

Ideal, defective, and gold-promoted rutile TiO₂(110) surfaces interacting with CO, H₂, and H₂O: Structures, energies, thermodynamics, and dynamics from PBE+*U*

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(Received 31 March 2011; revised manuscript received 7 June 2011; published 20 July 2011)

Extensive first-principles calculations are carried out to investigate gold-promoted TiO₂(110) surfaces in terms of structure optimizations, electronic structure analyses, *ab initio* thermodynamics calculations of surface phase diagrams, and *ab initio* molecular dynamics simulations. All computations rely on density functional theory in the generalized gradient approximation (PBE) and account for on-site Coulomb interactions via inclusion of a Hubbard correction PBE+*U*, where *U* is computed from linear response theory. This approach is validated by investigating the interaction between TiO₂(110) surfaces and typical probe species (H, H₂O, and CO). Relaxed structures and binding energies are compared to both data from the literature and plain PBE results, thus allowing the performance of the PBE+*U* approach for the specific purpose to be verified. The main focus of the study is on the properties of gold-promoted titania surfaces and their interactions with CO. Both PBE+*U* and PBE optimized structures of Au adatoms adsorbed on stoichiometric and reduced TiO₂ surfaces are computed, along with their electronic structure. The charge rearrangement induced by the adsorbates at the metal (oxide) contact are also analyzed in detail and discussed. By performing PBE+*U* *ab initio* molecular dynamics simulations, it is demonstrated that the diffusion of Au adatoms on the stoichiometric surface is highly anisotropic. The metal atoms migrate either along the top of the bridging oxygen rows or around the area between these rows, from one bridging position to the next along the [001] direction. No translational motion perpendicular to this direction is observed. Approximate *ab initio* thermodynamics predicts that under O-rich conditions, structures obtained by substituting a Ti_{5c} atom with an Au atom are thermodynamically stable over a wide range of temperatures and pressures that are relevant to applications in the realm of catalysis. Finally, it is shown that TiO₂(110) surfaces containing positively charged Au ions activate molecular CO, whereas a single negatively charged Au^{-δ} species bound to an O vacancy only weakly interacts with CO. Despite this, the calculations predict that the reactivity of gold nanoparticles nucleated at O vacancies can be recovered for cluster sizes as small as Au₂.