorption, while not the rate determining step is a key reaction that becomes more important as the particle size decreased.

APPES was used to study the chemical composition of the surface and of the gas phase in a variety of reactions, including CO+NO on Rh single crystals [1] and on PdRh nanoparticles [4], the partial oxidation of CH₃OH on Cu [5], and others. In all cases we could determine the surface composition as the reactions were taking place. Both adsorbates and metal atomic composition revealed unexpected changes that could not be obtained in any other way. With APPES we could also determine for the first time the phase diagram of Pd-O, the nature of the oxides formed and the conditions of thermodynamic equilibrium [6].

Significance

The results of our studies show the importance of understanding the atomic nature of the catalyst sites that are active in reactions, revealing that for example the traditional Langmuir model where dissociation of molecules varies as (1-x)ⁿ where x is the coverage and n the number of atoms or fragments that the molecule dissociates into, needs to be modified in many cases. The ability offered by our techniques of providing *in situ* spectroscopic characterization of catalyst under realistic reaction conditions is unprecedented..

References

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