INSIGHTS INTO CATALYSIS OVER SUPPORTED METAL PARTICLES AT REACTION CONDITIONS

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Abstract

The active sites that carry out catalytic transformations are controlled by the reaction conditions. Reaction conditions ultimately dictate the catalytic sites, reaction mechanisms and the measured kinetics. Herein we examine how the high pressures at which catalytic reactions are carried out lead to higher coverages and how adsorbates can assist in the activation of reactants for alkane activation, Fischer Tropsch synthesis and the hydrogenolysis of polyols over supported metal particles.

Introduction

Advances in theory and computing power over the past two decades have enabled first principle quantum chemical simulations to provide direct insights into the molecular transformations that occur over model catalytic surfaces and elucidate the potential mechanisms responsible. Theory and simulation are now routinely used together with experiment to understand how reactions occur over well-defined surfaces under idealized reaction conditions. While this information advances our understanding of elementary bond- making and breaking steps, it is limited in describing the catalysis over supported catalysts at the temperatures and pressures that the reactions are actually carried out at. Metal particles often behave quite different than metal surfaces especially at the higher coverages observed in most catalytic systems. In addition to coverage effects, cluster size, morphology and metal support interactions can also significantly influence the sites and the mechanisms that control catalysis. Herein, we discuss the importance of adopting more realistic models of supported metal catalysts that explicitly examine nm-sized metal clusters, metal-support interactions and the influence of reaction conditions. We do so by examining different catalytic systems including the oxidation of methane, the oxidation of CO and the hydrogenation of CO in Fischer Tropsch synthesis.

Methods

First principle density functional theory calculations were carried out using the Vienna ab initio (VASP) program to determine reaction energies, activation barriers and activation entropies. The results are used in a 3D ab initio-based kinetic Monte Carlo algorithm to simulate catalysis over metal particles and elucidate particle size effects.

Results and Discussion

Reliable simulations of catalytic systems require an accurate accounting of what is on the surface under working conditions. The reaction conditions act to set the chemical potentials of the different reagents which subsequently dictate adsorbate surface coverages under working conditions. These coverages ultimately control the distribution of different sites on the surface along with the mechanisms by which reactions proceed. Many catalytic reactions are carried out on surfaces that are highly covered under reaction conditions. The oxidation of methane over Pt, Pd, and Rh, for example, results in over four different kinetic regimes depending upon the reaction conditions.[1-3] High ratios of P_{O2}/P_{CH4} result in the formation of an O*-covered metal surfaces or oxide formation. Lower P_{O2}/P_{CH4} result in the formation of metal-O* and/or metal-metal site pairs that carry out the

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conversion of methane. Particle size effects are different in each of the kinetic regimes.

The reactions of CO with oxygen (CO oxidation)[4] and hydrogen (Fischer Tropsch synthesis) [5] demonstrate similar sensitive dependencies of the reaction rates and selectivities on the chemical potentials of CO as well as O_2 and H_2, respectively. Higher partial pressures of CO lead to fully covered surfaces that require desorption of CO to create vacant sites along with the direct reaction O_2 (Fig. 1a) or atomic hydrogen (Fig. 1b) to aid in the activation of the C-O bond. The high coverages of CO prevent the direct activation of CO but act instead to assist in the associative activation of CO.

Simulations at high coverages on model single crystal surfaces become an issue as there are characteristic differences in single crystal surfaces and metal particles. Single crystal surfaces undergo significant strain due to the lateral repulsive interactions and tend to reconstruct. Metal particles, on the other-hand, expand in order to remove strain. This leads to very different reactivity between the ideal single crystal surfaces and the surfaces of nanometer size particles. Structure-sensitivity and particle size effects require a detailed analysis of the different sites on the surface and ensemble averaging. Different sites show different site-dependencies. Reactions dominated by dissociative reactions tend to favor coordinatively unsaturated sites found on smaller particles where reactions that are dominated associative mechanisms found in adsorbate-assisted reaction favor larger particles (as shown in Fig. 1c.)

Summary

These simulations provide some of the first steps toward modeling catalysis over supported metal particles under working conditions. They demonstrate that the catalytic performance is rather sensitive the reaction conditions which dictate the sites available to carry out particular reactions, the mechanisms by which the reactions are carried out and the effects of particle size.

References
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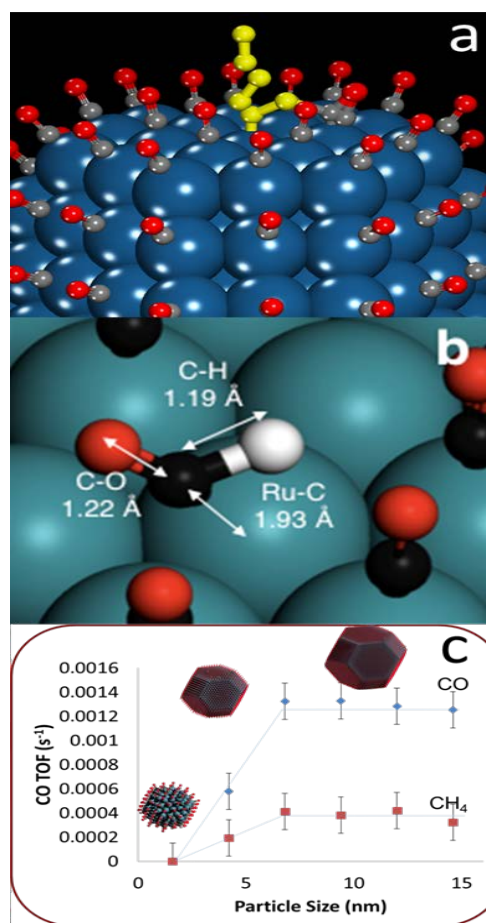5. Loveless, B.T. C. Buda, M. Neurock, and E. Iglesia, J. Am. Chem. Soc., 135, 16, 6107-6121, 2013.

Figure 1. DFT-calculated reaction path for the: (a) oxidation of CO (with O2) on Pt clusters and (b) the hydrogenation of CO with hydrogen (H*) on Ru clusters. (c) The effects Ru particle size on the catalytic activation of CO with hydrogen and methane formation.

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