Supporting Information

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When the reporter induces the effect:
CO on Au₁/MgO(100)/Mo(100) *

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Experimental details
Experiments were performed on 20 ML thick MgO(001) films grown on a Mo(001). The Mo substrate was cleaned by oxidation with O₂ at 1500 K and subsequent flashes to 2300 K. The MgO films were prepared by deposition of Mg in an oxygen ambient (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. Color centers were produced by electrons with an energy of 100 V extracted from a filament. Infrared 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. †

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Computational details

The supercell calculations are based on spin polarized DFT using the Vienna Ab initio simulation program (VASP)\(^2\) with a plane waves basis set, a projector augmented wave method (PAW)\(^3\) for the treatment of core electrons and a kinetic energy cutoff of 400 eV. The generalized gradient approximation (GGA) has been chosen to represent the exchange-correlation potential in the formulation of Perdew and Wang (PW91).\(^4\) The MgO(100) surface has been modeled by a three-layers slab and 4x4 supercells containing 96 atoms. The upper two layers are relaxed in the geometry optimization while the atoms in the third layer are frozen in their lattice positions (Mg-O distance fixed at the optimized bulk value, 2.126 Å, to be compared to the experimental value of 2.104 Å\(^5\)). The atomic structure is optimized at Γ point until all atomic forces are less than 0.01 eV/Å. Au adsorbates are situated on one side of the slab with 12 Å of vacuum separation.

In the cluster model calculations the MgO surface was simulated by O\(_9\)Mg\(_9\) clusters embedded in about 3000 point charges ±2 (PC) which reproduce the Madelung potential at the adsorption site. To avoid the artificial polarization of the O\(^2-\) anions at the cluster border, the positive PCs at the interface have been replaced by effective core potential (ECPs) Mg* ions with no basis functions.\(^6\) DFT calculations have been carried out using the PW91 and the B3LYP hybrid exchange-correlation functionals.\(^7,8\) The atomic orbital basis sets used are: 6-31+G*\(^9,10\) for O atoms of the cluster, 6-31G*\(^9\) for the Mg atoms of the surface layer and for the CO molecule, and a 6-31G\(^9\) for the Mg atoms of the second layer. The Au atom has been described with a 19-valence electron relativistic ECP using the LANL2DZ basis set.\(^6\) We have optimized the geometry of the AuCO complex and of the surface O atom in direct contact with the gold atom. Vibrational frequencies have been computed by determining the second derivatives of the total energy with respect to the internal coordinates.

A last set of calculations has been carried out at the CCSD(T) level using the following large basis sets: uncontracted 5s6p3d2f on Au;\(^6\) Alrichs TZV+2d on C and O.\(^11\) Here, due the high computational cost, a minimum cluster model has been used to represent the surface. This consists
of a OMg₅* cluster embedded in PCs. The validity of this model has been tested by performing a
B3LYP calculation using the same OMg₅* cluster and basis set adopted for the CCSD(T) case, and
comparing the results with larger clusters or supercell calculations. The differences due to the
limited cluster size are very minor. The Au and AuCO adsorption properties are correctly
reproduced even with the minimum OMg₅* model. Attempts to perform the CCSD(T) geometry
optimization with analytical gradients failed for technical reasons, mainly due to the very large size
of the calculation. Therefore, the geometry optimization and the evaluation of the CO frequency has
been done by constructing a sufficiently dense grid. In particular we optimized separately r(O₅c-
Au), r(Au-C), α(Au-C-O), and r(C-O), in this sequence. The resulting structure is very similar to
that obtained with other approaches, see Table 1. Particular care has been used in the evaluation of
the vibrational frequency at the CCSD(T) level. The procedure used to fit the potential energy curve
using a polinomia of fourth or higher degree provides virtually the same values obtained based on
second derivatives. The cluster model calculations have been performed using the Gaussian-03
program package.¹²
References