Interaction of Gold Clusters with Color Centers on MgO(001) Films**

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For a long time gold was considered catalytically inactive. However, it came under scrutiny after experiments showed distinct catalytic activity for small, supported, gold-nano-particle catalysts.[1–3] This discovery has triggered a burst of activity to understand the microscopic mechanisms of these systems.[4,5] One strategy to unravel the details was to characterize model systems of gold atoms deposited on defined supports both experimentally as well as theoretically.[6–11] A variety of different effects were considered in which particle size and electronic effects were among the most important ones. In this respect, the interaction with the underlying support is of paramount importance for a detailed understanding. For the supported system the situation is rather complicated because of the large variety of surface sites that need to be taken into account. For oxide supports, such as MgO, low-coordinate sites as well as surface oxygen vacancies (surface color centers or F_S-centers) are considered particularly important, because it is expected that these sites may alter the properties of the adsorbed atoms and clusters with respect to regular surface terrace sites. Recent density functional theory (DFT) calculations show a strong binding of gold atoms and dimers at defects with the highest binding energies found for gold on singly charged (F^+) and neutral (F^0) color centers.[9] Furthermore, charge transfer from the defect site to the gold atom was also proposed.[9] This result is in agreement with calculations of Landman et al. for small gold clusters (Au_8). Based on theoretical predictions and IR spectra taken for Au_8 clusters deposited on MgO films with different roughness it was concluded that the observed difference in catalytic activity towards CO oxidation is due to an interaction of the Au_8 clusters with color centers on the MgO surface.[7]

However, a direct experimental correlation between the presence of color centers on the surface, their interaction with metal atoms and clusters, and the properties of the metal atoms and clusters adsorbed to these sites (as probed, for example, by the CO stretching frequency), has never been established. Herein we are aiming to demonstrate this correlation using color centers on single crystalline MgO and their interaction with gold as a prototype example. A combination of electron paramagnetic resonance (EPR) and scanning tunneling microscopy (STM) is used to verify the existence of color centers as well as the nucleation of Au onto these defects. These characterized systems then serve as reference systems in which the CO stretching frequencies can be correlated with the properties of Au clusters nucleated at regular as well as defect sites.

The upper STM image in Figure 1a was measured on a 3–4 monolayer (ML) thick, single-crystalline MgO(001) film grown on Ag(001) after electron bombardment. The image is characterized by rectangular MgO terraces which have edges running parallel to the [100] directions of the MgO lattice. The additional bright spots located at the edges, corners, and kinks of the MgO facets are introduced by electron-bombardment and were assigned to surface color centers.[12] Note that the non-electron bombarded, pristine film shows only a minute number of color centers. Subsequently, this film was
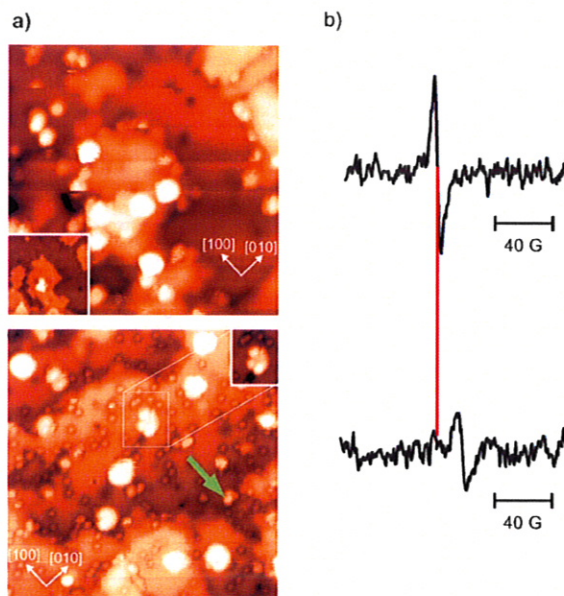
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Figure 1. a) STM images (30×30 nm^2). Top: 3–4 ML MgO(001)/Ag-(001) taken after electron bombardment, $V_s = -3.0$ V, $I_t = 8$ pA; inset: same area $V_s = 3.5$ V, $I_t = 9$ pA; bottom: the same preparation after deposition of 0.035 ML Au at 5–8 K; a dimer is indicated by a green arrow; inset: nucleation on a color center, with adjusted contrast; $V_s = 1.3$ V, $I_t = 10$ pA; 30×30 nm^2. b) EPR spectra around $g = 2$, top: MgO(001) film on Mo(001) after low-dose electron bombardment; bottom: the same preparation after deposition of 0.015 ML Au at 30 K. The red line indicates the position of the color-center signal in both spectra.

exposed to a small amount of Au atoms (0.035 ML) at 5–8 K. As seen from the lower STM image in Figure 1a, Au atoms and Au_2 dimers (e.g. marked by the green arrow) are found on the terraces of the MgO film. From the fine structure observed within the bright protrusions (see inset) as well as scanning tunneling spectroscopy it is inferred that small gold clusters of a few atoms nucleate on these centers.

The upper trace in Figure 1b shows the EPR spectrum around the free electron g-value of a 20 ML thick, single-crystalline MgO(001) film grown on Mo(001) after bombardment with electrons. The EPR signal was previously assigned to paramagnetic color centers located at edge sites of the MgO surface.[12] The signal only occurs after electron bombardment. The pristine film shows no EPR signal, which means that the number of paramagnetic color centers on this film is lower than 7×10^{11} centers cm^{-2}. This value is in accord with STM results from the MgO films grown on Ag. After deposition of 0.015 ML of Au at 30 K the EPR signal of the color center is quenched. This result is a direct consequence of the nucleation of Au at the color centers. This behavior arises from the coupling of the doublet ground states of the color center and the Au atom to a singlet ground state of the adsorption complex. However, the quenching of the signal is also consistent with the formation of small Au clusters at these sites, as seen by STM. Concomitant to the decrease of the color-center signal a new EPR signal appears at higher field. This line is part of a quartet of lines with a large isotropic hyperfine coupling constant of about 1400 MHz, which is characteristic of single Au atoms. A detailed analysis of angular dependence of the signals shows that these Au atoms are nucleated on the terraces of the MgO film, directly above the oxygen ions.[13] The Au dimers seen by STM cannot be detected directly by EPR spectroscopy, however, the presence of oligomers is inferred from dosage-dependent measurements. From these experiments it can be concluded that:

1. The pristine films do not exhibit a measurable amount of point defects (color centers).
2. Color centers are produced by electron bombardment and can be characterized by EPR and STM.
3. Au nucleates at color centers as well as on regular terrace sites.

These systems are now used to calibrate the stretching frequency of CO molecules bound to different Au centers. Figure 2a shows the IR spectrum of an electron bombarded MgO film grown on Mo(001) after deposition of 0.05 ML Au at 30 K and subsequent saturation dosage of CO at 30 K. The spectrum shows a broad peak around 2160 cm^{-1} which consists of a doublet of lines at 2163 and 2153 cm^{-1} arising from CO adsorbed to low-coordinate sites as well as regular terrace sites of the MgO surface, respectively.[14] In addition, two bands one at 2120 and a broad one around 2070 cm^{-1} are observed. These bands correspond to CO bound to Au as IR measurements on the bare, electron-bombarded film exposed to CO, but not Au, shows only the peaks at 2163 and 2153 cm^{-1}, and only differs from the spectrum of the CO-treated pristine film in that the relative intensity of the peak at 2163 cm^{-1} increases at the expense of the intensity of the peak
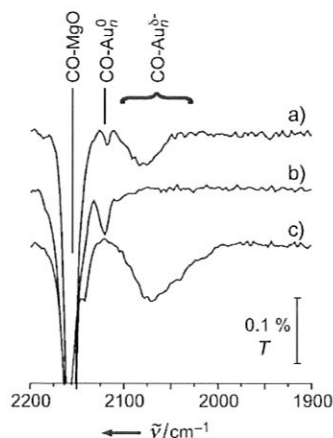

Figure 2. IR spectra after saturation coverage by CO on Au clusters formed on differently pretreated MgO films. a) film after medium-dose electron bombardment and deposition of 0.05 ML Au at 30 K; b) pristine MgO film after deposition of 0.025 ML Au at 80 K; c) film after high-dose electron bombardment and deposition of 0.025 ML Au at 30 K; film annealed to 90 K prior to CO adsorption; T = transmission.

at 2153 cm^{-1} (data not shown). The band at 2120 cm^{-1} is in perfect agreement with expectations for CO adsorbed to small, neutral Au clusters, which are known to show bands that are slightly blue shifted with respect to those of CO adsorbed to large Au clusters or Au single-crystal surfaces (2110 cm^{-1}).[4] For the amount of Au used in our experiment no signal arising from CO bound to single gold atoms is observed. A discussion of the unexpected properties of the IR signals of CO bound to single gold-atoms, is given in the next Communication in this issue.[15] To further corroborate the assignment, Au was adsorbed on a pristine MgO film without electron bombardment which, according to STM and EPR measurements, has a negligible amount of color centers. The IR spectrum of this preparation treated with CO (Figure 2b) shows a signal at 2120 cm^{-1}, in addition to the bands of the MgO film, confirming the assignment of this peak to CO adsorbed to neutral Au clusters. Notice the complete absence of bands in the 2000–2100 cm^{-1} range.

For the electron-bombarded sample, the signal observed at 2070 cm^{-1} (Figure 2a) can be readily explained by CO adsorbed to negatively charged Au clusters, which are predicted to be produced by the adsorption of Au to color centers. The red shift of the band is due to the greater π-back-donation from the negatively charged Au than from the neutral Au. Theoretically, a red shift of the CO stretching frequency of 25 to 80 cm^{-1} depending on the charge on the Au_8 clusters was predicted which corresponds rather well with the observed values.[7] From the width of the IR line it is clear that a variety of different species are present. This situation is even more pronounced for a film which was heavily bombarded with electrons (Figure 2c). First, the signal at 2120 cm^{-1} has vanished after this treatment indicating that the prolonged electron bombardment has decreased the amount of terrace sites considerably. Second, the signal for CO bound to the negatively charged Au clusters is even broader and extends down to 2000 cm^{-1}. The intensity distribution in the range between 2000 and 2070 cm^{-1} depends

on the amount of gold and the preparation (electron dosage, deposition temperature, annealing steps etc.). From a variety of different experiments it can be concluded that the lines at lower wavenumber correspond to CO bound to smaller gold particles. In addition, structural inhomogeneities of the various species will contribute to the width of the signal. The effect of cluster size on the stretching frequency is in agreement with a simple model: the influence of the charge on the stretching frequency should decrease with increasing cluster size owing to the distribution of the charge over the cluster. A similar behavior was also found for gold clusters in the gas phase.[16]

These results can be compared to values reported for Au particles on various catalytically interesting samples as shown in Figure 3.[4,17–19] The values presented herein for a well
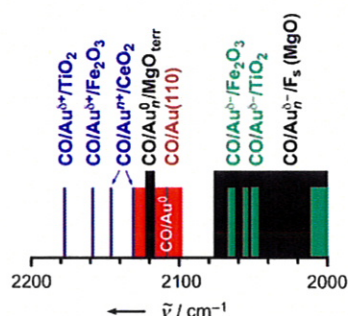
deposited at 30 K unless otherwise stated. The Mo substrate was cleaned by oxidation with O_2 at 1500 K and subsequent flash heating to 2300 K. The MgO films were prepared by deposition of Mg in an oxygen atmosphere (1×10^{-6} mbar) at a substrate temperature of 600 K and a rate of 1 ML MgO/min. The films were subsequently annealed to 1100 K for 10 min. The EPR spectra of Au atoms were measured with a microwave power of 2 mW in a TE_{102} cavity using a modulation amplitude of 4 G. IR spectra were taken with a spectral resolution of $4\;cm^{-1}$. 1000 scans were accumulated to obtain a reasonable signal-to-noise ratio. Details of the experimental setup are described elsewhere.[20] STM experiments were carried out in a custom-built low-temperature STM which has been described in detail elsewhere.[21] For the STM experiments a 3–4 ML thick MgO(001) film was grown on Ag(001) by reactive deposition of Mg at 550 K. Au was deposited at 5–8 K. In all cases color centers were produced by electrons with an energy of 100 eV extracted from a filament.

Figure 3. Comparison of IR stretching frequencies observed for the systems reported herein (back bars, terr = terrace) with measurements on other catalytically relevant systems (blue: positively charged Au particles; red: neutral Au particles; green: negatively charged Au particles).

defined model system fit perfectly with findings for neutral Au clusters on a variety of supports. The stretching frequencies for CO on the negatively charged Au clusters differ from those of CO on neutral clusters in a way that depends strongly on the size of the particles. The difference ranges from about $100\;cm^{-1}$ for very small clusters down to about $40\;cm^{-1}$ for larger particles.

In conclusion, these experiments provide the first direct correlation between the presence of color centers on a single-crystalline oxide surface, the nucleation of metal atoms to these centers, and the impact of the nucleation site on the properties of the metal particle as probed by the IR stretching frequency of adsorbed CO molecules. Based on the IR data it was shown that Au particles adsorbed to color centers are indeed charged as expected from theoretical predictions, while Au particles on regular terrace sites are neutral. In addition, we find good indications that the red shift of the stretching frequency for CO on negatively charged Au clusters is strongly dependent on the size of the Au particle as rationalized by simple electronic considerations.

Experimental Section

EPR and IR experiments were performed at 30 K on a 20 monolayer (ML) thick MgO(001) film grown on Mo(001). Au atoms were

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