

## **Nano is different: Catalysis by nanosized gold and confinement effect in siloxane nanocages**



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Unusual properties often develop when the dimensions of materials are in the nanoscale. Two systems exemplifying dramatic changes in chemical properties as a result of size reduction to the nanoscale, are investigated. The first one is the Au/TiO<sub>2</sub> catalyst used for low temperature oxidation of CO. The second exploits a novel siloxane nanocage (~2nm) recently developed in our group.

While bulk gold is chemically inert, supported gold nanoparticles are remarkably active catalysts for a variety of reactions, including the oxidation of carbon monoxide at low temperature. To identify the origin of this unusual activity, it is necessary to understand the nature of the active site as well as the reaction mechanism. Our approach is to construct a structure activity relationship by monitoring the structural changes during the activation of an inactive catalyst. In addition, the reaction pathway was investigated by identifying the surface species directly involved in the reaction and quantifying their transformation rates under transient and steady-state conditions. Combining in-situ XANES, EXAFS and FTIR with microreactor studies, it is demonstrated that metallic nanosized gold is a necessary component of the active site. Its role is to activate CO, which subsequently oxidizes at the catalytic centers. Information on the nature of the catalytic centers is obtained through the identification of adsorbed hydroxycarbonyl species, via a combination of in-situ FTIR, <sup>18</sup>O<sub>2</sub> isotopic exchange and mass spectrometry. All together, this study suggests that nanosized gold provides the necessary unsaturated sites for CO activation and also generates a higher density of active sites for reaction, as compared to larger particles.

The case of siloxane nanocages provide additional evidence of dramatic changes in chemical properties, occurring upon confinement at the nanoscale. The spherical nanocages (~2nm) consist of an atomic layer thick siloxane shell with propylamine groups tethered to its interior. Diffusion of molecules to and from the nanocage interior, occurs through ~ 5Å openings present on the nanocage surface. The properties of the nanocage as a ligand for Au<sup>3+</sup> were investigated via a combination of XANES, EXAFS, UV-VIS and cyclic voltammetry. A remarkable reduction on the Brønsted basicity of propylamine groups within the nanocage, consequence of their nanoconfinement, was observed (the protonation constant decreased by five orders of magnitude). As a result, the nanocage complexed Au<sup>3+</sup> at a pH five units lower than an equivalent amine free in solution. Under the proper conditions, it also acted as a chelating ligand forming multiple Au-N bonds per gold. This implies a high degree of flexibility of the propylamine groups affixed within the nanocage. Based on these observations, the potential of this material both as a catalyst and as a nanoreactor is discussed.



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