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Catalytic activity of gold nanoclusters supported by cerium oxide: interplay between cluster reactivity, size, and interface charge transfer revealed by DFT calculations STEFANO FABRIS, CNR DEMOCRITOS and SISSA, Trieste, Italy, MATTEO FARNESI CAMELLONE, CNR-DEMOCRITOS and SISSA — The parameters controlling the catalytic activity of oxide-supported Au atoms and clusters are studied by means of density functional theory calculations. $CeO_2(111)$ surfaces containing positively charged Au ions, either as supported Au^+ or as substitutional Au^{3+} ions, are shown to activate molecular CO and to catalyze its oxidation to CO_2 via participation of lattice O. For the Au^+ adatoms, the limiting rate is determined by the adsorbate spillover. The reaction proceeds with CO oxidation via O vacancy formation. These vacancies readily attract the Au^+ adatoms, turn them into negatively charged $Au^{\delta-}$ adspecies that prevent further CO adsorption, thus deactivating the catalyst. The reactivity of gold nanoparticles nucleated at O vacancies can be recovered for cluster sizes as small as Au_2. Substitutional Au3+ ions dispersed into the ceria lattice can instead sustain a full catalytic cycle maintaining their charge state and activity along the reaction process. The interplay between the reversible Ce^{4+}/Ce^{3+} and Au^{3+}/Au^+ redox couples underpins the high catalytic activity of dispersed Au atoms into the ceria substrate. Ab-initio surface thermodynamics is used to investigate the stability of different solid solutions and to predict more reactive catalysts.

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