Bridging the Environment Gap using First-Principles-Based Catalyst Modeling

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Introduction

Molecular-scale modeling based on density functional theory (DFT) is a common feature of the catalysis research landscape today. These simulations have contributed significantly to the understanding of catalytic reaction mechanisms, to trends in reactivity amongst metals, and even to the prediction of new catalyst compositions. One of the principle challenges in applying molecular simulation to heterogeneous catalysis is incorporating the often significant effect of the reaction environment—temperature, reactant and product concentrations, catalyst support, poison—on chemical composition and structure and thus on reaction mechanism and activity. While the historical concept of a catalyst is of a material that accelerates a reaction without itself being consumed, it has long been understood that heterogeneous catalysts are not static entities, and there are now numerous examples of catalysts whose activity are strongly linked to features of the reaction environment.

Catalytic oxidations provide some of the most obvious examples of an environment effect on reactivity. The mechanism and rate of CO oxidation to CO_2 is observed to depend on the competition between chemisorbed CO and O [1] and on the appearance of surface oxides [2]. Similarly, the catalytic activity of Pt towards NO oxidation to NO_2 can only be described by accounting for the effect of O coverage on the rates of surface reactions [3]. Despite the importance of these environment-induced reaction patterns, molecularly detailed models remain sparse. Here we review our work over the last several years to combine DFT simulations with first principles thermodynamic and chemical kinetic models to describe the reactivity of metal surfaces and particles as a function of oxidation environment.

Materials and Methods

DFT calculations are performed using the PAW-based supercell implementation of GGA DFT within the *Vasp* code.

Figure 1. Calculated coverage-dependent oxygen binding energies.

Results and Discussion

Oxygen binding energy provides a straightforward illustration of environmental effects on reactivity. Figure 1 displays calculated O binding energies to the (111) surfaces of the late transition metals as a function 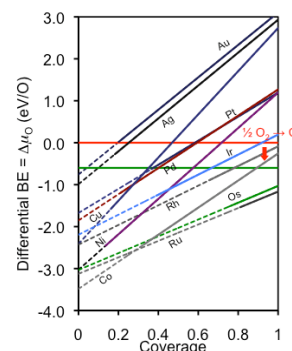of surface coverage. Increasing coverage, as induced by increasingly strong oxidizing environments, produces a monotonic decrease in binding energies arising from energetically costly adsorbate-adsorbate interactions [4]. Binding energies across a series of metals often correlate with the rates of surface reactions. Calculations show that such correlations also hold across the coverage axis: the calculated activation barriers to O_2 activation or O-NO formation, for instance,

$$O_2 (g) + 2 * \rightleftharpoons 2 O* (\theta) \qquad (1)$$
$$NO (g) + O* (\theta) \rightleftharpoons NO_2 (g) \qquad (2)$$
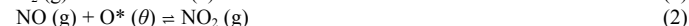
are found to be vary linearly with reaction energy. Because the latter transition state is more flexible the barrier is less sensitive to surface coverage—a feature we find to be critical to quantitative modeling of NO oxidation kinetics.

While often overlooked, similar ideas apply to discrete metal particles. Figure 2 shows calculated equilibrium structures of a Pt_3 particle as a function of oxygen "coverage" [5]. As on an extended surface, oxygen binding energy decreases with increasing coverage, but the simple trends are complicated by stable "magic" cluster compositions. These trends persist across particle sizes and are largely unaffected by interaction with an MgO support.
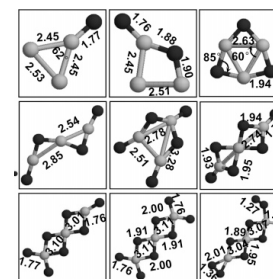

Figure 2. Pt_3O_x structures.

The solid to dotted transitions in Figure 1 mark the environments at which chemisorbed oxygen becomes metastable to metal oxidation. The transition between these two is important in catalytic activity under strongly oxidizing conditions but is poorly understood. Calculations show that the discrete clusters of Figure 2 provide a useful model for the surface structures that form along this transition.

Significance

Catalytic reactivity is intimately linked with reaction environment, primarily through the chemical changes the environment can impose on a catalyst material. With increased understanding, the environment may provide a complementary handle to catalyst composition in tuning reactivity.

References

1. Ertl, G. *Science* 254, 1750 (1991).
2. Ackermann, M. D., Pedersen, T. M., Hendriksen, B. L. M., Robach, O., Bobaru, S. C., Popa, I., Quiros, C., Kim, H., Hammer, B., Ferrer, S., and Frenken, J. W. M., *Phys. Rev. Lett.* 95, 255505 (2005).
3. Ovesson, S., Lundqvist, B. I. , Schneider, W. F., and Bogicevic, A., *Phys. Rev. B* 71, 115406 (2005).
4. Getman, R. B., Xu, Y, and Schneider, W. F., *J. Phys. Chem. C* 112, 9559 (2008).
5. Xu, Y., Shelton, W. A., and Schneider, W. F., *J. Phys. Chem. B* 110, 16591 (2006).