

Activity and Stability of Metal-supported Metal Adclusters

Jeffrey P. Greeley^{1*}, Dusan Strmcnik², Vojislav Stamenkovic², and Nenad Markovic²

¹Center for Nanoscale Materials, Argonne National Laboratory,

²Materials Science Division, Argonne National Laboratory,

Argonne, IL 60439 (USA)

*jgreeley@anl.gov

Introduction

Highly undercoordinated transition metal surface features have long been known to possess reactivity properties significantly different from those of idealized, close-packed metal surfaces. These unusual reactivities, in turn, suggest that undercoordinated features such as metal adclusters might serve as important active sites for various electrocatalytic reactions. However, to date, neither the electrocatalytic activity nor the stability of such clusters has been comprehensively studied for any electrochemical reactions of note.

In this contribution, we present a combined theoretical and experimental study of the electrocatalytic reactivity of Pt(111)-supported Pt adclusters for both the CO electrooxidation and the oxygen reduction reactions. First, we focus on one component of the overall reactivity, the catalytic *activity*. We demonstrate that highly undercoordinated clusters are extremely active for CO electrooxidation while, at the same time, being markedly inactive for the oxygen reduction. These results are interpreted in the context of elementary reaction energies and free energy barriers determined from rigorous Density Functional Theory (DFT) calculations. Second, we present an extensive series of calculations related to the *stability* of metal-on-metal adclusters; in particular, we show how cluster size and hydration/oxidation state contribute to their equilibrium dissolution potentials in acidic electrochemical environments.

Materials and Methods

Dacapo, a periodic, planewave DFT code[1], is employed for all calculations in the study; the RPBE functional with a planewave cutoff of 25 Ry is used. Cluster shapes and adsorbate geometries are fully optimized according to the Hellman-Feynman forces acting on the systems. Explicit water bilayers are included in the simulations to model the effect of the aqueous environment, and potential and pH effects are treated using the Theoretical Standard Hydrogen Electrode concept pioneered by Nørskov et al[2].

Results and Discussion

Our combined STM, cyclic voltammetry, and polarization measurements demonstrate that highly undercoordinated Pt adclusters on Pt(111) surfaces are uniquely active for the CO electrooxidation reaction; in fact, the activity of these clusters approaches that of the best state-of-the-art alloy catalysts for CO electrooxidation. Our computational analysis demonstrates that this increased activity is due to enhanced competition of OH for adsorption sites on undercoordinated adatoms compared to steps and terraces[3]; by incorporating the calculated energetics into simple Butler-Volmer rate models, we produce polarization curves in good agreement with our experimental results.

In contrast to the results for CO electrooxidation, our computational results strongly suggest that another important electrochemical reaction, the oxygen reduction reaction (ORR),

is inhibited by the presence of highly undercoordinated adclusters. The free energy barrier of the rate-limiting step is ~0.4 eV higher on Pt adatoms than it is on terraces; Pt(211) steps also show significantly lower predicted activity than do the terraces. These results are fully consistent with our measurements of ORR activity on adcluster-covered Pt(111) surfaces.

Although the electrocatalytic *activity* of supported clusters is of great practical interest, to fully understand the reactivity of these clusters, it is also critical to elucidate the fundamental principles governing the *stability* of the clusters in reactive environments. To this end, we present a comprehensive computational analysis of the dissolution potentials for both Pt-on-Pt adclusters and a full, periodic array of solute-on-host adclusters; the dissolution potential is determined as a function of the clusters' size and hydration/oxidation state. The equilibrium potential (and hence the clusters' stability with respect to dissolution) increases monotonically with cluster size for all solute/host pairs studied, and cluster hydration is found to significantly enhance the clusters' stability, as well. Nonetheless, for a significant percentage of host/solute systems studied, the cluster dissolution potential is substantially lower than the bulk dissolution potential of the element in question, suggesting that novel approaches will be needed to stabilize such clusters over long-term periods of electrocatalyst operation.

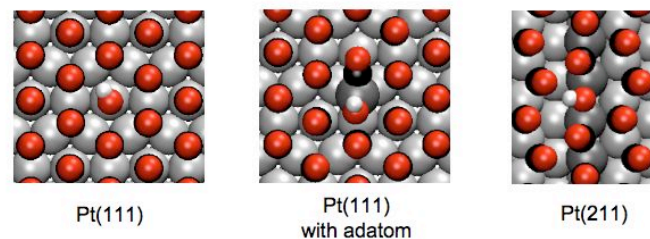


Figure 1. Optimized geometries of adsorbed OH moieties on various CO-covered platinum surfaces. For clarity, a stabilizing bilayer of water molecules is not shown.

References

1. Hammer et al., *Phys. Rev. B* **1999**, 59, 7413.
2. Nørskov et al., *JPCB* **2004**, 108, 17886.
3. Strmcnik et al., *J. Am. Chem. Soc.* **2008**, 130, 15332.

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