

Cluster Expansion and Empirical Models of Coverage-Dependent CO Binding on Pd(111) and Supported Pd

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Introduction

Palladium catalyzes the water-gas shift (WGS) reaction at low temperatures, and both models and measurements reveal that under reaction conditions the Pd surface is CO-covered [1,2]. Kinetic models must incorporate this coverage-dependence to even qualitatively capture observed WGS activity [1,2]. CO exhibits a complex coverage dependence on Pd, [3,4]. Density-functional-theory-based (DFT) models often neglect this site variation with increasing coverage. Available evidence also indicates that the metal-support boundary participates directly in WGS catalysis. The influence of supports on coverage-dependent adsorption has to our knowledge never been explored.

In this work we describe DFT and cluster expansion models to understand and interpret coverage-dependent CO binding on Pd(111). We report a three-site cluster expansion (CE) that captures the changes in CO site preference with increasing CO coverage.[3] We apply a previously reported charge decomposition analysis [5] to extract the dipole and steric contributions to this coverage dependence. And we map these results onto a model of the interface between an alumina support and the (111) facet of a Pd particle to infer the effects of support on this coverage dependence.

Materials and Methods

DFT calculations were performed using the Vienna Ab initio Simulation Package. The Perdew-Wang 91 implementation of the generalized gradient approximation was used to approximate the exchange-correlation functional. Atomic cores were simulated by the projector augmented wave method. Cluster expansions were fit using the Alloy Theoretic Atomic Toolkit.

Results and Discussion

We used CE fitting to identify adsorption sites and model adsorption energies of CO vs. coverage on Pd(111). CO prefers 3-fold sites at low coverage and populates lower coordination sites at increasing coverage. Representative adsorption configurations and energies are shown in Fig. 1.

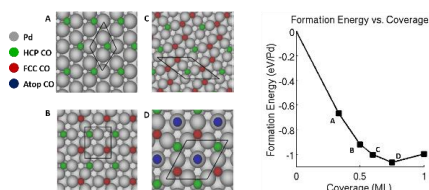


Figure 1. Ground state configurations and formation energies of the three-site Pd(111) model.

We computed CO dipole moments by partitioning the supercell charge density. We find that atop and hollow-bound CO have oppositely signed dipoles. We find a linear relationship between the dipole magnitude and the electric field induced by the dipole at an adjacent binding site. We used this relationship to quantify the dipole-dipole interaction energy as a function of site. As shown in Fig. 2, the dipole energies favor mixed site binding.

We computed steric interactions between CO as the energy to bring isolated molecules to a particular configuration in the absence of Pd. Steric interaction energies increase linearly with number neighbors. As shown in Fig.2, the steric interactions also favor mixed site over same site configurations. The combination of steric and dipole interactions account for the majority of the CO-CO interactions, suggesting that models that incorporate these two can describe the coverage-dependent adsorption energy.

We describe extensions of these results to a nanorod model of Pd on $\text{Al}_2\text{O}_3(0001)$. Results suggest that CO binding at low coverage is similar on a nanorod and (111) facet, but that lower metal coordination and greater metal flexibility allow CO coverages to reach higher values on the supported nanorod than on the facet.

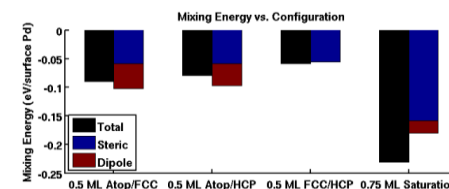


Figure 2. Steric, and dipolar contributions to mixed site configurations..

Significance

Microkinetic models of WGS, or any catalysis that occurs at high surface coverage, require reliable but simple models of coverage-dependent binding energies. Here we report an approach for extracting that coverage dependence from DFT results for CO on Pd, relate the coverage dependence to simple adsorbate-adsorbate interactions, and explore how these effects are modified at the metal-support interface.

References

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