When the Reporter Induces the Effect: Unusual IR spectra of CO on Au₁/MgO(001)/Mo(001)**

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Since Haruta's discovery that nanometer-sized gold particles supported on titanium dioxide act as effective catalysts for oxidation reactions,[1,2] a large number of experimental and theoretical studies has been dedicated to the origin of the enhanced chemical activity of nanosized gold (e.g. refs. [3–8]). Recently, Haruta et al. concluded that for high-activity Au catalysts, the contact structure between the Au particles and the support is more important than the mean particle size,[9] thus emphasizing the role of the oxide substrate in the chemistry of supported metal clusters. A key aspect in the activation of gold seems to be the charge transfer from the support to the metal. By studying size-selected Au₃ clusters on regular and defective MgO surfaces, Heiz and co-workers came to the conclusion that in the presence of surface defects the activity of Au₈ is considerably enhanced,[10] and proposed that oxygen vacancies (so-called color centers or F centers), an often addressed class of point defects on oxide surfaces,[11] efficiently transfer charge to the cluster thus increasing its chemical activity. A similar effect in terms of reactivity was found for negatively charged Au clusters in the gas-phase.[12] Even before this report it was clear that defects on the oxide support can have a crucial role in modifying the properties of a nanocluster and that it is important to quantify the extent of charge transfer to establish correlations with the chemical activity. However, the experimental determination of the

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charged state of an entity on a surface is challenging. It is mostly done by indirect measurements, for example photoelectron spectroscopy,[13] thus care must be taken when interpreting the results. For instance, for Au atoms adsorbed on regular terrace sites of MgO films, the isotropic hyperfine coupling constant as measured by electron paramagnetic resonance (EPR) spectroscopy is reduced by about 50% as compared to the gas phase.[14] This reduction is not due to charge transfer but to polarization and hybridization effects, in fact, gold atoms bound to the non-defective MgO surface are essentially neutral as shown by theoretical calculations.[6,14,15]

The IR stretching frequency of CO adsorbed to metal atoms or particles is a common way to probe the electron density of the metal centers.[16,17] For CO on metal surfaces the CO stretching frequency (2143 cm⁻¹ in the gas-phase) is shifted to 1950–2140 cm⁻¹ when CO is adsorbed on one metal atom (on-top position), to 1800–2000 cm⁻¹ for CO bridging two metal sites, and to 1700–1900 cm⁻¹ for CO on threefold-hollow sites (see e.g. ref. [18]). This trend correlates with the number of metal atoms interacting with CO, hence with the extent of back-donation into the CO 2π* antibonding orbital. It is, however, important to note that assignments based on this scheme have led to misinterpretations as shown by photoelectron diffraction experiments.[19] A large body of data exists for CO adsorbed on Au particles on oxides, and, depending on the nature of the support and on the size of the particles, the stretching frequency is always between 2000 and 2170 cm⁻¹.[20–23] Signals below 2090 cm⁻¹ were assigned to negatively charged Au nanoclusters nucleated at defect sites, while values between 2140 and 2100 cm⁻¹ are typical of neutral Au clusters. For isolated, supported, transition-metal atoms, such as Pd bound to regular terrace MgO sites, CO stretching frequencies above 2000 cm⁻¹ were found. Very low frequencies, in the range 1800–1900 cm⁻¹, are more typical of [MCO]⁻ transition-metal complexes in the gas phase.[17,24]

Herein we will compare the CO stretching frequencies of CO bound to Au atoms deposited on regular terrace sites with those of CO attached to Au atoms nucleated at color centers on MgO surfaces. The first situation was realized by deposition of 0.0125 monolayer (ML) Au at 30 K onto a well annealed, 20 ML thick MgO(001) film which was shown to be free of color centers.[25] From EPR spectroscopy it was unambiguously shown that under these conditions Au atoms are nucleated on the terrace sites of the MgO film. This situation is in agreement with STM results on MgO(001) films grown on Ag(001),[14] which exhibit similar surface morphology and adsorption sites compared to films appropriately prepared on Mo surfaces.[26–29] Saturation coverage of CO was dosed at 30 K and the system was annealed to 63 K to desorb CO bound to the terrace sites of MgO (see the typical IR band of low-coordinate sites of MgO at 2163 cm⁻¹, Figure 1).[28] Under these conditions two bands at 2122 and 1852 cm⁻¹ corresponding to Au species are observed (see Figure 1a). From the coverage dependence of the line intensities in combination with the EPR results it is readily deduced that the 1852 cm⁻¹ band is due to CO bound to Au atoms while the 2122 cm⁻¹ band is due to CO adsorbed on small Au clusters.[14] In addition, isotope mixing experiments (gray trace in
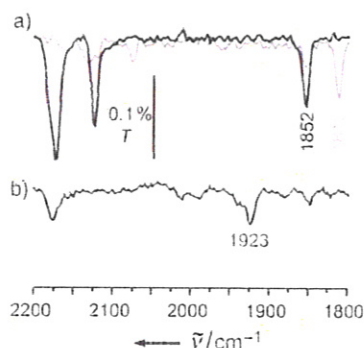
Figure 1. IR spectra of Au/CO complexes adsorbed on a) an annealed MgO(001) film (black trace 100% ^{12}CO; gray trace 25% ^{12}CO, 75% ^{13}CO) and b) an electron bombarded MgO(001) film (^{12}CO); T = transmission.

Figure 1a) show unambiguously the presence of a one-to-one complex of CO and Au. The band at 1852 cm^{-1} is an unusually low frequency for CO adsorbed on supported metal atoms. It is red-shifted by 291 cm^{-1} with respect to gas-phase CO, and is much below any other reported value of the CO stretching frequency on supported Au.[20–23] With respect to a matrix-isolated Au/CO complex, $\tilde{\nu}_e(CO) = 2039$ cm^{-1},[30] the line is shifted by about 180 cm^{-1}. This result indicates that the MgO terrace sites have a huge effect on the properties of supported Au/CO complexes.

This situation is compared to Au adsorbed on a film containing surface color centers. The color centers are produced by electron bombardment of films prepared according to the recipe used for the above experiment. The color centers are predominately located at steps, corners, and kinks, but almost never on terraces as previously shown by STM as well as by EPR spectroscopy.[25] 0.0025 ML Au was deposited at 30 K on these films and EPR as well as STM reveal a nucleation of Au atoms at the color centers as well as a small fraction on regular terrace sites of the MgO facets.[31] The IR spectrum shown in Figure 1b was taken after saturating the surface with CO at 30 K and subsequent annealing to 75 K to desorb most of the CO bound to MgO sites. In comparison to the spectrum in Figure 1a additional bands are found at 1923 cm^{-1} and between 1980 and 2020 cm^{-1}. The band at 1852 cm^{-1} is strongly diminished indicating that only a minority of Au atoms remains on the terrace sites, and the band at 2120 cm^{-1} is completely absent for this preparation condition. From coverage-dependent measurements the band at 1923 cm^{-1} can be attributed to Au/CO complexes formed on neutral (F^0) or singly charged (F$^+$) color centers while the blue-shifted signal, which extents up to 2070 cm^{-1} depending on the preparation condition (Au coverage, deposition temperature, annealing, etc), belongs to CO adsorbed to small Au clusters nucleated at color centers.[31]

The observed blue shift of the CO stretching frequency of the CO/Au/color-center complex as compared to gold adsorbed on

regular terrace sites is surprising because the color centers are usually considered the stronger Lewis bases and the frequency of CO adsorbed on these defects is normally red-shifted compared to the same atoms bound to oxide anions.[16]

This surprising result was investigated in a series of theoretical calculations. The methods used range from periodic supercell density functional theory (DFT) calculations (plane wave basis sets, PW91 exchange-correlation functional as implemented in the VASP code[32]) to embedded cluster DFT calculations (atomic orbital basis sets, PW91 or B3LYP exchange-correlation functionals), to coupled cluster calculations at the CCSD(T) level (Gaussian 03;[33] for full details of all the calculations see the Supporting Information). The reason for using so many different methods, and in particular the computationally intensive CCSD(T), is that pure DFT functionals tend to give too low an energy for the CO 2π* orbital and to overestimate the metal-to-CO back-donation (which greatly influences the CO stretching frequency), a problem partially resolved by the use of hybrid functionals. Figure 2a shows the optimized geometry of the
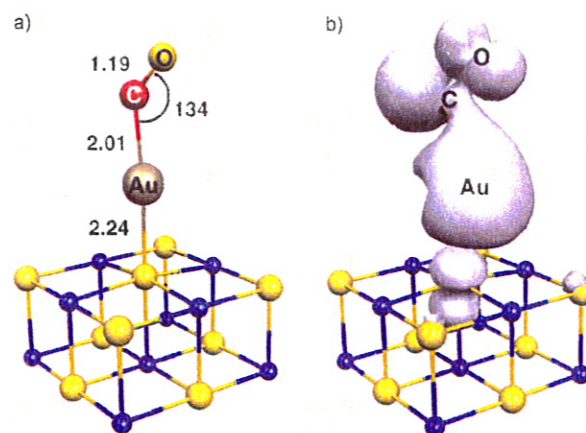

Figure 2. a) Optimal geometry and b) spin-density plot of an Au/CO complex adsorbed on-top of an oxygen anion on a MgO(001) terrace (embedded cluster calculations; distances [Å], angle [°]).

Au/CO complex on a five-coordinate oxygen anion (O$_{5c}$) of the MgO surface. The molecule is tilted (the Au-C-O angle is approximately 134°) and has an elongated C–O bond. As shown in Table 1, both the binding geometry and the CO stretching frequency vary little with the method used. All models predict large red-shifts of $\tilde{\nu}(CO)$, between 275 and 301 cm^{-1}. At the highest level of theory, CCSD(T), $\tilde{\nu}(CO)$ is 1863 cm^{-1} and $\Delta\tilde{\nu} = 298$ cm^{-1} (with respect to the gas phase);

Table 1: Properties of Au/CO complex formed at the (001) surface of MgO obtained with various computational methods.

Model	Method	α(Au-C-O) [°]	r_e(C–O) [Å]	Δr_e(C-O) [Å]	$\tilde{\nu}(CO)$ [cm^{-1}]	$\Delta\tilde{\nu}^{[a]}$ [cm^{-1}]
supercell	DFT(PW91)	137	1.182	0.040	1848	−281
O$_3$Mg$_9$	DFT(PW91)	134	1.187	0.049	1854	−275
O$_3$Mg$_9$	DFT(B3LYP)	132	1.175	0.037	1910	−301
OMg$_5$	CCSD(T)	136	1.181	0.044	1863	−298

[a] With respect to free CO. r_e = Equilibrium bond length.

these values are in nearly quantitative agreement with experiment.

The large red-shift of the CO stretching frequency reflects a substantial charge transfer from Au to CO. The unpaired electron is about 10% on the surface O_{5c} ion, 30% on Au, and 60% on CO, see Figure 2b; in the surface complex the $2\pi^*$ orbital of CO becomes occupied thus resulting in a large vibrational shift. The Lewis acidic CO promotes charge flow from the O^{2-} ion to Au (an atom with high electron affinity, 2.3 eV) and from Au to CO. The occurrence of a net charge transfer is confirmed by the fact that a $[AuCO]^-$ gas-phase complex, computed at the B3LYP level, has a $\bar{\nu}(CO)$ red-shifted by 271 cm^{-1} compared to free CO. Note that the tilt of the CO molecule is very unusual for CO bound to metals. It is also a direct consequence of the charge transfer. The molecule NO, which is valence isoelectronic with CO^-, also binds to metals by forming nonlinear bonds (e.g. refs. [34,35]).

The net charge transfer, however, occurs only after CO adsorption; the gold atom adsorbed to a terrace site of MgO is neutral[6,14,15] This situation means that the CO stretching frequency measures a final-state effect and cannot be considered as a reporter of the properties of the Au/MgO complex as usually assumed.

The occurrence of a large charge transfer on the defect-free MgO surface explains why no further red-shift is observed for the Au/CO complex bound to color centers; experimentally a blue shift of approximately 60 cm^{-1} is observed with respect to the terrace sites. This result has been modeled by adsorbing an Au/CO complex on an F^0 center on a MgO terrace (in this respect the calculation is not fully representative of the experiment as F centers are located on steps and corners). Periodic supercell calculations as used above show a linear complex with $\bar{\nu}(CO) = 1876$ cm^{-1}, which is 28 cm^{-1} higher than for the same complex formed on a terrace, fully consistent with the experimental results. The electron-withdrawing ability of the Au/CO complex is so strong that it can withdraw an electron more easily from the five-coordinate oxygen anion on an MgO terrace than from an F^0 center.

In conclusion, we report on the large influence of CO on the properties of Au atoms adsorbed on MgO terrace sites. The atoms adsorbed to O_{5c} anions of the MgO terraces are neutral, but change their chemical nature dramatically by simple adsorption of the Lewis acid CO. This adsorption induces a net charge transfer from the surface to the Au/CO complex, leading to a dramatic red-shift of the CO stretching frequency. In fact, the charge transfer is so large that the Au/CO complex adsorbed to electron-rich defects such as color centers shows a blue-shifted band with respect to the complex on regular terrace sites. It is possible that other π ligands can induce similar effects and thus may result in a modified chemical activity. Finally, it is important to stress that the CO stretching frequency does not serve as a reporter of the nature of the adsorbed Au atoms; CO induces significant chemical modifications of the supported gold species. Thus, care is required in the interpretation of vibrational spectra of CO.

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