Initial Formation of Positively Charged Gold on MgO(001) Thin Films: Identification by Experiment and Structural Assignment by Theory

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ABSTRACT: Infrared spectroscopy experiments using CO as a probe and X-ray photoelectron spectroscopy were used to study the initial nucleation of gold on the surface of MgO(001)/Ag(001) thin films at 90 K. The most intense CO infrared signal observed at low gold coverage was at 2154 cm⁻¹, indicating the formation of positively charged Au species. Both infrared and photoemission data reveal details about the thermally induced sinter behavior of metallic and positively charged gold species on the MgO(001) surface. Density functional theory was used to examine different defect types on the MgO surface for their



ability to form positively charged Au species and to assign the observed IR stretch vibration to Au_n^+ -CO species on specific binding sites on the MgO(001) surface.

1. INTRODUCTION

Identifying local binding sites on oxide supports that give rise to unique chemical and physical properties of catalytic metals, well dispersed into atoms and clusters, has proven to be difficult and is one of many significant challenges facing surface science of heterogeneous catalysis today. The study of dispersed metal particles supported on well ordered oxide films allows fundamental insight into the relationship between atomic structure and the chemical and physical properties of the supported metals.¹⁻⁵ In recent years, gold atoms and clusters supported by thin MgO films that are grown on Mo(001) or Ag(001) have attracted particular attention as prototypical model catalyst systems. The properties and catalytic activity of these systems have been extensively studied experimentally by scanning probe microscopy, vibrational spectroscopy, electron paramagnetic resonance, and temperature programmed desorption,⁶⁻¹⁰ as well as computationally using density functional theory (DFT) calculations. $^{11-14}$ Despite the enormous interest in the Au/MgO model system, there remain many unanswered questions. This study addresses the origin of the observed positive shift in the frequency of CO adsorbed on Au/MgO(001).

The electronic nature of gold clusters deposited on oxide surfaces and in particular the charge state of these aggregates, be it neutral, positively, or negatively charged, have attracted a lot of interest and stimulated several experimental and theoretical studies.^{15–21} The situation is complicated by the fact that different charge states of Au may result from different preparation conditions (oxidative or reducing environment), the nature of the oxide support (reducible or nonreducible), or the existence of defects on the support. It is not surprising, therefore, that there is no single answer to the question of what is the charge state of a

small gold cluster deposited on an oxide surface. Also, the identification of the charge state of a gold nanoparticle is not trivial. Adsorption of CO "probe" molecules and the measurement of their vibrational properties is, together with analysis of binding energy shifts from X-ray photoelectron spectroscopic studies, often employed to identify the oxidation state of metal atoms or nanoparticles grown on oxide surfaces.²² A CO frequency of about 2100-2120 cm⁻¹ is typical of neutral Au particles or of the Au surface.^{23,24} Frequencies in the range 2130–2180 cm⁻¹ correspond to the formation of gold clusters in positive oxidation state,²⁵ while, for clusters with an accumulation of negative charge due, for instance, to the interaction with surface defects, the frequency is red-shifted and may vary considerably but is typically around $2040-2080 \text{ cm}^{-1.8,10,26}$ The explanation of this trend is rather simple and is based on the classical Blyholder model.²⁷ Analysis of the dependence of the CO frequency shift with respect to different Au-CO bonding contributions reveals a direct relationship between the CO stretching frequency and the amount of electronic charge back-donated from the metal to the CO $2\pi^*$ molecular orbital. In turn, this depends on the charge state of the metal, being largest for electron-rich species.² Exceptions to these "rules" do also exist. Recently, it has been shown that when CO interacts with a neutral Au atom deposited on the MgO surface its stretching frequency, instead of being close to that of the gas-phase molecule, is red-shifted by almost 300 cm^{-1} .^{29,30} This is due to an induced net charge transfer of one electron from the Au 6s valence orbital to the CO $2\pi^*$

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molecular orbital, which occurs spontaneously upon CO adsorption, and is caused by the Pauli repulsion between the neutral Au atom's 6s electron and the closed shell oxygen ion in the oxide surface. In this case, the CO molecule does not probe the charge state of the as deposited Au atom but instead the strong chemical rearrangement following CO adsorption.²⁹ In the meantime, CO stretching frequencies between the limiting value for the Au atom and the value range of $2100-2120 \text{ cm}^{-1}$ found for neutral Au aggregates have been observed for negatively charged Au atoms and clusters and neutral Au dimers and trimers.³¹

Another important aspect in this matter is the perturbation of the electronic nature of the small metal aggregates that are formed on the surface by the interaction with the support. Charge transfer at the interface between the oxide and the metal cluster is not the only mechanism that determines the final shift in the CO frequency. CO is very sensitive to the details of the cluster electronic structure and, in particular, to the polarization of the metal electrons; an increase in the Pauli repulsion between CO and the metal cluster can result in a blue shift of the frequency even in the absence of a positive charge. Furthermore, exposed cations and anions at the surface of ionic oxides generate local electric fields which may interact with the CO multiple moments, resulting in non-negligible shifts in the CO vibrational frequency. All of these effects, charge transfer, electron polarization, Pauli repulsion, and local electric field, play an important role for supported metal clusters containing just a few atoms, while their effect is expected to rapidly vanish for particles containing tens or hundreds of atoms.

In this study, we present and discuss the origin of a blue-shift in the frequency of CO molecules adsorbed on Au atoms or small clusters deposited at 90 K on thin MgO films grown on Ag(001)single crystals. According to the above discussion, this is indicative of the formation of gold species in a positive oxidation state. Since MgO is a basic, nonreducible oxide, this result is unexpected and must be related to specific interactions of the gold species with local sites on the oxide surface. The Article is divided into two sections: First, we identify experimentally by IR spectroscopy of CO probe molecules and X-ray photoelectron spectroscopy the cationic gold species on model surfaces of Au/MgO(001) prepared under controlled conditions by physical vapor deposition. Second, DFT calculations are used to assign the cationic IR stretch frequencies to specific Au_n^+ – CO species at unique binding sites of the MgO(001) support. Combined, this report presents a detailed study addressing the origin of the positive shift in the frequency of CO adsorbed on Au/MgO(001).

2. EXPERIMENTAL METHODS

The experiments were preformed in a UHV chamber equipped with a hemispherical electron energy analyzer together with a twin anode X-ray source for X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). A small cell connected to the main UHV chamber was used for infrared experiments in reflection absorption geometry (IRAS). A Ag(001) sample was attached by Ta wires to Mo rods on the manipulator, which allowed for resistive heating to 700 K or liquid nitrogen cooling to 90 K. The temperature was monitored via a chromel—alumel thermocouple spot-welded to the backside of the crystal. The Ag(001) single crystal was cleaned by repeated sputter—anneal cycles until a sharp 1×1 LEED pattern was obtained and the XPS measurements showed no sign of surface contaminants. MgO(001) films were grown on the Ag(001) substrate by reactive deposition of Mg in an oxygen ambient of 1×10^{-6} mbar O₂ at a substrate temperature of 573 K and a deposition rate of 1 monolayer (ML) per minute. The surface quality of the MgO(001) film was verified with LEED and the stoichiometry with XPS. Gold was deposited on the surface of MgO in varying amounts (0.006, 0.02, 0.04, and 0.2 ML, 1 ML \approx 1 \times 10^{15} $atoms/cm^2$) at 90 K in UHV by physical vapor deposition (PVD) from an electron beam evaporator at a rate of 0.04 ML/min. IR spectra using ¹²CO as a probe molecule were collected at 90 K (unless explicitly stated) using a Bruker IFS66v/S spectrometer and a liquid nitrogen cooled MCT detector. Each spectrum was obtained by averaging 1200 interferrograms with a spectral resolution of 4 cm⁻¹. Background measurements were collected from the MgO prior to gold deposition. Photoelectron spectra were collected using Al K α radiation (1486.6 eV) at an electron take-off angle of 60°. The hemispherical energy analyzer was set to a constant pass energy of 20 eV.

3. COMPUTATIONAL METHODS

The properties of Au_n-CO complexes formed at the MgO surface have been studied by means of embedded cluster models and DFT calculations using the B3LYP hybrid functional.^{32,33} In order to properly account for the formation of strong dipoles on the surface, resulting from possible charge transfers at the interface between the Au atoms or clusters and the MgO surface, the electronic relaxation of the substrate was accounted for over a wide region using the shell-model approach where the MgO surface is described by a nanocluster of about 5000 atoms. The central part, treated quantum-mechanically (QM), is surrounded by a region of about 300 classical ions whose polarizability is described by a shell model (SM).³⁴ Cations in the SM region at the interface with the QM region are replaced by ions (Mg*) on which a semilocal effective pseudopotential (ECP) is centered, in order to reproduce the Pauli repulsion and avoid the nonphysical polarization of QM interface anions. Region I (QM and SM) is then surrounded by a large array of point charges (PC) in order to reproduce the long-range electrostatic potential. This scheme is implemented in the GUESS code³⁵ interfaced with the Gaussian 03 code,³⁶ and the total energy of the hybrid system is calculated as a sum of classical and QM contributions. All centers in the QM region and Mg* interface atoms have been allowed to move during the optimization, while only shells, not cores, have been relaxed in the SM region.

A number of possible adsorption sites where Au atoms or clusters can be stabilized have been considered. These include regular (001) terrace sites, edges, and anionic reverse corners (ARC), as examples of morphological defects or point defects. Oxygen vacancies (F centers) have been considered in 0, +1, and +2 charge states, and their formation has been considered on terrace, edge, and corner sites. Neutral Mg vacancies have been considered at edge and corner sites only. The list of potential point defects where gold can be stabilized is completed by OH groups at edge sites. The OH group has been modeled by adding a dissociated H₂O molecule to an edge site. Specifically, an OH⁻ group has been added to a Mg²⁺ cation and a proton, H⁺, has been added to a O²⁻ anion. The whole system is thus charge neutral.

Typical QM clusters considered in this work are $Mg_{10}O_{10}$ - Mg_{14}^* (edge), $Mg_{26}O_{14}Mg_{4}^*$ (terrace), and $Mg_{17}O_{17}Mg_{22}^*$ (reverse corner). The basis sets used are 6-31G on Mg, 6-31G* on the O atoms of MgO, 6-311+G* for C and O of the CO



Figure 1. IR spectra of adsorbed CO for different coverages of Au deposited at 90 K on 13 ML MgO(001)/Ag(001). The gray spectrum is the result of dosing a mixture of 67% ¹²CO and 33% ¹³CO.

molecule, and $6-311+G^{**}$ for H, while the Au atoms were described with the small core, 19-electron, effective core potential, ECP, of Hay and Wadt³⁷ and an unsegmented [5s6p3d/ 3s3p2d] double- ζ basis set.

Harmonic frequencies of the normal modes were determined for CO adsorbed on the Au clusters in the gas phase or supported on MgO by solving the full secular matrix. Anharmonic contributions for free CO molecules are small³⁸ and are similar for charged and neutral AuCO clusters.²⁸ With the present approach, the free CO ω_0 (harmonic) is 2212 cm⁻¹; the experimental ω_e (anharmonic) and ω_0 (harmonic) frequencies are 2143 and 2170 cm⁻¹, respectively. Therefore, a scaling factor of 2143/2212 = 0.9688 has been applied to all computed frequencies to take into account anharmonic effects and to directly compare computed and measured C-O stretching frequencies. The accuracy of the approach can be evaluated on well characterized $[Au_nCO]^+$ systems. The computed (scaled) value for $[AuCO]^+$, 2242 cm⁻¹, is very close to that reported for the same complex isolated in a neon matrix, 2237 cm^{-1,39} The planar $[Au_3(CO)_3]^+$ complex has a CO stretching frequency at 2182 cm⁻¹ in experiment⁴⁰ and 2185 cm⁻¹ in the present calculations. This shows that the reported values for gas-phase complexes are rather accurate and that the errors should not exceed ± 10 cm⁻¹. This may no longer be true when MgO supported clusters are considered. Here, small changes in charge transfer from the oxide to gold or local electric fields due to the embedding potential can easily result in CO vibrational shifts of a few tens of cm^{-1} .

4. RESULTS: EXPERIMENT

a. Au Coverage Dependence. The nucleation of gold on the surface of a 13 ML thick MgO(001) film was studied with infrared spectroscopy using CO as a probe molecule for various amounts of Au deposited at 90 K. Figure 1 shows the IR spectra collected at 90 K of CO adsorbed on Au species on MgO(001)

for increasing Au coverage. At the lowest coverage, 0.006 ML Au, the main contribution to the spectrum is an absorption band centered at 2154 cm⁻¹, exhibiting a shoulder at 2170 cm⁻¹. Two additional small signals appear at 2121 and 1850 cm^{-1} . As the coverage is increased to 0.02 ML Au, all absorption bands increase in intensity. The band centered at 2170 cm^{-1} is now clearly resolved in this spectrum, and the two absorption bands at 2154 and 2121 cm⁻¹ are nearly equal in intensity. At 0.04 ML Au, the band centered at 2121 cm⁻¹ is the most intense of the spectrum. At this coverage, a shoulder on the low frequency side of this signal is observed at 2102 cm^{-1} . The intensity of the absorption band at 1850 cm⁻¹ remains almost constant compared with the 0.02 ML Au sample, while those of the bands at 2154 and 2170 cm⁻¹ are significantly reduced. At the highest Au coverage studied here, 0.20 ML Au, CO adsorption results in two intense bands at 2121 and 2102 cm^{-1} . The signals at 2170, 2154, and 1850 cm^{-1} , which were present at lower Au coverage, are not observed on the 0.20 ML Au sample.

The IR signals observed at 2121, 2102, and 1850 cm^{-1} are well-known for CO adsorbed on MgO(001)-supported Au atoms and clusters. A combined experimental and theoretical study has identified the species giving rise to a stretching frequency of 1850 cm^{-1} as CO adsorbed on single Au atoms.² The other two components are observed for Au clusters on various oxide supports and are assigned (i) to CO adsorbed on neutral Au clusters $(2102 \text{ cm}^{-1})^{23,24}$ and (ii) to either very small Au clusters or partially positively charged Au sites at the cluster/ oxide periphery (2121 cm⁻¹).^{41,42} Frequencies in the range 2150–2180 cm⁻¹ are typical for CO adsorbed on the cations of the MgO support.⁴³ However, according to the classification mentioned in the Introduction section, positively charged gold species also give rise to CO stretching frequencies in this range. Since CO adsorption on MgO is in general weak, a comparison of the thermal stability of adsorbed CO is a way to distinguish between adsorption on the substrate and on the gold particles.

b. Thermal Stability of Adsorbed CO and Au Sintering. The thermal stability of the CO adsorption complexes giving rise to the absorption bands centered at 2170, 2154, 2121, and 1850 cm^{-1} was determined for the 0.02 ML Au sample. Figure 2a shows IR spectra taken following exposure of CO at 90 K as a function of annealing temperature. The spectra were collected at the temperatures shown in Figure 2a without additional exposure to CO. Additionally, to present the data in a more graphical manner and to include all annealing temperatures (too many to show in the top panel), the same data is displayed in the lower panel of Figure 2a as an image plot. The signal assigned to CO on single gold atoms at 1850 cm⁻¹ disappears at around 140 K, in agreement with a previous study.⁴⁴ The absorption band centered at 2121 cm⁻¹ is stable to 220 K, whereas the two bands centered at 2170 and 2154 cm^{-1} merge into a single band at 2160 cm^{-1} by 120 K that is then stable to 240 K.

The experimental result shown in Figure 2a clearly indicates that the signals observed at 2154 and 2170 cm⁻¹ are due to CO adsorption on Au particles on the MgO support. Both the frequency as well as the thermal stability of adsorbed CO is in line with the interpretation of these species as being due to CO adsorbed on positively charged Au species. The CO adsorption experiment using a 12 CO/ 13 CO isotopic mixture presented in Figure 1, where only one additional band at 2107 cm⁻¹ according to the expected isotopic shift of the 2154 cm⁻¹ signal is observed, provides clear evidence for monocarbonyl complexes of CO on



Figure 2. (a) IR spectra of CO adsorbed on 0.02 ML Au/13 ML MgO(001)/Ag(001) as a function of temperature. The spectra were collected at the indicated temperature. The lower panel presents the results as an image plot with red being intense and blue representing no absorption. (b) IR spectra of CO adsorbed on 0.02 ML Au/13 ML MgO(001)/Ag(001) as a function of annealing temperature. The spectra were collected after recooling to 90 K and dosing with CO. (c) Model of the Au/MgO(001) surface representing the nature of Au species formed at various annealing temperatures as deduced from the IR spectra shown in part b.

the positively charged gold species. It is interesting to note that the 2120 cm⁻¹ state is lost at a similar high temperature of 220 K, considerably higher than the typical CO desorption temperature from regular Au clusters on MgO (~150 K).⁴⁵ This is in line with the interpretation as CO adsorption sites in small Au clusters or cluster/oxide perimeter sites. Combining the results of Figures 1 and 2a leads to the conclusion that the initial nucleation of Au on the surface of the MgO(001) film at 90 K occurs at sites that give rise to positively charged Au species. These sites are occupied almost completely at the smallest Au coverage studied here. Therefore, their abundance is estimated to be below 0.5% ML. As the coverage is increased, single Au atoms (1850 cm⁻¹) and small Au clusters (2121 cm⁻¹) are stabilized on the surface, and finally, large Au particles with bulk-like properties (2102 cm⁻¹) are formed.

The desorption temperature of 240 K observed for CO adsorbed on the positively charged Au species should be considered a lower bound because annealing is a dynamic experiment that affects the morphology of the Au particles initially formed at 90 K. In order to study the thermally induced agglomeration behavior of the Au particles, IR spectra were recorded following each annealing step after recooling the sample to 90 K and redosing CO. The result of this experiment is presented in Figure 2b, where the topmost spectrum represents the initial state of 0.02 ML Au after deposition at 90 K with four IR bands at 2170, 2154, 2121, and 1850 cm^{-1} . Up to an annealing temperature of 200 K, the IR spectra in Figure 2a and b are almost identical, which indicates that the spectral changes can primarily be ascribed to morphological modifications due to enhanced diffusion and particle agglomeration. Single Au atoms are least stable on the surface and are lost at \sim 140 K. The sharp signal at 2121 cm⁻¹ due to small Au particles becomes broad and shifts to lower wavenumber in the course of annealing to 200 K. We attribute this to thermally induced restructuring of the Au particles, which introduces heterogeneity in the adsorption site distribution and CO adsorption geometry. Sintering and agglomeration proceed

in the temperature range 200–300 K and lead to the disappearance of the positively charged Au species. Only a very weak CO signal at ~2110 cm⁻¹ remains after 300 K annealing (Figure 2b). Upon further annealing to 500 and 600 K, a sharp and intense CO absorption signal is restored with ω (CO) = 2090 cm⁻¹.

The weak IR absorption observed at 246 and 300 K in Figure 2b is ascribed to CO adsorption on Au particles with distinct morphology that are formed during annealing. Figure 2c summarizes the annealing induced morphological changes of Au on the MgO surface. At low deposition temperature, sharp CO absorption signals result from the presence of single Au atoms, small Au clusters, and particles nucleated at sites that give rise to positively charged Au. As the temperature is increased, enhanced diffusion leads to the formation of larger particles, which, at temperatures between 250 and 300 K, are flat and only 2-3 atomic layers high.⁶ CO adsorption is only possible on the edge sites of these particles, since the binding energy is too small for adsorption on the (111) top facet.⁴⁶ In addition, CO molecules adsorbed on the edge sites might be strongly tilted toward the surface, resulting in only weak IR absorption due to the metal surface selection rule. Only if the annealing temperature is increased above 300 K is the thermal energy sufficient for Au to form large, regular metallic nanoparticles that give rise to CO adsorption with the typical CO stretching frequency around 2100 cm⁻¹. It has to be noted that the apparent loss of CO IR signals at intermediate annealing temperatures is only observed for very small initial Au coverage. If this annealing experiment is performed with a sample containing 0.20 ML Au, where large three-dimensional particles are present already after deposition at 90 K, the spectral changes in CO absorption signals are much less pronounced.45

The general conclusion drawn from the IR spectra about nucleation and sintering of Au on MgO(001)/Ag(001) thin films is corroborated by corresponding X-ray photoemission studies. Panels a and b of Figure 3 show the XPS spectra obtained from 0.02 ML Au deposited on 13 ML MgO(001)/Ag(001) at 90 K



Figure 3. XPS spectra of 0.02 ML Au/13 ML MgO(001)/Ag(001) at 90 K (a) and of the same sample after annealing to 573 K (b). (c) Binding energies of the Au $4f_{7/2}$ components as a function of annealing temperature after initial deposition of 0.02 ML Au on 13 ML MgO(001)/Ag(001) at 90 K.

(Figure 3a) and from the same sample after annealing to 573 K (Figure 3b). The Au 4f binding energy region overlaps in energy with the Mg 2s of the support. The shape and full-width-at-halfmaximum of the Mg 2s have been determined for the clean MgO sample prior to Au deposition and were later used in the fitting procedure for the gold containing samples. The XPS spectrum of the annealed sample is characterized by a single Au component (two spin-orbit split states, $4f_{7/2}$ and $4f_{5/2}$, 4:3 intensity ratio, and 3.67 eV splitting) with a Au $4f_{7/2}$ binding energy of 84.0 eV (Figure 3b), which corresponds to that of bulk Au and is characteristic for metallic Au in sintered particles. By contrast, perfect fitting of the XPS spectrum taken immediately after deposition of Au at 90 K requires two components with Au $4f_{7/2}$ binding energies at 85.6 and 84.4 eV, respectively (Figure 3a). The origin of the binding energy shift with respect to bulk Au is different for the two components and can be explained by initial and final state effects.⁴⁷ We attribute the Au 4f_{7/2} component with a binding energy of 84.4 eV to very small, metallic gold clusters, where insufficient screening of the core hole (final state effect) contributes to the binding energy shift of +0.4 eV. On the other hand, a shift of +1.6 eV, as observed for the second Au $4f_{7/2}$ component with a binding energy of 85.6 eV, is significantly higher than the shift expected for purely final state effects.⁴⁸ Therefore, we attribute this shift as arising from an initial state effect due to the presence of cationic Au. Figure 3c summarizes the XPS results for 0.02 ML Au on 13 ML MgO(001)/Ag(001) obtained for various annealing steps between 100 and 573 K. A slight binding energy increase of the metallic Au 4f7/2 is observed at an initial heating step to 130 K caused by slight geometrical rearrangements on the surface. The downward trend in binding energy with increasing annealing temperature reflects the sintering induced changes of Au particles on the MgO surface. Agglomeration of Au in the temperature range 130-220 K leads to dilution of the positive charge in cationic Au clusters as well as to an increased final state screening in the metallic Au particles. Hence, a decrease in the Au $4f_{7/2}$ binding energy is observed for both components. By 240 K, cationic and metallic Au cannot be distinguished anymore, and from there on, the spectra are reasonably well fit by a single, metallic Au component. At 300 K, the binding energy is 84.1 eV, indicating a remaining small contribution from particle size effects (final state), which is completely absent after annealing to 573 K, where large Au particles with a diameter of several nanometers have formed. The loss of the cationic Au component at 240 K is perfectly in line with the disappearance of the IR band at 2160 cm⁻¹ and further corroborates the assignment of this IR signal to CO adsorbed on cationic Au.

While the observed sintering behavior follows general expectations for the Au/MgO(001) system, the initial formation of



Figure 4. IR spectra of CO adsorbed on 0.02 ML Au deposited at 90 K on MgO/Ag(001) films of different thicknesses.

positively charged gold species upon deposition of small quantities of Au, which results in rather high stretching frequencies of adsorbed CO, raises some questions about the nature of Au nucleation centers present on the surface of MgO thin films. Frequencies in the range 2130-2180 cm⁻¹ are commonly observed for powder samples of oxide-supported Au clusters after oxidative treatment and have been assigned to CO adsorption on positively charged or oxidized Au particles.⁴⁹ At very small Au coverage, CO frequencies in this range have also been observed on model systems comprising gold on single crystalline transition or rare earth metal oxide supports such as Fe₃O₄ or CeO₂.^{50,51} While for those the positive charging of Au might be explained by the redox chemistry between the support on the one hand and gold on the other,⁵² such a mechanism is difficult to imagine as being responsible for the formation of positively charged gold species on the MgO support. Instead, the interaction of Au with particular defects on the MgO surface seems to be more likely.

In this respect, it is worth noting that deposition of Mg on MgO powders and thin films leads to spontaneous oxidation of Mg and the formation of electrons trapped at defects on the MgO surface.^{53–55} Since these defects are no longer available for additional ionization processes, the nucleation behavior of Au on Mg/MgO is expected to be slightly modified. In fact, the IR band at 2170 cm⁻¹ cannot be observed on a MgO thin film sample onto which Mg has been deposited prior to Au (data not shown), suggesting a similar role of the underlying defect in the activation of Mg and Au.

c. Morphological Aspects. In Figure 4, we present IR results for Au nucleation at 90 K on MgO films of different thicknesses probed by CO adsorption. Our previous computational studies and low-temperature scanning tunneling microscopy experiments have shown that Au adsorption on metal-supported MgO(001) is strongly influenced by the MgO film thickness, resulting in the formation of negatively charged Au atoms in the limit of ultrathin films.^{56,57} The absence of a CO absorption band at 1850 cm^{-1} on the 4 ML MgO film, which is due to neutral Au atoms on the MgO surface, strongly supports this result (Figure 4). The fact that no additional IR signal is observed due to CO binding to Au⁻ is explained by its small CO binding energy, which prevents observation at 90 K.58 However, the CO-IR spectrum of Au/4 ML MgO/Ag(001) also indicates the formation of positively charged gold species with $\omega(CO) = 2154 \text{ cm}^{-1}$. The intensity of this signal decreases significantly if the film thickness is increased to >10 ML. In parallel, the signal contributions due to single Au atoms (1850 cm^{-1}) and small Au particles (2121 cm^{-1}), as well as from the Au⁺-related signal at 2170 cm⁻¹, gain intensity.

It can be expected that the surface morphology of the MgO films becomes better as thicker films are grown, a fact that is related to the strain imposed by the lattice misfit between Ag(001) and MgO(001) on the ultrathin films, which fades away with increasing film thickness.⁵⁹ This is especially true for the average size of MgO(001) islands, which explains the observed increase in intensity of "regular" Au–CO species (2121, 2100, and 1850 cm⁻¹) for thicker films. The signals due to positively charged gold species at $\omega(CO) = 2170$ and 2154 cm⁻¹ obviously follow different trends: while the former increases with film thickness, the abundance of the latter is strongly reduced. This suggests that the abundance of the underlying nucleation centers, which are obviously of different nature, changes with MgO film thickness.

At this point, we note that slight differences in surface morphology and, hence, defectivity of MgO films of varying thickness may influence the amount of hydroxyl groups on the MgO surface due to dissociation of residual water during the course of the experiment. We expect that this effect is more pronounced for thinner films. Previous experiments have shown the formation of partially positively charged metal particles upon deposition on hydroxylated oxide surfaces.⁶⁰ In fact, for Au deposited on intentionally hydroxylated MgO surfaces, the formation of positively charged Au particles can be unambiguously demonstrated.⁶¹ Beside the role of particular defects, an active participation of hydroxyl groups, which might be present even on a nominally clean MgO surface in amounts exceeding 0.01 ML,⁶² in the formation of positively charged Au species can, therefore, not be disregarded.

In order to identify possible sites that might give rise to positive charging of gold, the properties of Au-CO at various defect sites on MgO(001) have been examined with DFT. The results of these studies are reported in the following.



Figure 5. Structures of $[Au_nCO]^+$ gas-phase species.

 Table 1. Properties of CO Adsorbed on top of Positively

 Charged Gas-Phase Au Atoms and Clusters

	Figure 5	r(C-O)/Å	$D_{\rm e}/{\rm eV}$	$\omega_{\rm e}/{\rm cm}^{-1}$	$\Delta \omega_{\rm e}/{\rm cm}^{-1}$
$[AuCO]^+$		1.117	1.99	2242	+99
$\left[\mathrm{Au}_{2}\mathrm{CO} ight]^{+}$	а	1.120	1.69	2215	+72
$[Au_3CO]^+$	b	1.121	1.48	2200	+57
$[\mathrm{Au}_4\mathrm{CO}]^+$	с	1.122	1.30	2139	-4
$[\mathrm{Au}_4\mathrm{CO}]^+$	d	1.121	1.10	2145	+2

5. RESULTS: THEORY

a. Gas-Phase [Au_nCO]⁺ Complexes. We first consider the vibrational properties of a CO molecule adsorbed on a Au⁺ ion and on small Au_n^+ free clusters, Figure 5 and Table 1. The problem has been investigated previously⁶³ and is considered here only for comparative reasons. CO was adsorbed on top of Au atoms because this is energetically preferred.⁶⁴ CO is strongly bound to positively charged gold atoms and clusters, but the bond strength (D_e) rapidly decreases with the delocalization of the positive charge on more than a single atom, Table 1. $D_{\rm e}$ goes from 1.99 eV in $[AuCO]^+$ to 1.30 eV in $[Au_4CO]^+$. Experimentally, the adsorption energy of CO to Au_6^+ is ~1.1 eV,⁶³ consistent with this trend. Also, the C-O stretching frequency follows a similar behavior: It is strongly blue-shifted, $+99 \text{ cm}^{-1}$ in [AuCO]⁺; the shift decreases in charged gold clusters containing 2 or 3 atoms where it is still positive $(+72 \text{ and } +57 \text{ cm}^{-1})$ respectively, Table 1). However, on the most stable isomer of $[Au_4CO]^+$, Figure 5c, a very small negative shift is found, Table 1. The other less stable isomer, Figure 5d, has a very small positive shift of $\omega_{\rm e}({\rm CO})$. Notice that for Au₅⁺-Au₈⁺ gas-phase clusters, values around $2150-2160 \text{ cm}^{-1}$ have been reported by Fielicke et al.;²⁶ in particular, $[Au_8CO]^+$ shows a CO frequency of 2150 cm⁻¹, i.e., only slightly blue-shifted compared to free CO (2143 cm^{-1}) . This is perfectly in line with the results reported in Table 1.

Assuming that an excess of oxygen could be present in the chamber at the moment of Au deposition, we also considered the properties of CO adsorbed on small gas-phase Au_nO_m clusters, Table 2 and Figure 6. The presence of oxygen results in partially oxidized gold atoms and in strong Au–CO bonds, but the CO frequencies are moderately shifted with respect to the free molecule and only in one case, Au_3O –CO, Figure 6b, a small positive shift of +5 cm⁻¹ is observed.

b. MgO Supported Au_nCO Complexes. On the MgO surface, Au atoms are essentially neutral.^{9,12} Nevertheless, when CO adsorbs to a gold atom on MgO, the C–O frequency drops to

Table 2. Properties of CO Adsorbed on top of Gas-Phase Au_nO_m Clusters

	Figure 6	r(C-O)/Å	$D_{\rm e}/{\rm eV}$	$\omega_{ m e}/{ m cm}^{-1}$	$\Delta \omega_{ m e}/{ m cm}^{-1}$
Au ₂ O-CO	а	1.124	1.92	2116	-27
Au ₃ O-CO	Ь	1.129	1.89	2148	+5
Au ₃ O-CO	с	1.132	1.77	2128	-15
Au ₃ O ₂ -CO	d	1.130	0.95	2135	-8



Figure 6. Structures of Au_nO_m-CO gas-phase species.

1850 cm⁻¹ due to the already mentioned transfer of the Au 6s electron to CO, yielding a Au⁺CO⁻ complex.^{29,30} So far, calculations on this species have been performed only for Au sitting on the O_{5c} ions of the MgO(001) terraces.²⁹ Here, we considered also morphological defects such as an anionic reverse corner (ARC), Table 3. On this site, AuCO exhibits similar properties to those found on terrace sites, i.e., a large red-shift in the CO frequency. Therefore, the previous assignment of the band at 1850 cm⁻¹ to isolated neutral Au atoms^{29,30} is valid also for other Au adsorption sites.

Next, we consider positively charged $[Au_nCO]^+$ species on the MgO surface. Of course, there are several sites where these complexes could be stabilized, but we restrict the analysis to terrace and edge sites, a hydroxyl group (OH) formed along an edge site, and an ARC. When Au⁺ is adsorbed on an O_{5c} terrace site, Figure 7a, CO is strongly bound, 1.94 eV, and the CO frequency is shifted by $+60 \text{ cm}^{-1}$. The O_{5c} has low "basic" character, so that the positive charge on Au is only partly screened by the oxide support. Still, there is a reduction of about 40 cm^{-1} in the CO frequency going from free to supported $[{\rm AuCO}]^+;$ see Tables 1 and 3. In the second site considered, an edge O_{4c} ion, Figure 7b, CO is also strongly bound to Au⁺, 1.91 eV, but the more "basic" nature of the site⁶⁵ leads to an efficient screening of the positive charge and the CO frequency is shifted by only $+10 \text{ cm}^{-1}$, Table 3. The third case is that of a Au⁺ ion bound to an OH group at an edge, Figure 7c; here, [AuCO]⁺ interacts simultaneously with an O4c edge ion and with the OH group. The interaction with two under-coordinated O atoms results in a very efficient screening of the positive charge. This is also true when [AuCO]⁺ forms on an ARC site, Figure 7d: here, the Au atom interacts simultaneously with three O ions of the surface. Here, CO remains strongly bound, Table 3, but the C–O frequency is now *red-shifted* by -67 cm^{-1} on the OH site and by -77 cm^{-1} on the ARC. Therefore, on sites where [AuCO]⁺ interacts with more than a single O atom, the frequency is red-shifted, not blue-shifted.

Positively Charged Au Atoms and Clusters Supported on the MgO Surface Figure 7 $r(C-O)/Å D_e/eV \omega_e/cm^{-1} \Delta \omega_e/cm^{-1}$ AuCO terrace^a 1.175 0.57 1850 -292

Table 3. Properties of CO Adsorbed on top of Neutral and

		Figure 7	r(C-O)/A	$D_{\rm e}/{\rm eV}$	$\omega_{\rm e}/{\rm cm}$	$\Delta \omega_{\rm e}/{\rm cm}^{-1}$
AuCO	terrace ^a		1.175	0.57	1850	-292
	ARC		1.174	0.90	1820	-323
$[AuCO]^+$	terrace	а	1.117	1.94	2242	+60
	edge	b	1.129	1.91	2153	+10
	OH edge	с	1.139	1.85	2076	-67
	ARC	d	1.140	1.38	2066	-77
$[Au_2CO]^+$	terrace	e	1.132	1.27	2154	+11
$[Au_3CO]^+$	terrace	f	1.128	0.32	2165	+22
	edge	g	1.127	0.37	2144	+1
$[Au_4CO]^+$	terrace	h	1.132	0.57	2110	-33
^a From ref 25.						

We now consider small $[Au_2CO]^+$, $[Au_3CO]^+$, and $[Au_4CO]^+$ clusters formed on terrace or edge sites, Figure 7 and Table 3. In $[Au_2CO]^+$, the Au–Au bond is considerably elongated with one fragment, $[AuCO]^+$, adsorbed on top of an O_{5c} ion and a neutral Au atom sitting on an adjacent O_{5c} site, Figure 7e. On the contrary, $[Au_3CO]^+$ and $[Au_4CO]^+$ stay intact but exhibit a strongly reduced CO binding energy (from 1.5 to 1.7 eV in the gas phase, Table 1, to 0.3–0.6 eV on the surface, Table 3). Additionally, the CO frequency is affected by the interaction with the oxide support. On $[Au_3CO]^+$, the $\omega_e(CO)$ is blue-shifted by +22 cm⁻¹ (terrace) or +1 cm⁻¹ (edge) (+57 cm⁻¹ in the gas phase), while, on $[Au_4CO]^+$, there is a red shift of -33 cm⁻¹ (-4 cm⁻¹ in the gas phase). On this basis, we conclude that the positive shift in CO frequency for gold deposited on MgO films could be due to Au⁺ atoms or tiny gold clusters (dimers, trimers) stabilized at terrace or edge sites.

We now consider the interaction of gold with specific point defects, starting with Mg vacancies. The removal of a Mg atom from the surface leaves two unsaturated O atoms. If an Au atom "replaces" the missing Mg, it will be formally oxidized, and this could justify the observed CO frequency shift. However, while the presence of O vacancies (F centers) on the MgO surface has been demonstrated,^{66,67} the presence of Mg vacancies remains to be unambiguously shown. On a Mg vacancy at a corner, Figure 8a and Table 4, Au is partly oxidized and CO is strongly bound, by 1.4 eV. The CO frequency is, however, slightly red-shifted, by -30 cm^{-1} , Table 4. Thus, the level of Au oxidation is not such to produce a strong positive shift in the CO stretching frequency. This result is also found when Au substitutes Mg at an edge site, Figure 8b. Despite the formal positive charge on Au (about +0.5 according to the Bader analysis), the CO stretching frequency is red-shifted by -75 cm^{-1} , Table 4. We also considered a Au₂ dimer formed at a corner Mg vacancy, Figure 8c, but also in this case the shift is not positive. On this basis, we can exclude that Mg vacancies play a role in the observed phenomena.

The defect on the MgO surface that has attracted the greatest attention is by far the O vacancy or F center.⁶⁸ We have considered color centers on both terrace and edge sites. We first consider the neutral variant, F^0 , with two trapped electrons, Figure 9a and b and Table 5. This defect is a strong electron donor⁶⁹ and as such cannot explain the CO blue shift. In fact, our results show that, when Au is bound to a F^0 center at a corner or an edge site, CO is weakly bound (because of the large Pauli



Figure 7. Structures of MgO supported $[Au_nCO]^+$ complexes: (a) AuCO⁺ on a terrace; (b) AuCO⁺ on an edge; (c) AuCO⁺ near an OH group at an edge; (d) AuCO⁺ on an anionic reverse corner; (e) Au₂CO⁺ on a terrace; (f) Au₃CO⁺ on a terrace; (g) Au₃CO⁺ on an edge; (h) Au₄CO⁺ on a terrace. The spin density is shown for open shell systems (Au₂CO⁺ and Au₄CO⁺).



Figure 8. Structures of Au_nCO complexes bound to a Mg vacancy: (a) AuCO on a corner; (b) AuCO on an edge; (c) Au_2CO on a corner. The spin density is shown for open shell systems (AuCO).

Table 4. Properties of CO Adsorbed on top of Au, COComplexes Bound to a Mg Vacancy

		Figure 8	r(C-O)/Å	$D_{\rm e}/{\rm eV}$	$\omega_{\rm e}/{\rm cm}^{-1}$	$\Delta \omega_{\rm e}/{\rm cm}^{-1}$
AuCO	V _{Mg} corner	a	1.137	1.42	2113	-30
	V_{Mg} edge	b	1.138	0.58	2068	-75
Au ₂ CO	V_{Mg} terrace	с	1.134	2.66	2109	-34

repulsion) and its frequency is strongly red-shifted (by about -200 cm^{-1} , Table 5). This is due to the increased back-donation into the $2\pi^*$ antibonding molecular orbital of CO and to the consequent bond elongation. The situation is not very different for the paramagnetic F⁺ centers, Figure 9c and d. Au atoms bind strongly to these centers due to the coupling of the trapped electron in the vacancy with the Au 6s valence electron, and the consequence is that CO is virtually unbound, Table 5. We have considered also Au₂ on F⁺, Figure 9e. Here, CO is bound by 0.49 eV, but the excess electron in the vacancy results in an enhanced back-donation and in a large red-shift, -159 cm^{-1} . Clearly, F⁰ and F⁺ centers cannot explain the formation of positively charged Au species.

The existence of these defects on the MgO surface has been demonstrated recently, although their number is expected to be low.⁶⁷ Au atoms and clusters are strongly anchored to F²⁺ centers. On the contrary, CO is always weakly bound to Au atoms on F^{2+} centers, independent of the location of the defect, Table 5. The CO bonding is so weak that in some cases the molecule moves to the interface where it binds also with a Mg cation; see F^{2+} on the edge, Figure 9g. Therefore, Au atoms at F^{2+} centers are not expected to bind CO at 90 K. On the other hand, F^{2+} centers can act as nucleation sites for small Au clusters, as shown by the fact that the dimer binding energy (i.e., the energy gain when a diffusing Au atom binds to another Au atom at F^{2+}) is positive, 0.3 eV.⁷⁰ Au dimers at F^{2+} centers, Figure 9h and i, bind CO by 1.2-1.3 eV and give rise to large shifts in CO frequency, Table 5. In particular, for Au_2/F^{2+} (edge), the computed shift, $+43 \text{ cm}^{-1}$, is compatible with the 2170 cm⁻¹ IR band of the experiment.

The last kind of O vacancy is the electron deficient F^{2+} center.

6. DISCUSSION

The experimental results clearly indicate the presence of two IR bands associated to CO molecules adsorbed on positively charged Au species at 90 K, one at 2170 cm⁻¹ and one at 2154 cm^{-1} . The evolution of these bands as a function of Au coverage, annealing temperature, and film thickness provides some relevant information about their origin. First, these two bands are present only at very low coverage, indicating that they are due to Au atoms or very small Au clusters. As more gold is deposited, larger particles form and bands at 2121 and 2102 cm⁻¹, typical of gold nanoparticles, are observed. Around 120 K, the two bands at 2170 and 2154 cm^{-1} merge into a single band at 2160 cm^{-1} that is then stable up to 240 K. A desorption temperature of 240 K corresponds, using the Redhead equation and a frequency factor of $v_1 = 10^{13} \text{ s}^{-1}$, to a CO binding energy of about 0.5-0.6 eV. This indicates that Au and Au-CO species become mobile between 90 and 160 K and that aggregation of small clusters occurs on the sites where nucleation initiated. The MgO thickness dependence (Figure 4) shows that the band at 2154 cm^{-1} is more abundant on thinner films and, in general, is associated with a higher degree of defectivity and disorder. On



Figure 9. Structures of Au_nCO complexes bound to F^0 , F^+ , and F^{2+} defect centers: (a) AuCO on a F^0 corner; (b) AuCO on a F^0 edge; (c) AuCO on a F^+ corner; (d) AuCO on a F^+ edge; (e) Au₂CO on a F^+ edge; (f) AuCO on a F^{2+} terrace; (g) AuCO on a F^{2+} edge; (h) Au₂CO on a F^{2+} terrace; (i) Au₂CO on a F^{2+} edge; (j) Au₃CO on a F^{2+} edge. The spin density is shown for open shell systems (AuCO/ F^0 , Au₂CO/ F^+ , AuCO/ F^{2+} , Au₃CO/ F^{2+}).

Table 5.	Properties of CC) Adsorbed	on Au _n CO	Complexes
Bound to	$F^{0}, F^{+}, and F^{2+}$	Centers		

		Figure 9	r(C-O)/Å	$D_{\rm e}/{\rm eV}$	$\omega_{\rm e}/{\rm cm}^{-1}$	$\Delta \omega_{ m e}/{ m cm}^{-1}$
AuCO	F ⁰ corner	а	1.151	0.28	1897	-246
	F^0 edge	Ь	1.149	0.86	1948	-195
AuCO	$\boldsymbol{F}^{+} \text{ corner }$	с	1.127	0.02	2157	
	$F^+ \; edge$	d	1.128	0.01	2143	
Au_2CO	F^+ edge	e	1.146	0.49	1984	-159
AuCO	\mathbf{F}^{2+} terrace	f	1.123	0.21	2207	+64
	F ²⁺ edge	g	1.131	0.28	2110	-33
Au_2CO	\mathbf{F}^{2+} terrace	h	1.125	1.18	2208	+65
	F ²⁺ edge	i	1.124	1.27	2186	+43
Au ₃ CO	F^{2+} edge	j	1.125	1.20	2211	+68

the other hand, there is no band at 2170 cm^{-1} on ultrathin MgO films, while this feature appears for films of 10 ML or more. This suggests that the defect responsible for this feature is not stable on the very thin films, while it is present on the thicker samples.

With the help of the theoretical results, we provide a tentative assignment of the observed features, starting with the band at 2154 cm⁻¹. [AuCO]⁺ complexes at MgO terrace sites exhibit a high frequency shift, $+60 \text{ cm}^{-1}$, which is not observed in the experiment probably because of the aggregation of other species (Au atoms, dimers, etc.) to form larger aggregates. In fact, the barrier for diffusion of [AuCO]⁺ is estimated to be about 0.6 eV, not sufficient to induce mobility of the complex at 90 K. On the contrary, gold cations at edge sites, more strongly bound, exhibit a small positive shift of the CO stretching frequency, $+10 \text{ cm}^{-1}$, consistent with the band at 2154 cm⁻¹. The bonding of CO to isolated Au⁺ ions is about 2 eV. Therefore, by raising the temperature, [AuCO]⁺ diffusion on the edge sites will occur instead of CO desorption, leading to aggregation of clusters. On small Au_n^+ clusters, CO is weakly bound, by 0.4–0.6 eV, but still exhibits small blue shifts in the CO stretching frequency, two observations which can explain both the IR and the temperature dependent data. What remains to be answered is how positively charged gold clusters form on the surface of a nonreducible oxide such as MgO.

The Au atom has an ionization potential (IP) of 9.22 eV (9.42 according to the present calculations), which makes ionization of gold prohibitive under normal conditions. However, when deposited on a terrace site, the IP decreases considerably, to 5.14 eV. The IP decreases even further when Au is sitting on defect sites such as an edge (4.82 eV), an OH group (4.06 eV), or an ARC (2.32 eV). This means that, if sufficiently strong electron trapping sites are present on the MgO surface, it can be thermodynamically favorable to transfer electrons from Au atoms formed on the MgO surface to these sites, resulting in the formation of Au⁺ and trapped electrons. This is also true for small Au clusters; for instance, MgO-supported Au₃ has an IP of 3.46 eV, about 50% of the gas-phase value, 7.26 eV. CO adsorption can further stabilize the positively charged state or even induce it, as reported for other oxides.⁷¹

Several electron traps exist on the MgO surface, some shallow, with binding energies for electrons of 1 eV or below (e.g., Mg corner ions,⁷² neutral divacancies⁷³), others rather deep (F^{2+} and F⁺ centers, OH groups).⁷⁴ For instance, the vertical electron affinity of an OH group at an edge site is about 3 eV,⁷⁵ showing that these sites are potential candidates for the stabilization of trapped electrons. Recently, it has been shown that electrons can be trapped at grain boundaries between MgO islands,⁷⁶ and that these grain boundaries can bind a large number of electrons.⁷⁷ In fact, due to the lattice mismatch between Ag(001) and MgO-(001), misfit dislocations are introduced in the film to compensate for the lattice strain already at the early stages of MgO film growth, leading to the formation of mosaics. The tilt angle of the mosaics decreases significantly with increasing film thickness.⁵⁹ The formation of Au ions by the indirect effect of grain boundaries, or the presence of a slightly larger amount of OH groups, would be consistent with the higher intensity of the band at 2154 cm^{-1} on thinner MgO films.

The band at 2170 cm⁻¹ has a more subtle origin. The only sites which, according to the theoretical calculations, give such large shifts in the CO frequency are the F^{2+} centers. Au atoms bind so strongly to these sites that CO adsorption is inhibited, but, on the other hand, they have good nucleation properties and the formation of Au₂ species on this center is favorable. CO binds

to Au₂/F²⁺ at an edge by more than 1 eV and exhibits a CO frequency shifted by about +40 cm⁻¹, which would explain the band at 2170 cm⁻¹. The role of F²⁺ defects in determining the band at 2170 cm⁻¹ would also explain the MgO-thickness dependence of the IR data, Figure 3. In fact, on ultrathin films (1–5 ML), this center is expected to be unstable, to capture electrons from the support, and convert into F⁺ or F⁰ centers by electron tunneling through the thin dielectric barrier.⁷⁸ This effect is no longer present for thicker MgO films (>10 ML) where F²⁺ centers can form and exist. By increasing the Au coverage, larger clusters form and rapidly screen the presence of the positively charged defect, thus resulting in the shift of the 2170 cm⁻¹ feature to lower frequencies.

7. CONCLUSION

The results presented in this study provide a deeper insight into the initial nucleation of Au on the surface of MgO(001) thin films. Previous experimental and computational studies revealed the nature of neutral, single Au atoms on the regular MgO(001)surface,^{9,29} as well as the interaction of Au with artificially created defects, resulting in the formation of negatively charged Au species.⁸ Here, we show that the surface of an as-prepared MgO(001) thin film contains defects that lead to positive charging of vapor deposited Au. We believe that the formation of positively charged species in the initial phase of gold deposition on MgO(001)/Ag(100) films is related to (a) the formation of single Au^+ ions and tiny Au_n^+ clusters on edge sites due to a spontaneous electron transfer to electron trapping sites present at the surface (e.g., grain boundaries) and (b) to the direct role of specific defects (edge F^{2+} centers), in particular in nucleation and growth of some aggregates. Of course, due to the complexity of the system, we cannot exclude that other mechanisms take place. Although the abundance of these sites is expected to be limited, they might have a strong impact on the nucleation behavior of Au, especially if the properties of small Au clusters are investigated.¹⁰

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