



Supporting Information

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Experimental Section

The pure Au- and mixed Au/Sr-clusters are generated with a high-frequency laser evaporation source, producing high currents of singly positively charged clusters. In this setup the output (355nm) of a Nd:Yag-laser is focused on a rotating Au-, AuSr-target disk. A helium pulse thermalizes the produced metal plasma and the clusters are grown by nucleation when the helium-metal vapor undergoes supersonic expansion. Subsequently they are size-selected by a quadrupole mass filter and deposited onto a magnesium oxide thin film. The total energy of the deposition process is composed of the kinetic energy of the cluster ($E_{\text{kin}} < 0.2 \text{ eV/atom}$), the chemical binding energy between the cluster and the MgO surface, as well as a negligible Coulomb interaction of the incoming cluster ion and its induced polarization charge on the oxide film surface. Consequently, as the kinetic energies of the impinging clusters correspond to soft-landing conditions ($E_{\text{kin}} \leq 1 \text{ eV}$) and as the total energy gained upon deposition is smaller than the binding energy of the investigated clusters, fragmentation of the clusters is excluded. Upon impact the cluster ions are neutralized by charge tunneling through the thin MgO films. We deposited only 0.15 % of a monolayer clusters ($1 \text{ ML} = 2.25 \times 10^{15} \text{ clusters/cm}^2$) at 90 K in order to land them isolated on the surface and to prevent agglomeration on the MgO-films. In Monte-Carlo simulation the relative number of isolated clusters was estimated to be higher than 95% after landing the clusters on the surface and migration to the trapping centers.

The support is prepared *in situ* for each experiment by epitaxially growing thin films on a Mo(100) surface by evaporating magnesium in a $^{16}\text{O}_2$ background. By changing the preparation method, e.g. the Mg evaporation rate and the oxygen background, films with different defect densities can be prepared. In this way two kinds of films are prepared: defect-poor (Mg evaporation rate: 0.3-0.5 *ML/min*, O_2 background: $5 \cdot 10^{-7} \text{ Torr}$) and defect-rich (Mg evaporation rate: 2-5 *ML/min*, O_2 background: 10^6 Torr) films. Both films are annealed to 1200K and 840 K during 10 minutes, respectively. Auger electron spectroscopy (AES) measurements show a one-to-one stoichiometry for magnesium and oxygen and the absence of any impurity. Typical thicknesses are about 10 monolayers, as determined by AES peak intensities and by X-ray photoemission (XPS), using the intensity attenuation of the Mo 3d core level with increasing film coverage. Both films have also been studied by electron energy loss spectroscopy. In contrast to defect-poor films, which are characterized by a loss at about 6 eV in the EEL spectra (in good agreement with previous studies on MgO(100) single crystals), the EEL spectra of defect-rich films exhibit characteristic losses between 1 and 4 eV, lying within the MgO band gap. Similar loss structures have been observed before, and according to first-principle calculations using large cluster models, they have been attributed to transitions, characteristic for neutral surface F centers in various coordinations on flat terraces, at steps and at kinks. The density of these oxygen vacancies is estimated to be larger than $5 \times 10^{13} / \text{cm}^2$. In all the experiments presented here the clusters were deposited on defect-rich films, it is however worth noting, that Au₈ on defect-poor films show no reactivity above 200 K.

To obtain identical conditions for the study of the chemical reactivity of the clusters we first exposed the prepared model system by a calibrated molecular beam doser at 90 K to an average of 20 $^{18}\text{O}_2$ molecules per Au/Sr atom. This results in saturation coverages on the clusters, as evidenced by the desorption of physisorbed species from the oxide surface. Subsequently, we exposed the system to the same amount of $^{13}\text{C}^{16}\text{O}$. This is crucial, as it is well known from single crystal studies that the initial amount of oxygen and CO on the surface and the ratio of these molecules during oxidation may influence the reactivity. Isotopically labeled $^{18}\text{O}_2$ were used to disentangle the CO_2 production on the cluster surface from an eventual catalytic oxidation of CO involving MgO substrate oxygen atoms. In a Temperature Programmed Reaction (TPR) experiment we then detected the differently labeled CO_2 molecules, which are produced on the surface of the clusters. The chemical action is determined by integrating the TPR signal of the CO_2 molecule and normalizing to the number of deposited clusters. For this procedure the mass spectrometer has been calibrated using the known amount of desorbing CO from a Mo(100) single crystal and taking into account its different sensibility for CO and CO_2 . The number of deposited clusters was obtained by integrating the measured ion current on the substrate over the deposition time.

Theoretical Section

The active part of the model catalyst (comprised of the vicinity of the F-center of the MgO(100) surface, the adsorbed metal cluster, and the reactant molecules adsorbed on the cluster) is described via Born-Oppenheimer local-spin-density-functional simulations (see ref. 18) employing self-consistent generalized gradient corrections.^[19] The Mg($3s^2$), O($2s^2 2p^4$), C($2s^2 2p^2$), and Au($5d^{10} 6s^1$) valence electrons were described by *ab initio* pseudopotentials (20) with a scalar-relativistic treatment for gold.^[21,22] The Kohn-Sham electronic states are expanded in a plane-wave basis set with a kinetic energy cutoff of 62 Ry. The MgO surface with the F-center is modeled by a two-layer *ab initio* cluster $\text{Mg}_{13}\text{O}_{12}$, embedded in a point-charge lattice of about 2000 alternating charges (with nominal charges of +2 and -2 of Mg and O ions, respectively; those positive point charges that are nearest neighbors to the periphery O atoms of the $\text{Mg}_{13}\text{O}_{12}$ cluster have however been replaced by "empty" Mg pseudopotentials in order to prevent unphysical polarization effects) to model the long-range ionic Coulomb field. The lattice parameter of the embedding part is fixed to the experimental lattice constant (4.21 Å) of bulk MgO.

The relaxed configurations of the bare adsorbed clusters, and the clusters with O_2 , have been obtained by a spatial- and spin-unconstrained gradient optimization method; in the relaxation process the substrate Mg^{2+} ions which are nearest neighbors to the FC, the metal cluster, and the adsorbed O_2 molecule are treated dynamically. The metal clusters were initially placed about 4 Å above the surface plane and the system was relaxed to the nearest energy minimum; this procedure was repeated several times in order to explore the isomer space of the adsorbed clusters. In addition, the stability of the lowest energy structures was checked by short-time (a few ps) *ab initio* molecular dynamics simulations. It is worth noting that while it was recently found that gas-phase gold clusters (particularly anions) favor planar (2D) optimal structures up to sizes beyond 10 atoms (see ref. 22 and ref. 15 therein), the strong attraction by the FC always anchors one gold atom close to it and distorts the planar structures; in fact, the $\text{Au}_8/\text{MgO}(\text{FC})$ catalysts shown in Figures 2A and 2B correspond to low-energy 3D isomers of Au_8 in the gas phase.