

Au Dimers on Thin MgO(001) Films: Flat and Charged or Upright and Neutral?

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The catalytic activity of oxide-supported metal particles can vary considerably with properties such as size or shape, a fact which has been recognized already quite some time ago.¹ These variations are particularly significant for small particles whose properties cannot be deduced by scaling laws. Even for particles with only a few atoms, the diversity can be large and involves different isomers, different adsorption geometries, and consequently different electronic properties. Despite the substantial efforts that have been made to gain microscopic insight into the properties of oxide-supported metal particles,^{2–5} the number of studies capable to unambiguously provide evidence for essential properties such as stoichiometry, adsorption geometry, or electronic structure is rather scarce.^{6,7} This study exploits a combination of low temperature scanning tunneling microscopy (STM) used in imaging as well as in manipulation mode and theoretical calculations to investigate the simplest Au clusters, namely, dimers, supported on thin, single crystalline MgO(001) films grown on Ag(001). The thickness of the MgO(001) film was chosen such that charge transfer from the Ag substrate to the deposited Au is possible.^{8,9} The main focus of this paper is to explore the complexity of such a simple system with respect to adsorption geometry, adsorption sites, and electronic properties and show that a combination of the above-mentioned methods is capable to provide this information.

Figure 1a,b shows two STM images taken at 5 K after deposition of Au atoms (~0.03 monolayers (ML), 5–10 K) from the gas phase onto a 3 ML MgO(001) film deposited on Ag(001) using well-established recipes.^{10–12} The images show bright protrusions related to Au species on the terraces of the MgO film. A classification of the protrusions according to their height and lateral dimensions reveals that ~90% can be associated with Au atoms (monomers “M”) whose properties have been discussed elsewhere.^{13,14} For the tunneling conditions used here, the protrusions corresponding to monomers are circularly shaped and have a typical height of about 1 Å. Apart from the atoms, other circular features with about 20% increased height as compared to the atoms (“D[†]” in Figure 1b) and features with elongated shape (“D→” in Figure 1a) were found in the same image. Typical line profiles of the different Au species are shown in Figure 1c. Statistical considerations suggest the additional features correspond to small oligomers such as dimers. The ratio of circularly shaped versus elongated oligomers is about 2:3.

The stoichiometry of the species was deduced using the STM as a manipulation tool.^{15–17} The STM tip was placed above a species of interest, and a voltage pulse of 2 V was applied for several seconds while the feedback loop was on. An application of this procedure to the “higher” Au feature (“D[†]”) is shown in Figure 1d, e. The image after manipulation (Figure 1e) reveals a dissocia-

tion of the oligomer into two features that can be attributed to single Au atoms (line profiles, see Supporting Information). Thus, the oligomer designated as “D[†]” is a dimer. Conversely a tip-induced formation of these species is also feasible. Figure 1f–h shows a series of images showing that the two monomers present in Figure 1f coalesce to form an elongated dimer after the first manipulation step, Figure 1g (“D→”, see also Figure 1a), while a subsequent manipulation transforms it to a dimer with circular appearance (“D[†]”), Figure 1h.

To support the existence of different adsorption geometries, plane wave DFT supercell calculations were performed on MgO(2L)/Ag(001) films (for a comment on the different film thickness used here, see Supporting Information).¹⁸ Theoretically, the most stable configuration is a Au dimer with an upright geometry, while flat lying dimers are less stable by 0.4 eV (Figure 1i,j). The flat dimers represent local minima on the potential energy surface, and their observation in the experiment is a consequence of kinetic limitations during deposition at 5 K. The upright configuration is preferentially located on top of oxygen anions, while adsorption on Mg ions or hollow sites is significantly less stable by 0.8 and 0.6 eV, respectively. For the flat lying dimers, two azimuthal orientations along the [110] and the [100] direction and different registries of the dimer center on hollow and on top of Mg and O sites were considered. Many of these isomers are iso-energetic within 0.1 eV (see Supporting Information).

It is interesting to compare these findings with the experimental results. Information on the adsorption site can be obtained by overlying a grid with the dimensions of one ionic sublattice onto the STM images (Figure 1k,l) which was extracted from atomically resolved STM images taken prior to the Au deposition. The position of the dimers can only be determined with respect to the position of the Au monomers which, on ultrathin MgO films, populate Mg and O sites almost equally.^{14,19} Figure 1k shows the upright dimer to be centered on the same ionic sublattice as the monomers. From an analysis of several STM images, it is possible to conclude that the experiments are consistent with upright dimers adsorbed on oxygen sites as predicted by theory, but a direct confirmation is not possible (for details, see Supporting Information). The flat lying dimer shown in Figure 1l is oriented along the [100] direction of the MgO, and the dimer axis is located on a line which does not cross lattice sites. An evaluation of various images reveals several adsorption geometries, namely, clusters oriented in [100] and [110] directions with the center of gravity located in hollow as well as on ionic lattice sites. This is in line with the theoretical prediction of a flat potential surface experienced by the flat Au dimer.

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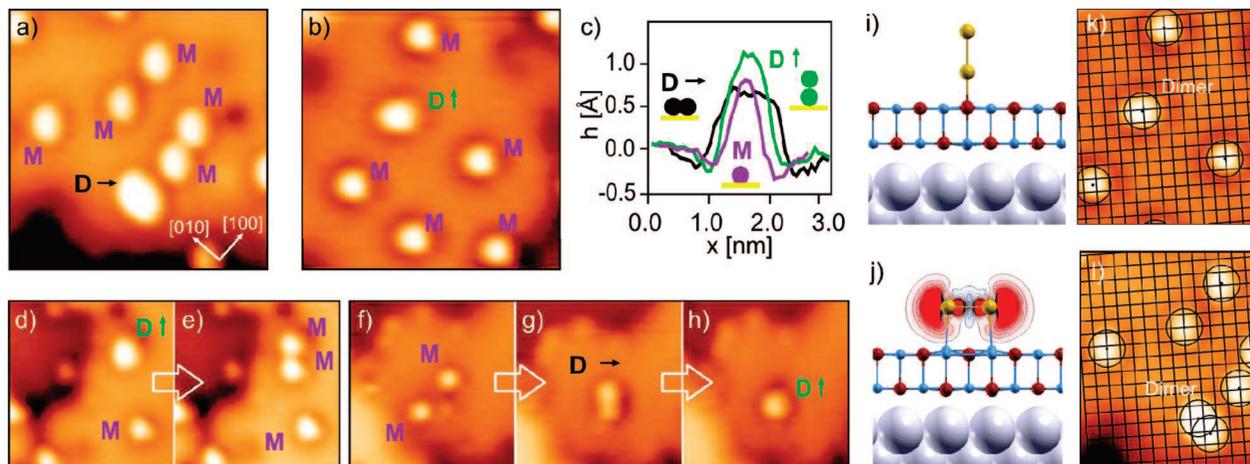


Figure 1. (a and b) STM images (6 nm × 6 nm) of Au on 3 ML MgO/Ag(001); single Au atoms (M) and Au dimers “D→” and “D†”; (c) corresponding line profiles. (d) STM image with Au atom “M” and Au dimer “D†”. (e) Same area as in (d) after applying a voltage pulse. (f and g) Series of STM images of the same area starting from the pristine surface (f) with two subsequent manipulation steps (g and h) showing the transformation of two single Au atoms into a flat dimer “D→” and an upright dimer “D†”. (i) Structure of an upright Au₂ (singlet ground state) adsorbed on an O site of 2 ML MgO/Ag(001). (j) Structure of flat Au₂⁻ on 2 ML MgO/Ag(001) (doublet ground state; Bader charge -0.8 e); Au atoms are nearly on top of Mg cations. The contour plot depicts the spin density. Notice the displacement of Mg and O ions (polaronic distortion); for details see Supporting Information. (k and l) STM images overlaid with a grid of one ionic sublattice showing the relative position of an upright and a flat lying isomer with respect to Au monomers.

Theoretically, a Au dimer like the one shown in Figure 1j, centered on a hollow site, exhibits a Au–Au distance of 2.64 Å. This is significantly longer than the computed bond length of the upright dimer (2.52 Å) and also longer than the one found for the same species on bulk MgO (2.52–2.53 Å).^{20,21} On a thin MgO/Ag(001) film, the flat lying dimer is only ~0.4 eV less stable than the upright one; on bulk MgO, however, a flat lying dimer is 0.6–0.8 eV higher in energy than the upright isomer and its bond length is significantly shorter, 2.56 Å.^{20,22} Why is the elongated flat lying dimer on the thin film more stable than its counterpart on the bulk oxide? The theoretical calculations show a charge transfer from the silver substrate onto the flat lying dimer. The extra electron is located in the antibonding σ^* orbital of the Au dimer explaining the elongation of the bond as compared to the neutral dimer.^{23,24} The charged state is stabilized both by polaronic effects within the MgO film and image charge effects in the silver substrate, which are missing in the case of bulk MgO. As expected for a Au₂⁻, the flat lying dimer has a doublet ground state. Figure 1j shows the spin density of the flat lying dimer, which clearly corroborates the charge transfer onto the small Au cluster, as seen by a Bader charge analysis (-0.8 e), too. The scenario is consistently found for all azimuthal orientations with small variations of the bond length between 2.64 and 2.67 Å. In contrast to that, the upright dimer is found to be neutral and shows a singlet ground state in close correspondence with results found on bulk MgO(001) surfaces. Thus, the two classes of isomers differ not only by their adsorption geometry but also by their electronic structure which can also influence the chemical properties considerably.

In summary, we have elucidated the adsorption behavior of Au dimers on a thin MgO film in great detail. Au dimers exist not only in an upright geometry—as theoretically predicted to be the most stable configuration—but also as flat lying dimers which populate a manifold of different azimuthal orientations. These are not just two adsorption configurations but involve rather different electronic structures: while upright dimers are neutral, flat ones are charged. This result highlights the peculiar properties of ultrathin, metal-supported MgO films which alter the characteristics of deposited Au atoms and particles significantly as compared to their counterparts on bulk MgO. Similar effects are conceivable for more complex bulk oxides, which

implies that very small clusters of well-defined stoichiometry may exhibit a large spread in electronic and in turn chemical properties.

Acknowledgment. The authors acknowledge support by COST (action D41), the DFG (CoE “unifying concepts in catalysis”), the Fond der chemischen Industrie, and the Barcelona supercomputing center (BSC).

Supporting Information Available: Details on the experimental and theoretical methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA8024388