

## Adsorption of O<sub>2</sub> and oxidation of CO at Au nanoparticles supported by TiO<sub>2</sub>(110) – A DFT study [1].

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Recently, oxide supported Au nanoparticles have attracted considerable attention due to their catalytic activity at low temperatures [2]. One of the interesting effects observed for these systems, not yet fully understood, is the influence of the type of support material, with larger activity for Au particles supported at reducible oxides like e.g. TiO<sub>2</sub>. To get some insight into the reasons that make such type of materials more active we have studied within the framework of Density Functional Theory (DFT) the adsorption of O<sub>2</sub>, coadsorption of CO, and the CO+O<sub>2</sub> reaction at the interfacial perimeter of Au nanoparticles supported by rutile TiO<sub>2</sub>(110) (see Fig. 1a). Both stoichiometric and reduced TiO<sub>2</sub> surfaces are considered, with various relative arrangements of the supported Au particle with respect to a bridging oxygen vacancy. The simulations were performed using a plane-waves basis set and pseudopotentials, together with the RPBE exchange-correlation functional. It was found that the use of a four tri-layers TiO<sub>2</sub> slab is mandatory in order to get an accurate description of the O<sub>2</sub>-TiO<sub>2</sub> binding.

The results show, in general, that the presence of a supported Au particle strongly stabilizes the adsorption of O<sub>2</sub> (see Fig. 1b). The binding of O<sub>2</sub> to clean stoichiometric TiO<sub>2</sub>, strongly endothermic, becomes exothermic when there is a supported Au rod nearby. The O<sub>2</sub> bond length is increased to 1.41 Å, indicating a sizable charging of the molecule. By analyzing the electronic states around the Fermi level (see Fig. 1c-d) we find that the Au cluster is able to donate electrons to O<sub>2</sub> through the oxide. The same effect is also observed in the case of a reduced TiO<sub>2</sub> surface (see Fig. 1e,f), although in this case most of the charge is transferred from the bridging oxygen vacancy. The binding energy is also considerably stronger.

On binding to the Au/TiO<sub>2</sub> interface, O<sub>2</sub> can adsorb in two different configurations, either on top of a Ti trough atom (Fig. 1f) or "leaning" against the Au particle (Fig. 1g). Each of them is characterized by a different charge state, with O<sub>2</sub> in a superoxo O<sub>2</sub><sup>-</sup> state while leaning against the Au particle, and in a peroxo O<sub>2</sub><sup>2-</sup> state while adsorbed in the Ti trough. Although the leaning configuration is clearly less stable than the Ti trough one, we nevertheless believe that it can be attainable under surface conditions where the vacancies possess less charge available for transfer to O<sub>2</sub> (presence of impurities, or high O<sub>2</sub> coverage). Finally, it has been also found that the binding features of O<sub>2</sub> at the Au/TiO<sub>2</sub> interface practically do not depend on the relative position of the vacancy with respect to the Au particle (either below the particle or outside of it) or the shape of the Au particle (either "sharp", as in Fig. 1f,g, or "rounded", as in Fig. 1h).

After O<sub>2</sub> adsorption, the next stage of the CO oxidation reaction is presumed to be the adsorption of CO on the Au particle, and subsequent reaction with O<sub>2</sub> at the perimeter interface. We have modeled the coadsorption of CO and O<sub>2</sub> at either "sharp" or "rounded" Au edges, finding that the adsorption properties of CO are relatively independent of the presence of coadsorbed O<sub>2</sub>. However, unlike O<sub>2</sub>, the binding of CO is very sensitive to the shape of the particle; steric repulsion effects make unfavourable the binding of CO at "sharp" particle terminations, while on the contrary CO binding at "rounded" particle terminations is quite strong (≈0.5 eV).

Finally, as rounded Au particles are the only case where strong CO-Au binding is found, we have simulated the reaction between CO adsorbed at the upper Au edge of the particle and O<sub>2</sub> adsorbed at the Au/TiO<sub>2</sub> interface in a leaning configuration (see Fig. 1h). We find that CO is able to move down from the upper Au edge and react with O<sub>2</sub> by overcoming a very small energy barrier of around 0.15 eV. Then CO<sub>2</sub> is formed without formation of any metastable CO·O<sub>2</sub> complex, unlike the case of Au particle supported on MgO [4].

Comparing MgO and TiO<sub>2</sub> supports, a fundamental difference is found between them: while for MgO the reaction follows an Eley-Rideal mechanism (with O<sub>2</sub> coming from the gas phase and its binding being assisted by preadsorbed CO), in the case of TiO<sub>2</sub> a Langmuir-Hinshelwood mechanism is possible, with both CO and O<sub>2</sub> having stable adsorption configurations and reacting once they have reached them. Overall, the role of substrate interactions is much more dramatic for a reducible oxide as TiO<sub>2</sub>, with a higher activity to be expected given the ability of the oxide to adsorb O<sub>2</sub> and transfer it to the active sites.

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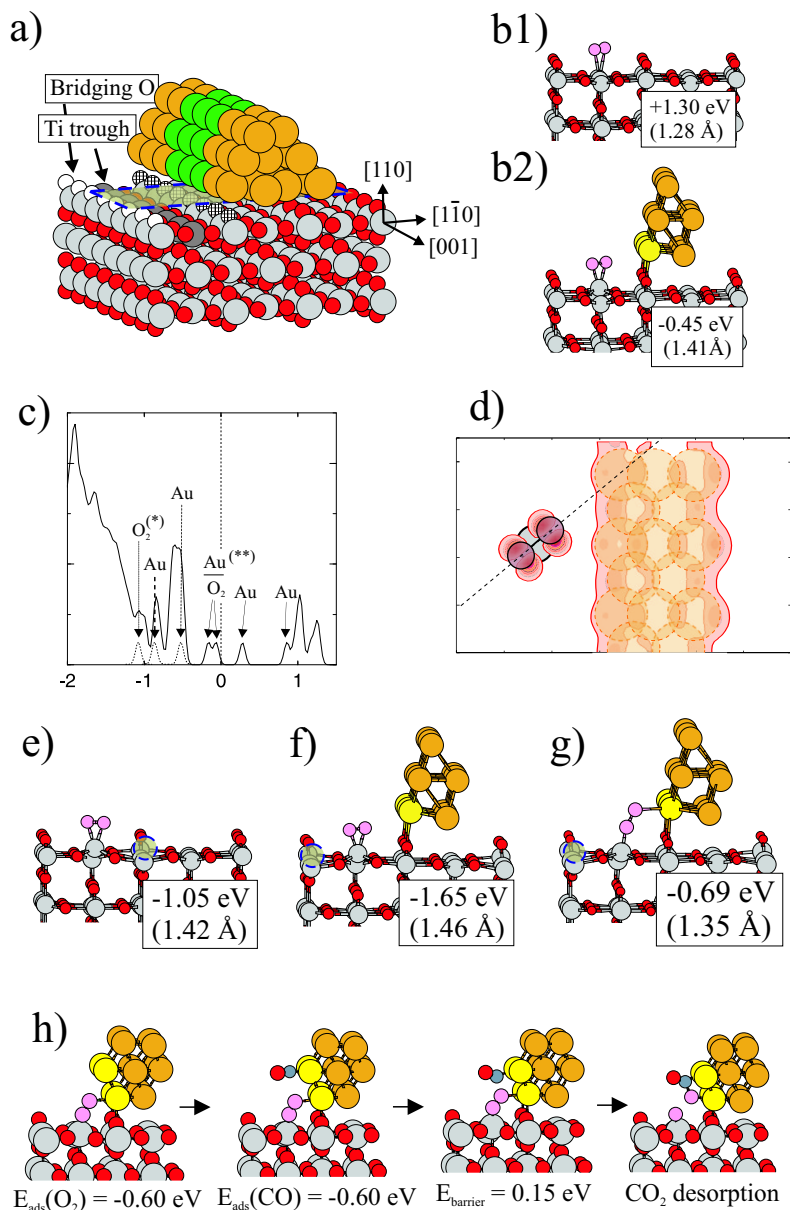


FIG. 1: a) View of a 1D Au rod supported on the  $\text{TiO}_2(110)$  surface, aligned along the  $[001]$  direction. b) Relaxed structures, adsorption potential energies and O-O bond lengths for  $\text{O}_2$  adsorption at stoichiometric  $\text{TiO}_2$  either clean (b1) or with a supported Au rod (b2). c) Density of states (DOS) around the Fermi energy for the (b2) case. Labels indicate the individual character of each  $\text{O}_2$ -derived or Au-derived eigenstate. d) Square modulus of the two occupied states closest to the Fermi energy in c) (labeled as (\*\*)), showing the charge transfer from the Au rod to  $\text{O}_2$ . e) Relaxed structure, adsorption potential energy and O-O bond length for  $\text{O}_2$  adsorption at reduced  $\text{TiO}_2$ . f,g) The same for a Au rod supported on reduced  $\text{TiO}_2$ , with  $\text{O}_2$  bonded either at a Ti trough atom or "leaning" against the Au rod. h) Structures and reaction energetics for the oxidation of CO at the perimeter of a Au nanoparticle with "rounded" shape.

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