

O-enhanced CO Photodesorption from Pd(111)

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Introduction

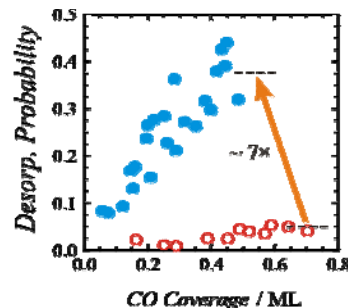


Figure 1. CO photodesorption probability of (CO+O)/Pd(111) and CO/Pd(111) as a function of CO coverage.

The catalytic oxidation of CO to CO₂ is an important elementary surface reaction that is ubiquitous in energy-related catalysis in the production and utilization of carbon-based fuels. This reaction is also widely studied as a prototype surface reaction for developing new catalysts, exploring structure-activity correlations and evaluating theoretical models. Very recently, we have explored the use of ultrafast laser excitation for initiating CO oxidation on a Pd(111) surface pre-covered with CO and O-atoms with well defined coverages [1]. One of the unusual findings of this study was the observation of enhanced CO desorption from an O-atom covered surface compared to CO alone (see Figure 1). In an effort to understand this behavior, we used density functional theory (DFT) to examine the CO binding energy on a Pd(111) surface as a function of CO coverage and binding site, and the presence of O-atoms. The results are expected to be relevant to both

thermal and photoinduced CO oxidation processes where the binding site and binding energy of CO are an important factor in determining the reaction mechanism and activity.

Materials and Methods

All calculations were performed using the Vienna *ab initio* simulation package (VASP) [2,3]. The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) was employed for the exchange and correlation functional. The electron-ion interaction was described using the projector-augmented-wave (PAW) method with plane waves up to a cutoff energy of 500 eV. Brillouin-zone integrations were performed on a grid of 4×4×1 Monkhorst-Pack special **k**-points, using a Methfessel-Paxton (MP) smearing of $\sigma = 0.1$ eV. The substrates were modeled by a three-layer slab with a $p(2\times 2)$ unit cell, separated by a vacuum space of 15 Å. The bottom two layers were fixed in their optimized bulk positions while the top layer was allowed to relax.

Results and Discussion

DFT calculations were performed to determine the most stable CO adsorption sites and CO differential binding energies on both O-saturated and CO-only Pd(111) at different CO

coverage. The CO differential binding energy without coadsorption was defined as $E[\text{nCO}/\text{Pd}(111)] - E[\text{Pd}(111)] - nE[\text{CO}]$ (n = the number of CO in a unit cell). In the presence of coadsorbed O, that was defined as $E[(\text{nCO} + \text{Oa})/\text{Pd}(111)] - E[\text{Oa}/\text{Pd}(111)] - nE[\text{CO}]$.

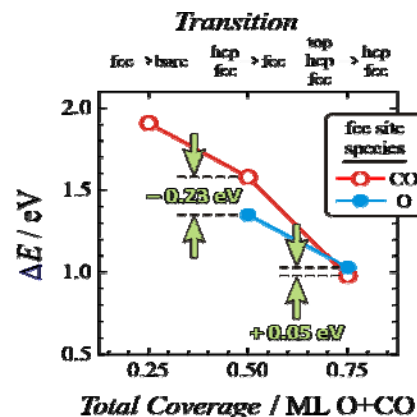


Figure 2. Binding energy differences for CO in the presence and absence of O.

The room temperature O-saturated Pd(111) surface consists of a 0.25 ML (2×2) adlayer with O atoms occupying face-centered cubic (fcc) sites. The (2×2) periodicity is unchanged by the adsorption of CO. According to our calculations, on an O-saturated Pd (111) surface, CO would occupy hexagonal close-packed (hcp) sites at the 0.25 ML coverage and both hcp and top sites when the surface is saturated with 0.5 ML CO. On a clean Pd (111) surface, CO would occupy hcp sites at 0.25 ML coverage, hcp and fcc sites at 0.5 ML coverage, hcp, fcc and top sites when the surface is saturated with 0.75 ML CO. It was found that the binding energy of top-site CO is not changed significantly (0.05 eV, see Figure 2) by the coadsorbed O. Therefore, the enhancement of CO desorption is not simply due to the changes in the top-site binding energy. However, hcp-site CO is significantly weakened by coadsorbed O (0.23 eV), which

predicts a marked increase in the probability of desorption from hcp sites. Nonetheless, the observed enhancement effect still can not be explained quantitatively and therefore we cannot rule out other mechanisms involved which would also contribute to the enhancement of CO desorption.

Significance

Our DFT studies are an important first step in understanding the bimolecular dynamics in this model catalytic system.

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