

THEORETICAL STUDY OF O₂ AND CO ADSORPTION ON GOLD CLUSTERS IN GAS PHASE AND SUPPORTED ON ALUMINA CLUSTERS AND SURFACES.

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Aiming to understand the role of the substrate in the adsorption of oxygen and carbon monoxide on small gold clusters supported on metallic oxides, we have started a systematic study of these processes on different substrates. Here we present results concerning adsorption on gold clusters in the gas phase, as well as supported on two different Al₂O₃ substrates: a fully relaxed stoichiometric cluster with 100 atoms, and the alpha-alumina (0001) surface. These results are obtained by means of first-principles density functional calculations based on norm-conserving pseudo-potentials and numerical basis sets.

Firstly, we have investigated the reactivity toward O₂ and CO of neutral gold clusters with 5-10 atoms. The initial geometries of the clusters substrate are taken from our previous work [1],[2]. The O₂ adsorption energy shows odd-even effects, with even clusters being more active (see figure 1 upper panel). This correlates with the excess electronic charge on O₂, the increase of O-O bond distance, and the lowering of vibrational frequency. Dissociative adsorption is energetically favourable for Au₆ and Au₇. The molecular adsorption does not modify significantly the geometry of the gold substrate, which remains planar. Instead, the dissociative adsorption causes the substrate geometry to relax drastically.

On the other hand, the adsorption energy of CO on gold clusters does not present odd-even effects (see figure 1. lower panel), and adsorption occurs on top of the least coordinated Au atom, except for Au₅ and Au₇ where the bridge position is preferred. Contrary to the trends obtained for O₂ adsorption on Au_n, there is no clear correlation among the adsorption energy, charge transfer, bond distance and stretch frequency of CO adsorbed on Au clusters. For CO on bridge sites, both the CO electronic charge and bond distance increase, whereas the vibrational frequency decrease, as compared with charge, bond distance, and stretch frequency of CO adsorbed on top sites. These effects are rationalized by analyzing the partial density of states (PDOS) of bridge and top isomers of COAu_n clusters with n=5, 6, 7 atoms. These PDOS are represented in Fig. 2. The region between -5 eV and the Fermi level is composed of σ and π states of C and O, which hybridize with states from (mainly) d orbitals of gold. The peak near the Fermi level has pure π character for the bridge isomer with a small σ component for the top isomer. This peak is notably larger for the bridge isomer than for the top one. The two unoccupied states of CO closer to the Fermi level have pure σ and π character. The π one is very small for the bridge isomer. Considering that these states correspond to the anti-bonding unoccupied π^* and σ of free CO, we see that the π^* back-donation to states below the Fermi level is larger for bridge than for top isomers.

As a second step, we compare the adsorption properties of a gold atom on i) a fully relaxed (Al₂O₃)₂₀ cluster, and ii) a nine layer slab of the Al terminated (0001) surface of alpha-alumina, with a 4x4 cell having 240 atoms. The fully relaxed slab is used as the initial substrate for Au deposition. Adsorption geometries are obtained by allowing for the full relaxation of the three first layers of the slab (80 atoms). We obtain many isomeric states of the complex Au-(Al₂O₃)₂₀. From the corresponding adsorption energy of Au, we infer that the preferred adsorption site is on top of a low coordinated Al atom, followed by a hollow site surrounded by three oxygen atoms. The adsorption of Au affects only the inter-atomic

distances of a few neighbouring atoms, but the structure of the initial cluster substrate is not changed otherwise. We analyze the preferred adsorption sites in relation to the average Al-O bond distance and local charge of Al, O, and Au atoms in the cluster or slab geometries, as well as the environment of the adsorbed gold atom.

Finally, preliminary results for the absorption energy of an 8 atom gold cluster on both, slab and cluster alumina substrates will be presented.

References:

[1] E. M. Fernández et al, Phys. Rev. B, 70, 165403 (2004).

[2] E. M. Fernández et al, Chem. Phys. Lett. (Accepted).

Figures:

