

## V.D.7 Reactivity and Stability of Multimetallic Nanocatalysts in Acid Medium

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### Objectives

We aim at determining trends for reactivity and stability against dissolution of bimetallic and trimetallic nanocatalysts exposed to acid medium. The reaction tested is the oxygen reduction. Reactivity and stability trends are sought as a function of surface composition and atomic distribution in the first 2-3 surface layers. Possible mechanisms for metal dissolution are investigated.

### Technical Barriers

We expect to contribute to the development of nanocatalysts of improved activity and durability. We expect our investigations to have general applicability to other problems of technological importance such as corrosion. Development of new computational methods such as our approach to describing complex interfaces may also benefit other scientific fields where the chemistry on substrates plays a primary role.

### Abstract

Reactivity trends for the reduction of oxygen are analyzed as a function of surface composition, geometry of the active sites, and atomic distribution in the first 2-3 layers of multimetallic catalysts. Trends of stability of Pt-alloy surfaces in acid medium as a function of composition are obtained via analysis of dissolution reactions. Possible mechanisms for metal dissolution are investigated via analysis of the initial oxidation stages of the dissolution process. Alternative biomimetic catalysts are explored emulating active sites of metalloenzymes.

### Progress Report

#### 1. Catalytic activity

Binding energies of oxygen reduction intermediates: OOH radical, O, and OH radical are used to evaluate catalytic activity in clusters and extended bimetallic surfaces, using a thermodynamic analysis proposed by us [1]. In small  $Pt_xPd_y$  clusters of various compositions, we investigated the effect of the atomic distribution (mixed vs. ordered structures) on reactivity. Polarization effects such as charge transfer from the Pd atoms both to Pt atoms and to adsorbates, and the different orbital electronic population in an "average" atom clearly allows us to differentiate the activity behavior of mixed vs. ordered clusters [2]. We have also done a similar analysis in extended surfaces[3] focusing on the differences of reactivity between clusters and extended surfaces for identical overall compositions due to geometric effects. Other bimetallic systems ( $Pt_3Co$  and  $Pd_3Co$ ) were also investigated on extended surfaces [4], where reactivity trends were found to follow the d-band model [5] predictions. Since the surface atomic distribution in nanocatalysts could be very different than that expected in bulk alloys, we studied the effect of nanoparticle size of Pt-Pd alloys of several overall compositions [6]. We have investigated the adsorption and dissociation characteristics of hydrogen peroxide, an undesired intermediate of the oxygen reduction reaction which can generate radical species that cause degradation of the polymer electrolyte membrane in fuel cells [7].

Solvent effects at the catalytic interface were incorporated to investigate water behavior near sulfonic sites in the vicinity of the nanocatalysts. We found three different structural and dynamical regimes as a function of the water/sulfur ratio [11], and further studies were oriented to determine the electronic characteristics of the water/sulfonic groups in contact with a few catalytic sites [12]. Significant effort was also invested by our team on developing new computational approaches to characterize the catalytic interface[13,14]. In addition, we have performed systematic studies of testing and developing corrections to DFT functionals for a large number of molecules[15,16]. The new results have chemical accuracy, which is essential for achieving computationally-guided designs.

Most recently we have also found interesting similarities between the bimetallic ionic sites found in metalloenzymes and those of bimetallic nanocatalysts [8] and we have analyzed the interactions of charged species with the intermediates and products of the oxygen reduction reaction. These studies (as well as the polarization effects found in small clusters) suggest that metal ions may be less expensive and more efficient active sites than metal atoms. Along the same lines we are characterizing ionic complexation in dendrimers and dendrimer fragments [9,10], and we are now testing those sites as catalytic centers.

## 2. Catalytic stability

Metal nanoparticles in acid medium can become unstable and dissolution of metallic atoms has been detected experimentally [17]. We have developed a systematic thermodynamic analysis based on density functional theory calculations [18], which allows us to determine the stability against dissolution of platinum and other elements in mono- or multimetallic ensembles. This technique can be utilized as a screening tool to determine the potential characteristics of a Pt-based alloy regarding catalytic stability. However, we are also interested on unraveling the molecular mechanisms by which such dissolution process takes place. We have just finished a complete study of the effect of the presence of subsurface oxygen on the structure of the platinum lattice, including the determination of barriers for diffusion of oxygen from the surface to the subsurface, as a function of coverage and exposed crystallographic face [19]. Our current work includes the analysis of the effect that other adsorbates (especially OH and H<sub>2</sub>O) have on the interplay between subsurface and surface oxygen and on the distortion of the metal structure and the investigation of the possible mechanism for separation of the metal cation from the metal structure.

## Future Directions

We intend to determine the effect of the electrolyte phase in first approximation by considering the effect that the acid medium (acidic water) and the presence of certain ions – present in the electrolyte to facilitate proton transport – may have, for instead altering the change of oxidation state of the platinum atoms and facilitating its dissolution, under the oxidized conditions established from our current studies. Once we have a better understanding of the dissolution process for platinum, we plan to extend the characterization of the mechanism of the metal dissolution process, clarifying the role that certain elements (as we have shown for iridium [18]) may have to increase the durability of platinum. Thus, we will expand our

current studies of the effects of subsurface and surface oxygen to multimetallic surfaces. In addition, we will investigate the effect of the nature of the exposed surface by examining different crystallographic faces and calculating their surface energies.

Regarding alternative catalysts, we plan to continue our investigations of biomimetic systems, and the characterization of host-guest structures with ions as active sites. Our new developed computational approaches to characterize the interfacial region will be further tested including potential dependence for the analysis of reactivity of multimetallic catalysts.

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