Gold Catalysts

Nanocrystalline CeO_2 Increases the Activity of Au for CO Oxidation by Two Orders of Magnitude **

Silvio Carrettin, Patricia Concepción, Avelino Corma, José M. López Nieto, and Victor F. Puntes*

More than twenty years ago it was shown that gold, despite its limited adsorption properties, catalyzes reactions such as CO oxidation,[1] alkene hydrogenation,[2] and ethylene hydrochlorination.[3] However, strong interest in gold for catalysis emerged only recently owing to the seminal work of Haruta et al.[4] These authors showed that when gold is deposited on a metal–oxide support by a coprecipitation method, the metal exhibits high catalytic activity for CO oxidation at low temperatures. Moreover, they found that the distinctive behavior of the gold catalysts was due to the presence of nanosized Au particles.

In a recent review, Bond and Thompson[5] showed that, in the case of Au-supported catalysts, factors such as Au particle size, preparation method, pretreatment conditions, and choice of the support play an important role in the CO oxidation activity of the final catalyst. Indeed, when nanoparticles of Au are deposited on TiO_2,[4b,6a] Co_3O_4,[4b,6b] ZnO,[7] Fe_2O_3,[4b,6a] or MgO,[8] the catalysts are particularly active for the above-mentioned reaction. In contrast, nanoparticles of Au were much less active when other supports were used.[5,9] These results suggest that a synergetic effect between the metal oxide support and Au may exist at the interface such that the metal oxide does not simply act as an inert carrier, but intervenes in the catalytic process.

We thought that if gold nanoparticles on the order of 3 to 5 nm were essential for the catalysis (owing to the presence of a large number of surface gold atoms with properties different from those of bulk gold) and if a synergetic mechanism occurs at the gold and metal oxide interface, the characteristics of the metal oxide surface should be of paramount importance. In other words, if the support could be prepared in the form of discrete, well-defined nanoparticles, this should have an influence on the surface electronic properties and consequently on the gold–support interaction.

Cerium oxide has been reported to be inadequate for preparing active gold catalysts for CO oxidation at low temperatures.[5] Nonetheless, this oxide support appeared to be interesting for water-gas shift reactions.[10] It has been reported[11,12] that coprecipitation of Au and CeO_2 gave CO oxidation catalysts that are active at 100 °C or higher, whereas Au on TiO_2[4b,6] or Fe_2O_3[4b,6] is already active below 0 °C. It was therefore clear to us that CeO_2 would be a good candidate to test if its impact on the catalytic activity of gold could be improved by preparing nanocrystals of CeO_2 within a very narrow particle size distribution.

The X-ray diffraction pattern of the support shows that CeO_2 is crystalline with the characteristic diffractogram of fluorite (see the Supporting Information). The CeO_2 particle size was determined from the half-height width of the (111) signal by using the Scherrer equation, and a mean ceria particle size of 3.3 nm was calculated. This value is much smaller than that previously reported for precipitated CeO_2 (15.9 nm).[13] Transmission electron microscopy (TEM) showed that the support is made up of very regular nanoparticles of about 4 nm. Owing to the small size of the nanoparticles, the BET (Brunner–Emmett–Teller) surface area of the support is very high (180 m^2g^{-1}).

Figure 1 shows the TEM analysis of the Au/CeO_2 catalyst. In the image on the right, the Au particles are bright white whereas the rest of the sample appears dark. The observed Au nanoparticles have diameters as low as 1 nm with a mean diameter of approximately 4 nm (see the Supporting Information); they are not agglomerated and are located on the CeO_2 support. The lattice spacing of the crystalline nanoparticles are observed in the HREM (high-resolution electron microscopy) images (see the Supporting Information). To determine the lattice spacing, an inversion of the radius of the dots or rings which appear in the fast Fourier transforms (FFT) of the image was carried out. Thus, the following crystal structures were observed: fcc Au, Cerianite CeO_2, and monoclinic Ce_6O_{11}. The presence of partially reduced CeO_2 could be due to electron irradiation under the high vacuum of the microscope. However, other samples and the analysis do not consistently show the presence of Ce_6O_{11} as is the case here, suggesting the lower degree of oxidation or strong tendency of the synthesized ceria to be reduced. We also

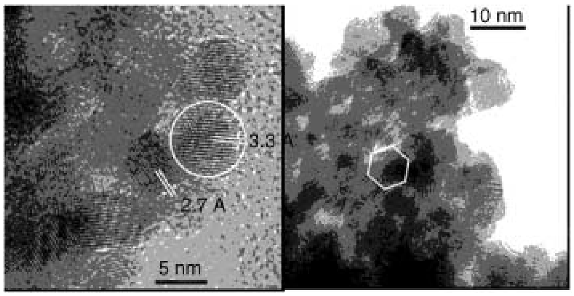

Figure 1. A high-resolution TEM image of the 2.8 %Au/CeO_2 sample. Left: the white lines correspond to the (202) Ce_6O_{11} (3.3 Å) and the (200) CeO_2 (2.7 Å) lattice spacing. Right: a hexagonal faceted (111) Au crystal is indicated.

DOI: 10.1002/ange.200353570

investigated samples after the catalytic test. Based on TEM, no evolution of the samples (collapse of the mesopores or growth of the Au crystals) was observed.

The resulting catalyst gave 100% conversion of CO at 10°C, and no catalyst deactivation was observed during the 10 h of the run (see the Supporting Information). To compare its activity with that of other previously reported good catalysts, we chose samples of 1.5% Au/TiO_2 and 5% Au/Fe_2O_3 supplied by the World Gold Council.[14] The specific rates per gram of Au are given in Figure 2. It can be seen that the specific rate with nanocrystalline CeO_2 was almost twice that with the other catalysts. When the reaction was carried out at -10°C, the activity of our Au/CeO_2 catalyst (2.8% Au) was 2.2×10^{-6} mol CO s^{-1} $gcat^{-1}$, which compared very well with that of the best catalyst reported by Tsubota et al.[6] Using Au/TiO_2 (3.3 wt% Au) they achieved about 3.5×10^{-6} mol CO s^{-1} $gcat^{-1}$ under similar reaction conditions. On the other hand, when we placed Au on a conventional CeO_2 support prepared by precipitation ($S_{BET}=70\,m^2g^{-1}$), the specific rate was almost two orders of magnitude lower when the reaction was carried out at 5°C (CO conversion 1.8%). Therefore, the fact that the CeO_2 support is in the form of nanocrystalline particles appears to be a key factor for achieving high activity in the oxidation of CO to CO_2 when Au is placed on a support.

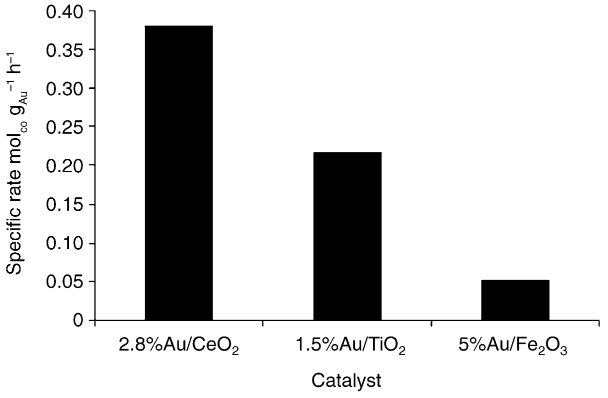

Figure 2. Graph showing the specific rate for CO oxidation on supported gold catalysts. The reference catalysts 1.5% Au/TiO_2 and 5% Au/Fe_2O_3 were supplied by the World Gold Council.[15] Reaction conditions: the molar ratio for CO/air/He was 0.2:19.8:80, with a contact time (W/F) of 94 $g_{cat}\,h\,mol_{CO}^{-1}$; reaction temperature 5°C.

It is well known the Au active catalysts can selectively oxidize CO to CO_2 in the presence of H_2 at low temperatures.[15] However, when the reaction temperature is increased to those of interest for fuel cells operation (60°C), the selectivity can be negatively affected.[15b,16] Our Au/CeO_2 catalyst shows excellent selectivity for CO oxidation in the presence of H_2 at 60°C (Figure 3). As is the case for Au on other active supports,[17] the CO conversion decreases when H_2 is introduced in the reaction mixture. However, with our catalyst 99.7% of the oxygen was consumed for the oxidation of CO, and only 0.3% of the oxygen reacted with H_2 to give water. In other words, Au on nanocrystalline particles of CeO_2 is also a very selective catalyst for the oxidation of CO in the presence of H_2.

To conduct infrared (IR) spectroscopy, CO was adsorbed on the 2.8% Au/CeO_2 sample in the IR cell. An intense band with a maximum at 2103 cm^{-1} together with a broad shoulder on its high-frequency side, with maxima at 2124 and 2133 cm^{-1}, were observed (see the Supporting Information). A low-frequency band at 2103 cm^{-1} was assigned to CO adsorbed on Au^0 sites in defect positions at the perimeter of the contact area between the Au particles and the support or to metallic Au with a lower degree of coordination.[18] Bands at 2124–2133 cm^{-1} were assigned to positively charged gold species.[19] Furthermore, CO interacting with Ce^{3+} ions of the CeO_2 support also gave a characteristic IR band at 2133 cm^{-1}.[20] In fact with X-ray photoelectron spectroscopy (XPS) we have observed the presence of Ce^{3+} ions on the catalyst surface.

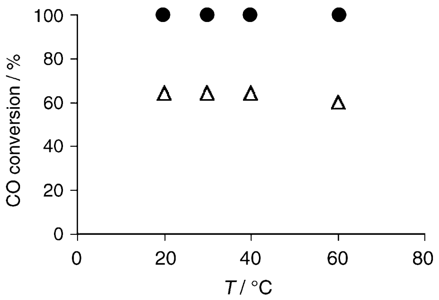

Figure 3. Plot displaying the selective oxidation of CO on 2.8% Au/CeO_2 catalyst in the absence (●) and in the presence (△) of H_2. Reaction conditions: the molar ratio for $CO/O_2/He/X$ was 0.8:0.4:40.4:58.4 ($X=H_2$, N_2), with a contact time (W/F) of 18.6 $g_{cat}\,h\,mol_{CO}^{-1}$.

When O_2 was allowed to react at 25°C with the adsorbed CO (see the Supporting Information) only the IR bands at 2103 and 2124 cm^{-1} decrease in intensity, and the rate of decrease is faster for the former. As previously indicated, the IR band at 2103 cm^{-1} is associated to CO adsorbed on Au sites located at the perimeter of the contact area of the metal particle with the support, which can be highly unsaturated.

From the IR adsorption and adsorption–reaction experiments conducted with CO and $CO+O_2$, it appears that Au and $Au^{\delta+}$ species are present in the catalyst and both can intervene in the oxidation process. The high degree of CO adsorption on Au particles located at the perimeter of the contact area between Au and the cerium oxide support, and the presence of Ce^{3+} ions (i.e. oxygen vacancies) on the surface of the nanocrystalline support that are able to adsorb and activate O_2 may explain the enhanced reactivity of the catalyst.

In conclusion, we have shown that by depositing Au on nanocrystalline particles of cerium oxide it is possible to achieve an increase of two orders of magnitude in the catalytic activity relative to the Au/CeO_2 catalysts prepared by coprecipitation or by Au deposition on a regular cerium oxide support. These results show that the properties of the support can change drastically when the particle size is decreased to the nanosize region, turning a support that was previously considered to be inadequate for preparing Au catalysts for CO oxidation into a highly active species. Moreover, owing to the high selectivity of Au/CeO_2 for the oxidation of CO in presence of H_2 at higher temperatures, the catalyst may have possibilities for use in fuel cells.

Experimental Section

A colloidal dispersion of CeO_2 nanoparticles was prepared by thermolysis of an acidified $Ce(NO_3)_4$ solution followed by redispersion, according to a previously described method.[21] The dispersion was purified and concentrated using an ultra-filtration cell equipped with a 3 KD membrane. The purification was monitored by the residual acidity of the dispersion, determined by an acid titration of the supernatant after ultra-centrifugation at 50000 rpm for 6 h.[22]

Au was deposited on the nanoparticulated cerium oxide by the following procedure: A solution of $HAuCl_4$ (0.140 g) in deionized water was brought to pH 10 by the addition of 0.2 M NaOH (7.5 g). Once the pH value was stable the solution was added to a slurry containing CeO_2 (1.260 g) in H_2O (25 mL). After adjusting the slurry to pH 10 with 0.2 M NaOH (1.4 g), the slurry was vigorously stirred for 18 h at room temperature. The solid was then isolated by filtration and washed until free of chloride and dried for 16 h at 100 °C. After this, the catalyst was not calcined. The total Au content of the final catalyst (2.8% Au/CeO_2) was 2.8% as determined by chemical analysis. The catalysts were tested in a quartz reactor (9 mm i.d.), and the products were analyzed by gas chromatography using Porapack and Molecular Sieves columns in combination.

Received: December 18, 2003 [Z53570]

Keywords: cerium · gold · heterogeneous catalysis · nanostructures · oxidation

- [1] S. Galvagno, G. Parravano, *J. Catal.* **1978**, *55*, 178.
- [2] a) G. C. Bond, P. A. Sermon, *Gold Bull.* **1973**, *6*, 102; b) P. A. Sermon, G. C. Bond, P. B. Wells, *J. Chem. Soc. Faraday Trans. 1* **1979**, *75*, 385.
- [3] a) B. Nkosi, M. D. Adams, N. J. Coville, G. J. Hutchings, *J. Catal.* **1991**, *128*, 333; b) G. J. Hutchings, *Gold Bull.* **1996**, *29*, 123.
- [4] a) M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* **1987**, 405; b) M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, *J. Catal.* **1989**, *115*, 301.
- [5] G. C. Bond, D. T. Thompson, *Catal. Rev. Sci. Eng.* **1999**, *41*, 319.
- [6] a) S. Tsubota, T. Nakamura, K. Tanaka, M. Haruta, *Catal. Lett.* **1998**, *56*, 131; b) M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet, B. Delmon, *J. Catal.* **1993**, *144*, 175.
- [7] F. Boccuzzi, A. Chiorino, M. Tsubota, M. Haruta, *Catal. Lett.* **1998**, *56*, 195.
- [8] D. A. H. Cunningham, W. Vogel, H. Kageyama, S. Tsubota, M. Haruta, *J. Catal.* **1998**, *177*, 1.
- [9] M. Haruta, *Cattech* **2002**, *6*, 102.
- [10] Qi Fu, A. Weber, M. Flytzani-Stephanopoulos, *Catal. Lett.* **2001**, *77*, 87.
- [11] W. Liu, M. Flytzani-Stephanopoulos, *J. Catal.* **1995**, *153*, 304.
- [12] P. Bera, M. S. Hegde, *Catal. Lett.* **2002**, *79*, 75.
- [13] A. Sepulveda-Escribano, F. Coloma, F. Rodriguez-Reinoso, *J. Catal.* **1998**, *178*, 649.
- [14] Gold reference catalysts, *Gold Bull.* **2003**, *36*, 1.
- [15] a) M. R. Torres Sanchez, A. Ueda, K. Tanaka, M. Haruta, *J. Catal.* **1997**, *168*, 125; b) M. J. Kahlich, H. A. Gasteiger, R. J. Behm, *J. Catal.* **1999**, *182*, 430.
- [16] B. Qiao, Y. Deng, *Chem. Commun.* **2003**, 2192.
- [17] R. J. H. Grisel, C. J. Weststrate, A. Goossens, M. W. J. Crajé, A. M. van der Kraan, B. E. Nieuwenhuys, *Catal. Today* **2002**, *72*, 123.
- [18] a) F. Boccuzzi, A. Chiorino, S. Tsubota, M. Haruta, *J. Phys. Chem.* **1996**, *100*, 3625; b) N. A. Hodge, C. J. Kiely, R. Whyman, M. R. H. Siddiqui, G. J. Hutchings, Q. A. Pankhurst, F. E. Wagner, R. R. Rajaram, S. E. Golunski, *Catal. Today* **2002**, *72*, 133.
- [19] a) J. D. Grunwald, M. Maciejewski, O. S. Becker, P. Fabrizioli, A. Baiker, *J. Catal.* **1999**, *186*, 458; b) F. Boccuzzi, A. Chiorino, *J. Phys. Chem. B* **2000**, *104*, 5414.
- [20] A. Bensalem, J. C. Muller, D. Tessier, F. Bozon-Verduraz, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 3233.
- [21] J. Y. Chane-Ching, EP 208580, **1987**.
- [22] J. Y. Chane-Ching, F. Cobo, D. Aubert, H. Harvey, M. Airian, A. Corma, unpublished results..