Monolayer Protected Gold Nanoparticles on Ceria for an Efficient CO Oxidation Catalyst

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Since the pioneering work of Haruta et al.[1] in 1987 it has been demonstrated that gold nanoparticles (AuNPs) on appropriate supports are excellent catalysts to promote oxidation processes.[2] Critical features are the size and the oxidation state of the gold atoms of the clusters. It is well accepted that only gold particles with diameter lower than ∼5 nm are catalytically active. The crucial point is the development of simple strategies for preparing catalysts containing clusters small enough to maximize the number of metal atoms interacting with the support, in order to increase their reactivity and the catalyst stability. No general consensus exists on the oxidation state of the gold atoms at the active site. In fact, small Au clusters, cationic gold atoms at different oxidation states [Au(I), Au(III), Au($\delta+$)], and gold atoms at the supporting interface have been claimed to be responsible for oxidation reactions.[3]

The control of the NP size in the catalyst has been attempted using different methodologies such as chemical vapor deposition (CVD),[4] reduction of Au(III) precursors in the presence of the support,[5] and more recently, preformation of AuNPs and their impregnation[6] or anchorage to selected support.[7] The latter presents the advantage to tune the particle size in a precise manner by choosing appropriate reaction conditions. Herein we report the use of monolayer protected AuNPs supported on ceria as precursors of active and thermally stable catalysts for hydrogen purification reactions.

Monolayer protected AuNPs have been prepared following the procedure of Brust et al.[8] using $HAuCl_4$ as the precursor, dodecanethiol ($HSC_{12}H_{25}$) as the ligand, and $NaBH_4$ as the reducing agent. A 1:2 Au/RSH molar ratio and reduction at 0 °C have been used to obtain NP with an average diameter of 1.9 nm. The NPs have been purified by gel permeation chromatography on Sephadex LH 60 to remove unbound thiols as demonstrated by proton NMR spectra. The composition of these AuNPs was determined by transmission electron microscopy (TEM) and thermogravimetric analysis (TGA; Supporting Information, Figure S1). CeO_2 has been prepared by precipitation from $Ce(NO_3)_3$ solution in NH_4-OH and calcined at 700 °C for 5 h to obtain a thermally stable support under the catalytic conditions. This material has been impregnated with a solution of AuNP in ethyl acetate to obtain 1% metal loading. After removal of the solvent the material has been dried overnight at 100 °C and then calcined at 250 °C for 5 h. This treatment guarantees the complete removal of the organic monolayer as suggested by TGA of the unsupported NP and by temperature-programmed oxidation of the material. The catalyst shows a BET surface area of 44 m^2/g, a total pore volume of 0.13 mL/g, and an average pore diameter of 11 nm. The X-ray diffraction pattern indicates a cubic fluorite structure for CeO_2. Gold diffraction peaks were not observed because of the low metal loading. Temperature programmed reduction experiments (Supporting Information, Figure S2) indicate that the presence of AuNPs strongly promotes CeO_2 reduction. This suggests the occurrence of spillover phenomena involving either hydrogen activated on the metal phase or lattice CeO_2 oxygen. TEM and extended X-ray absorption fine structure (EXAFS) analysis have been used to fully characterize the material for complementary observations. The similar contrast of Au and CeO_2 particles makes identifying the gold crystals among the ceria ones difficult and observing a significative number of clusters to determine a particle size distribution impossible. Nevertheless, by means of energy dispersive X-ray spectroscopy (EDX) a number of gold particles of 3−4 nm could be located. Representative TEM images of AuNPs on the calcined catalyst shown in Figure 1 suggest a cubic octahedral arrangement. No significant modification of the average dimensions of the AuNPs was observed after CO preferential oxidation (PROX) activity (Figure 1).

X-ray absorption near-edge structure spectra of the catalyst at the Au L_{III} edge (Supporting Information, Figure S3) indicate the presence of Au(0) whereas after catalytic performance traces of Au oxide or hydroxide can be suggested by the shoulder-like shape in the white-line region corresponding to the 2p 5d transitions characteristic of those species (see Supporting Information). The results of the

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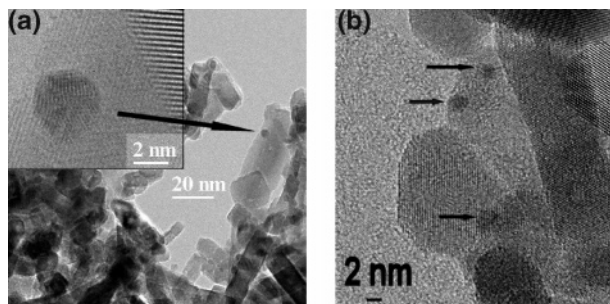
Figure 1. Representative TEM images of AuNP on ceria (a) after calcination at 250 °C and (b) after PROX activity up to 200 °C (1% CO, 1% O_2, 50% H_2, 20% CO_2, 5% H_2O, 8 h, balance He).
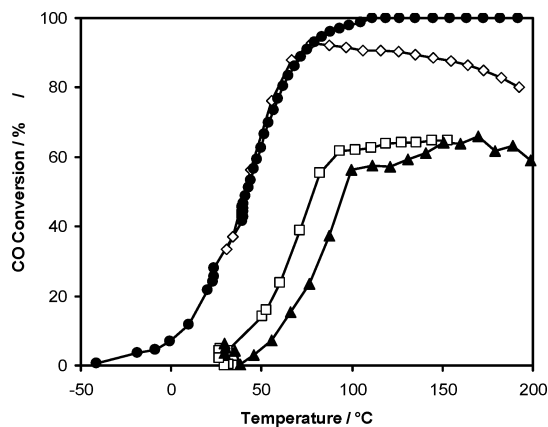
Figure 2. CO conversion over 1% Au/CeO$_2$. Conditions: 1% CO + 1% O_2 (●); 1% CO + 1% O_2 + 50% H_2 (◇); 1% CO + 1% O_2 + 50% H_2 + 20% CO_2 (□), and 1% CO + 1% O_2 + 50% H_2 + 20% CO_2 + 5% H_2O (▲) (balance He). 40 mg catalyst; flow rate 50 mL/min; heating rate 1 °C/min.

Table 1. Best Structural Parameters from the Fits of EXAFS Signal of 1% Au/CeO$_2$ and Estimated Metal Particle Diameters

sample	shell	N	σ_{DW} (Å)	R (Å)	d (Å)
calcined	O	2.0(3)	0.093(7)	2.560(3)	40
	Au	9.7(4)	0.091(1)	2.832(8)	
PROX aged	O	1.8(5)	0.081(2)	2.49(1)	24
	Au	7.4(6)	0.078(1)	2.836(8)	

EXAFS fits, calculated with FEFF8.1 theoretical phases and amplitude functions, are reported in Table 1. The Au−Au coordination numbers and the distances shorter than in the bulk metallic Au confirm the presence of small metal particles with average diameters of 2−4 nm. The higher Debye−Waller factor of the calcined sample suggests the presence of a relevant structural or morphological disorder when the metal particles are formed by thiols removal. The Au−O coordination number of about 2, with atoms at longer distances than in the Au oxide and hydroxide systems, indicates a relevant contribution from the oxygen atoms of surface ceria.

The catalytic performance of our Au/CeO$_2$ was tested for CO oxidation and PROX in the presence of H_2, CO_2, and H_2O (Figure 2). Notably, these are the main components of the gas mixtures obtained from H_2 production reactions, which requires purification from CO. As it is well-known, CO oxidation occurs below room temperature on highly dispersed gold nanoclusters. The presence of hydrogen reduces the selectivity of the catalyst only above 75 °C,

where a small fraction of hydrogen reacts with oxygen to form water. This is a significant observation since the ability of the catalyst to oxidize CO more readily than H_2 is a fundamental prerequisite for PROX activity. CO_2 addition leads both to a high-temperature shift of about 50 °C in the light-off temperature and a drastic decrease of the maximum CO conversion. A further deactivation is observed after addition of water. The major effect is the suppression of the low temperature activity. This fact can be interpreted as a strong competitive adsorption of water on the surface of the catalyst.

Catalyst stability has been investigated under various conditions. Minor deactivation was observed during CO oxidation in run-up experiments up to 300 °C, while activity drops after aging at 400 °C (Supporting Information, Figure S5). Deactivation of the catalysts can occur either through sintering of the AuNPs or buildup of carbonate species which block active sites.[9] We observed that the activity can be only partially restored by oxidation at 400 °C, suggesting that gold particle growth may contribute to the decrease of the activity. Isothermal CO PROX (1% CO, 1% O_2, 70% H_2, balance He) at various temperatures between 80 and 150 °C (Supporting Information, Figure S6) indicates good stability for up to 8 h. Addition of CO_2 leads to catalyst deactivation (Supporting Information, Figure S7), which can be reasonably associated to carbonate deposition. Indeed, some gradual recovery was observed during isothermal reaction at 200 °C (Supporting Information, Figure S8). Finally, in the simultaneous presence of CO_2 and H_2O (Supporting Information, Figure S9), the catalyst becomes progressively less active, to a lower extent with respect to the case without H_2O. This is consistent with the reported role of H_2O in preventing carbonate accumulation. Notably, the EXAFS analysis suggests the occurrence of some AuNPs disgregation processes during the more severe PROX aging conditions. While these phenomena are well-documented in the case of Rh/Al$_2$O$_3$,[10] it has not previously been observed for AuNP and requires further investigation.

In summary, the results reported highlight the great potential of the use of size-tunable preformed AuNPs for the preparation of active catalysts. The use of preformed metal clusters and the mild reaction conditions are not favorable to the formation of ionic Au species. The experimental results suggest that the catalytic sites for CO oxidation are the metal NPs and not ionic Au species.

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