



Reactivity of Au nanoparticles supported over SiO₂ and TiO₂ studied by ambient pressure photoelectron spectroscopy

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ABSTRACT

The influence of the metal cluster size and the support on the reactivity of gold-based catalysts has been studied in the CO oxidation reaction. To overcome the structural complexity of the supported catalysts, gold nanoparticles synthesized from colloidal chemistry with precisely controlled size have been used. Those particles were supported over SiO₂ and TiO₂ and their catalytic activity measured in a flow reactor. The reaction rate was dependent on the particle size and on the support, suggesting two reaction pathways in the CO oxidation reaction. In parallel, ambient pressure photoelectron spectroscopy (APPS) has been performed under reaction conditions using bidimensional model catalysts prepared by supporting Au nanoparticles over planar polycrystalline SiO₂ and TiO₂ thin films. The nanoparticles were transferred from a water surface where they have been dispersed by means of the Langmuir–Blodgett (LB) technique. In this way, the catalytically active surface was characterized under real reaction conditions, revealing that during CO oxidation gold remains in the metallic state.

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1. Introduction

Bulk gold is known for its inertness in chemical reactions [1]. Nevertheless, in the late 1980, Haruta discovered that gold nanoparticles dispersed in an oxide support are active for the low temperature CO oxidation [2]. Since then, an increasing number of reports dealing with many different reactions catalyzed by supported gold catalysts have followed [3,4]. Investigations using *in situ* characterization of supported gold catalysts under reaction conditions are, however, in an early stage. Most of these studies deal with the CO oxidation because of its potential for practical applications, like the purification of H₂ streams by preferential oxidation of CO (PROX) in order to avoid the deactivation of Pt in fuel cell-related catalysts. Supported gold nanoparticles are extremely active in this reaction at temperatures as low as 200 K [5]. The effect of the Au particle size was first studied by Haruta et al. with supported catalysts, showing that the Au cluster size is a key factor for the

catalytic activity [6]. It is now well established that the size of the gold nanoparticles must be below 5 nm in order to obtain an active catalyst [7]. It is not clear yet if the particle size is a primary variable affecting the activity or if the particle morphology or structure of the metal-support interface is the key parameter [8]. Some authors have pointed out that the support plays an important role in the CO oxidation reaction and that more active catalysts are obtained when the gold clusters are deposited on reducible oxides, especially TiO₂ [4,9,10]. By contrast, Norskøv et al. have suggested that the support does not play any role in the CO oxidation reaction. The low coordinated gold atoms are responsible for the catalytic activity instead [11].

Furthermore, different proposals can be found on the literature about the nature of the active site(s) responsible for the CO oxidation in supported gold catalysts. The high reaction rate has been attributed to either metallic gold atoms at the Au-support interface [12] and/or to low coordinated atoms in the gold clusters [13]. Bond and Thompson [14] have suggested that the active sites are gold ensembles incorporating metallic and cationic (3+) gold atoms, the latter located at the metal-support interface. It has been proposed that metallic [15], cationic [16], and even anionic gold species [17] could be the active sites responsible for the high activity observed with Au catalysts in CO oxidation. *In situ* infrared

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spectroscopy has been used to elucidate the nature of the gold in the active catalysts. Dekkers et al. studied the CO adsorption on Au/TiO₂ catalysts and concluded that the active phase is metallic Au because in the most active catalysts there is predominance of the band at 2112 cm⁻¹ [18]. However, Avalos and coworkers found different gold species in a Au–mordenite catalyst used for CO oxidation [19]. They proposed that these different species are responsible of the activity of gold at different temperatures

The typical supported gold catalyst consists of Au nanoparticles of different sizes and shapes dispersed on an amorphous support, usually a high area metal oxide powder. There have been some attempts to overcome the inherent structural complexity of supported catalysts by preparing “model samples”. These models consist of planar support surfaces (usually a single crystal) [3,20] with gold clusters deposited on top. On these samples, surface characterization techniques operating in ultrahigh vacuum can be used. These systems have the limitation of lacking some important characteristics of potential practical catalysts, such as support hydroxyl groups and/or water. The use of clusters of gold with selected sizes provides a way to control on of the variables of the system [21]. In this work, we used gold clusters with a narrow size distribution and polycrystalline flat supports which mimic the characteristic of powder ones, such as the high area or the presence of surface hydroxyl groups. Moreover, we use a novel *in situ* technique, ambient pressure photoelectron spectroscopy

(APPS), capable of providing spectroscopic information on the chemical state of the surface and the influence of reactant gases during reaction conditions.

2. Experimental

Colloidal gold nanoparticles with sizes in the range between 2 and 5.5 nm were synthesized by the reduction of gold(III) chloride hydrate (99.999%) with tetrabutyl ammonium borohydride (TBAB, 98%) in the presence of didodecyldimethylammonium bromide (DDAB, 98%) and dodecylamine (99%), as previously described by Jana and Peng [22]. In a typical synthesis, 0.1 mmol of HAuCl₄ were dissolved in 10 ml of a 0.1 M DDAB solution in toluene. Next, 1 mmol of dodecylamine was added to the solution and dissolved by sonication. Finally, a solution of 0.3 mmol TBAB dissolved in 2 ml of 0.1 M DDAB in toluene was rapidly injected into the gold chloride solution under vigorous stirring in a similar way as described in Refs. [23,24]. As a product of this reaction, 2–3 nm gold nanoparticles were obtained. Larger particles, up to 5 nm, were obtained by seeded growth from this initial sample. Gold nanoparticles were grown by introduction of an additional gold precursor, which was slowly reduced using a hydrazine solution. Following the synthesis process, the samples were cleaned several times by means of precipitation with alcohols and re-dispersion in chloroform. After the synthesis, 0.5 mmol hexadecanethiol were

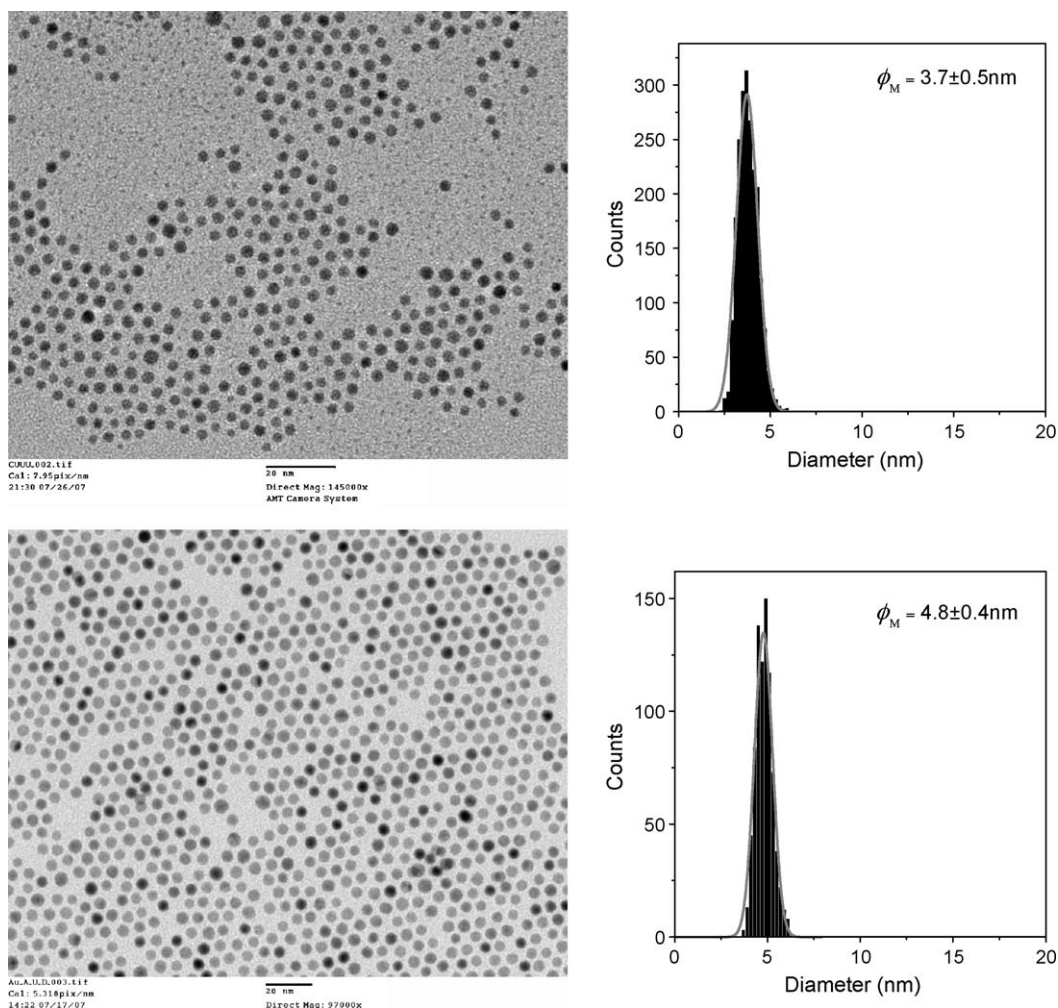


Fig. 1. Transmission electron microscopy of 3.7 and 4.8 nm gold nanoparticles with particle size distribution.

added to the nanoparticle solution to prevent aggregation. The synthetic route allowed the preparation of gold nanoparticles with size distributions around 10%. Fig. 1 shows a typical TEM micrograph of 3.7 ± 0.5 and 4.8 ± 0.4 nm Au particles and the corresponding histogram of the particle size distribution. The other samples (with different Au cluster size) display Au particles of similar shape and narrow distribution.

For CO oxidation experiments gold nanoparticles dispersed in chloroform were supported on high area commercial SiO_2 (Cab-O-Sil H-5 Cabot Corporation, $300 \text{ m}^2/\text{g}$) or TiO_2 (Degussa P25, $42 \text{ m}^2/\text{g}$). The method used for dispersing the particles in the support has been previously described [25]. Briefly, the support and the nanoparticles were mixed in an aprotic solvent, specifically chloroform, and sonicated for 60 min. Next, the mixture was filtered and dried in an oven at 80°C for 16 h. The samples were characterized before and after reaction by X-ray photoelectron spectroscopy, XPS (PHI 5400) and transmission electron microscopy (JEOL 2100-F 200 kV). In this instrument it is possible to perform high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field (HAADF) scanning transmission electron microscopy. The intensity of the electrons collected in the last technique is approximately proportional to Z^2 , allowing z-contrast imaging.

The catalytic activity of selected samples (displayed in Table 1) was measured in a U-shaped quartz reactor. The reactor was placed in an oven connected to a PID temperature controller (Watlow). The gas flow was regulated by mass flow controllers (Porter Instruments). Before measuring the catalytic activity, the hexadecanethiol molecules protecting the Au clusters were removed by submitting the sample to a temperature-programmed treatment in O_2/Ar (10 vol.%) at 300°C (heating rate $5^\circ\text{C}/\text{min}$) and dwell time of 60 min. After the pretreatment, the samples were cooled down in O_2/Ar and the rate of carbon monoxide oxidation was measured at increasing temperatures (from 20 to 100°C) and 0.1 MPa of total pressure. The gas flow rate was $40 \text{ ml}/\text{min}$ ($5 \text{ CO}/50\text{O}_2/20\text{Ar}$). The evolution of the concentration of the different compounds was monitored by selected m/z fragments that were analyzed by means of a quadrupolar mass spectrometer connected on line to the reactor outlet.

For spectroscopy studies we have used films of Au nanoparticles deposited on a flat substrate by the Langmuir–Blodgett (LB) method [26,27]. The substrate was either SiO_2/Si wafers (native oxide layer over a silicon wafer) or nanoporous TiO_2 films over a Si wafer [28,29]. Before the spectroscopic measurements, the samples were characterized by scanning electron microscopy (Zeiss Gemini Ultra-55 Analytical Scanning Electron Microscope) and XPS (described above). To remove the thiols, the samples were cleaned with an UV/ozone cleaner during 60 min.

APPS experiments were performed using a spectrometer capable of operating at ambient pressures in the Torr range at the beamline 9.3.2 at the Advanced Light Source (Berkeley, USA) [30,31]. The spectrometer consists in a chamber with a differentially pumped electrostatic lens system that focuses the electrons

emitted by the sample into the focal plane of a hemispherical electron energy analyzer.

The catalytic activity of Au for CO oxidation with O_2 could be monitored using a mass spectrometer connected to the second pumping stage of the instrument, just before the analyzer. Photoemission spectra of the Au4f, C1s, Ti2p, O1s, Si2p, core levels were recorded using photon energies of 400 eV (Au and Si), 600 eV (C), 720 eV (Ti) and 850 eV (O), respectively, which produce photoelectrons emitted approximately the same kinetic energy (300–350 eV), thus, ensuring the same analysis depth. The binding energy scale in all experiments was calibrated using the known value Ti3p (37.5 eV) as a reference [32]. A Shirley background was subtracted from all spectra before deconvolution. The peaks were fitted using Gaussian–Lorentzian curves. The separation between the spin-orbit coupled peaks Au $4f_{7/2}$ and Au $4f_{5/2}$ was found to be 3.67 eV with a branching ratio of 4:3. The area of the peaks has been normalized by the incident photon flux.

3. Results and discussion

3.1. Powder samples characterization

Fig. 2 shows selected TEM and HRTEM micrographs of gold nanoparticles supported on silicon oxide and titanium dioxide (before the oxygen treatment). On SiO_2 the nanoparticles were randomly distributed. Their shape is mainly spherical although some faceted particles having hexagonal shape can be seen. Most of the gold nanoparticles were found at the edges of the anatase phase when supported on TiO_2 -P25 (evidence by electron diffraction). In this support, 70% of the titanium dioxide is present as anatase and 30% as rutile. The anatase particles are smaller and more faceted than the rutile ones and this could be the reason why most of the gold is supported over anatase. In all cases, the gold nanoparticles are single crystal metallic Au (face centered cubic, fcc). The large difference in atomic number between the gold ($Z = 79$) and the oxide supports (oxygen, 8; silicon, 14; and titanium, 22) allows detection of the nanoparticles with high contrast using the STEM-HAADF detector as it is very sensitive to the atomic weight (Fig. 3). In the Au/ SiO_2 samples the spatial distribution of Au particles is random, with no preferential location. On the other hand, when TiO_2 is used, the gold nanoparticles are evenly distributed over the support and located at the edges of the titania particles.

X-ray photoelectron spectroscopy of the as-prepared samples (Fig. 4) shows that the gold atoms are in the metallic state on both supports (SiO_2 and TiO_2). There is only one peak in the Au $4f_{7/2}$ region, located at 83.8 eV (metallic gold). It cannot be discarded the presence of an extra peak at higher binding energies, although the low signal to noise ratio makes the assignment difficult.

3.2. Catalytic activity

The thiols covering the gold nanoparticles were removed before testing the catalytic activity of the samples. This was performed by heating the samples in diluted oxygen (10% O_2/Ar) at $5^\circ\text{C}/\text{min}$ from room temperature to 300°C , and then keeping this temperature for 60 min [25]. During the thermal treatment the effluent gases were analyzed by mass spectroscopy. Water was first detected at 80 – 110°C . Next, CO_2 (formed by decomposition of the hydrocarbon chains of the surfactants) was detected at 150 and 300°C . To test if the heating treatment was sufficient to optimize the nanoparticles reactivity, the specific activity of the 2 nm sample for CO oxidation at 70°C was recorded as a function of the treatment temperature from 120 to 500°C (Fig. 5). The specific activity increases linearly with the temperature until 200°C . From this point, on further increases in the treatment temperature do not affect the reaction

Table 1
Powder catalysts used, particle size (determined by TEM) and loading (wt.%).

Sample name	Support	Size of gold nanoparticles (nm)	Loading (wt.%)	Mass of catalyst used (mg)
Au–Si–3.7	SiO_2	3.7	0.7	200
Au–Ti–2	TiO_2 P-25	2	1.9	154
Au–Ti–3.7	TiO_2 P-25	3.7	1.2	120
Au–Ti–4.1	TiO_2 P-25	4.1	0.6	190
Au–Ti–4.8	TiO_2 P-25	4.8	1.6	160
Au–Ti–5.3	TiO_2 P-25	5.3	2.0	200

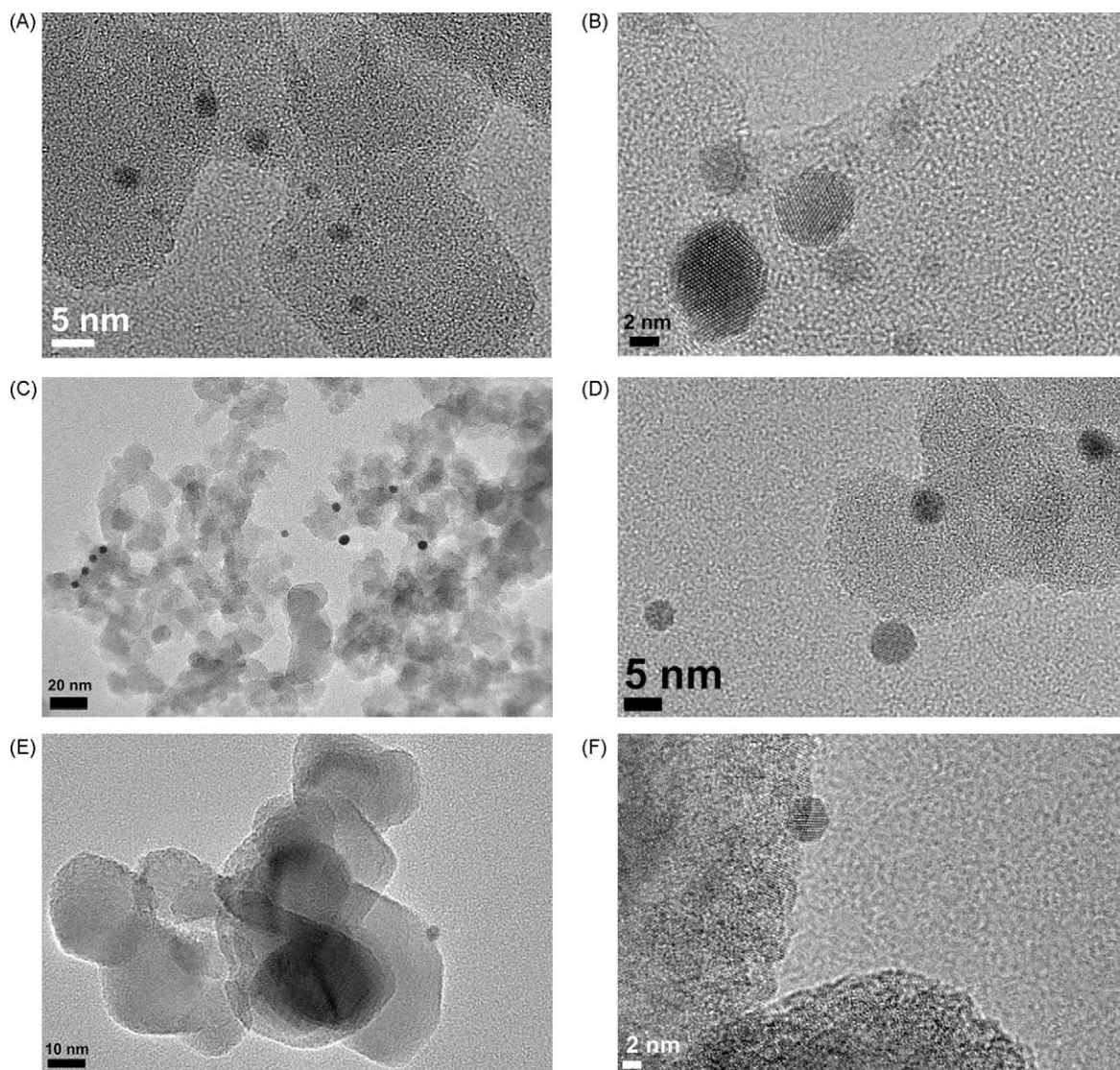


Fig. 2. TEM and HRTEM micrographs of supported gold nanoparticles before thermal treatment and catalytic activity measuring: (A and B) 2 nm supported over SiO₂, (C and D) 3.7 nm over SiO₂, and (E and F) 4.1 nm over TiO₂.

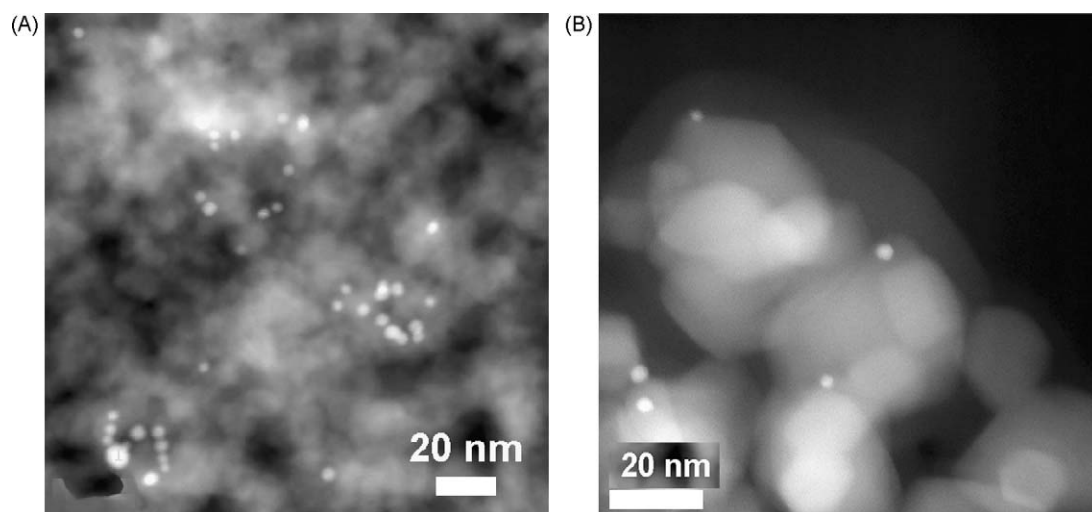


Fig. 3. HAADF micrographs of freshly prepared samples (before heating treatment and catalytic activity test). (A) 3.7 nm Au sample supported over SiO₂ and (B) 2 nm sample supported over TiO₂.

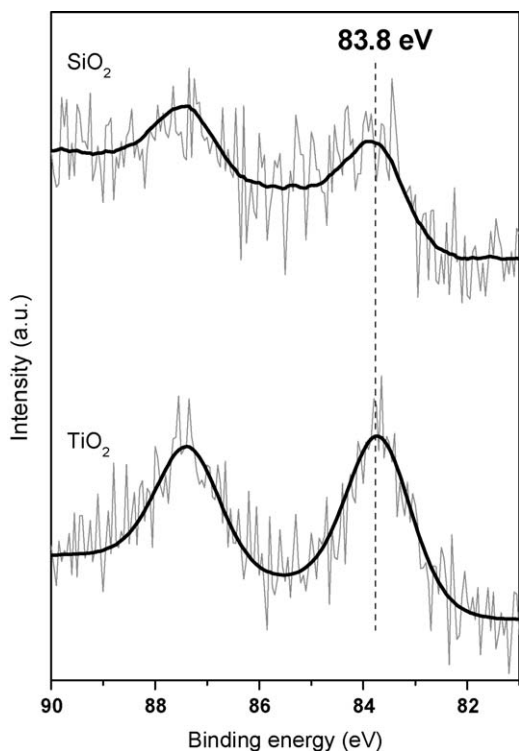


Fig. 4. Au4f region of 2 nm nanoparticles supported over powder SiO₂ and TiO₂.

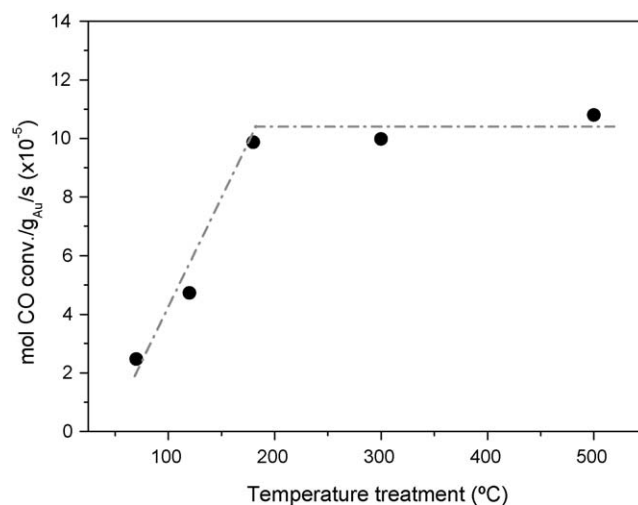


Fig. 5. Specific activity (CO converted by gram of gold) of TiO₂ supported 2 nm nanoparticles in the CO oxidation reaction at 70 °C (gas flow 1CO:1O₂:4Ar, 30 ml/min total flow rate) vs. the temperature of pretreatment in 10% O₂/Ar.

rate, with the activity remaining stable even when the sample was treated at 500 °C.

The first parameter investigated in the reactivity of the gold nanoparticles was the effect of the support. We chose the 3.7 nm sample and tested the catalytic activity for CO oxidation after the treatment in O₂/Ar at 300 °C. As shown in Fig. 6A, below 50 °C the specific activity of the gold nanoparticles is similar on both supports. When the temperature increases, the activity in the case of the silica support remains flat and even decreases. In contrast, on the titania support the activity rises rapidly with temperature. At 90 °C its activity is about seven times higher on TiO₂ than on SiO₂. These results clearly indicate that there is an effect of the oxide support in the reactivity of gold catalysts, at least at the higher temperatures, consistent with the results published by Arrii et al. [9]. In our experiment, the gold nanoparticles deposited over SiO₂ and TiO₂ come from the same batch, and therefore, there are no other external factors that could affect their reactivity. They have the same size, shape and probably the same amount of impurities. This fact is of great importance because the differences in the

catalytic activity when supported on different oxides are only due to the effect of the support. Most of the work published in gold catalysts comparing different supports use samples prepared by deposition precipitation, with gold nanoparticles of similar size (but not exactly the same) and different shape depending on the surface composition and morphology of the substrate [33].

Using the titania support, the effect of the particle size (2–6 nm range) was evaluated in the CO oxidation reaction at 70 °C (Fig. 6B). When the particle size decreases, the specific activity (per gram of gold) increases dramatically, in agreement with most of the published data on supported gold [34–36]. We did not observe however, the volcano plot (specific activity vs. cluster size) described by Chen and Goodman [20], although in those experiments the support was a single crystal and the particles were a peculiar 2D form (up to 1 nm in size and 2 monolayer thickness).

After reaction, the samples were characterized again by XPS and TEM. The XPS data showed that in the Au 4f region there is only one peak at 83.8 eV in all the samples, indicating that after reaction the gold nanoparticles remain in the metallic state. Fig. 7 displays TEM and HRTEM micrographs of selected used samples supported over SiO₂ and TiO₂. There is some agglomeration on the samples supported over silica, especially for the 2 nm gold particles. This agglomeration is more pronounced in the case of samples supported over titania, where particles showing different crystalline orientation can be distinguished in the 2 nm sample. The reason why the gold particles on TiO₂ show a higher degree of agglomeration might be due to the low surface area compared with the silica (42 and

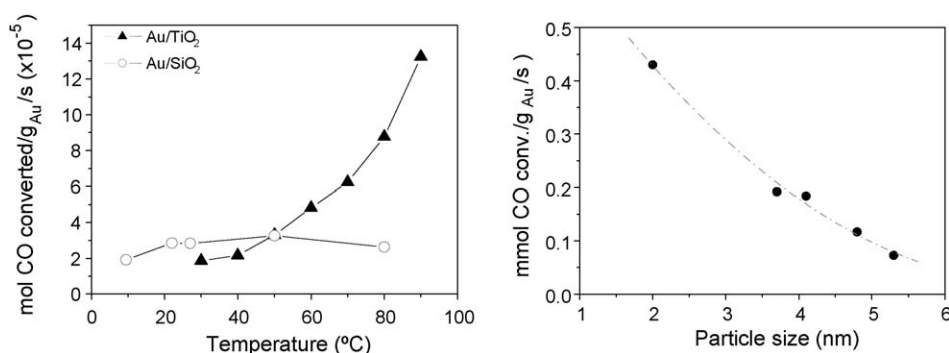


Fig. 6. Catalytic activity (expressed as CO converted by gram of gold) of supported Au nanoparticles in the CO oxidation reaction (gas flow 1CO:1O₂:4Ar, 30 ml/min total flow rate). (A) Effect of the support for the 3.7 nm particle size and (B) effect of the particle size for nanoparticles supported over TiO₂.

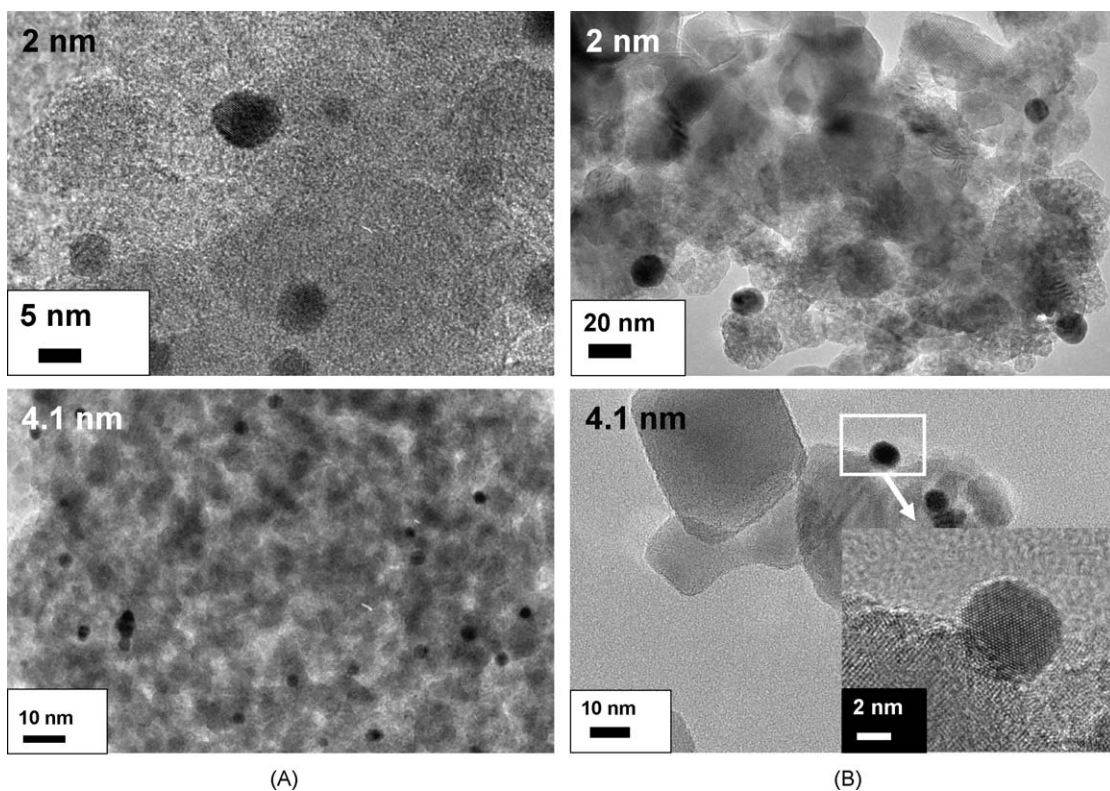


Fig. 7. TEM micrographs of 2 and 4.1 nm supported gold nanoparticles after reaction. (A) Samples supported over silicon oxide and (B) samples supported over titanium dioxide.

300 m²/g). Despite of this fact, the activity over TiO₂ is still higher than on silica. It is important to remark that in these samples the faceted particles have become spherical in shape.

At temperatures above 50 °C the gold nanoparticles display an activity that is clearly higher when supported on TiO₂, in

agreement with the theories proposing that the support has a strong influence in the catalytic performance. Liu et al. using DFT calculations [37] proposed that CO oxidation occurs at the interface between gold and the titanium dioxide. Bulk gold (single crystal or polycrystalline) does not adsorb molecular oxygen,

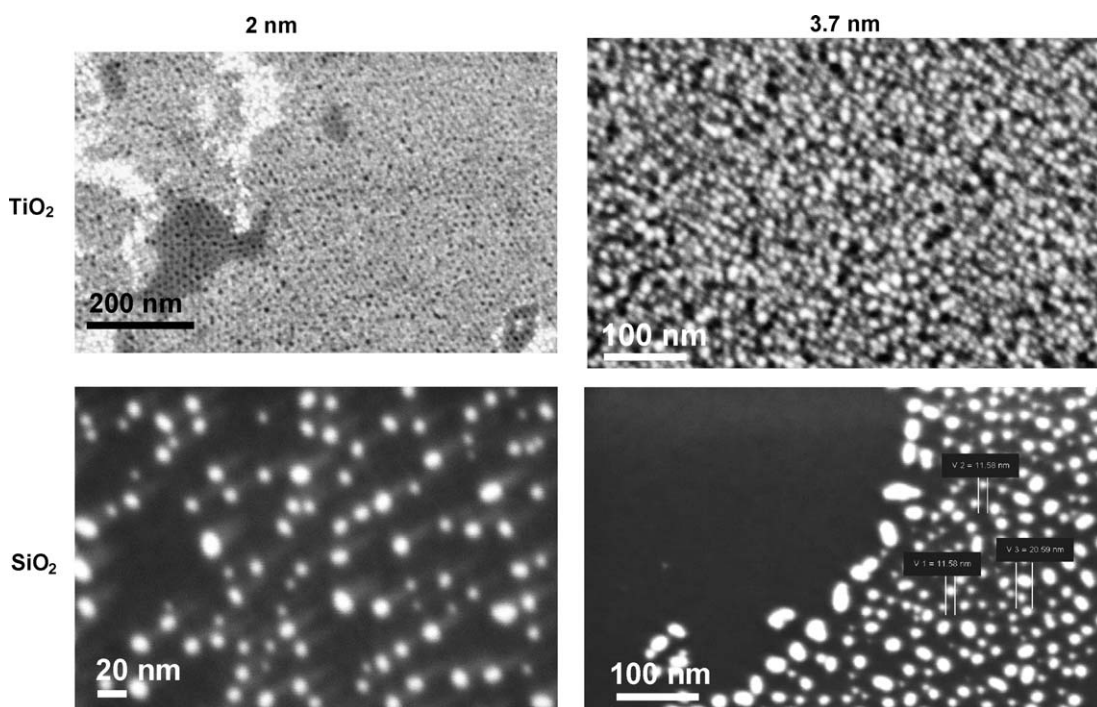


Fig. 8. SEM micrographs of planar model catalysts prepared by Langmuir–Blodgett using SiO₂ and TiO₂ thin films as supports and 2 and 3.7 nm gold nanoparticles. All the samples were cleaned with ozone for 60 min after preparation.

only small Au particles can do it. The CO, however, can be adsorbed on the surface as demonstrated theoretically and experimentally [38,39]. Therefore, it is necessary to activate the O₂ molecule to initiate the CO oxidation [40]. The interaction between the gold nanoparticles and adsorbed oxygen is thought to be produced by electron donation and back donation between the orbitals 6s and 6p of the Au and the π^* orbital of the oxygen molecule that weakens the O–O bond. The promoting effect of the support oxide could consist in the enhancement of this electron transfer [37]. This is in line with theoretical studies that propose that molecular oxygen can adsorb forming a peroxo species onto gold clusters. This chemisorption can also cause a change in the shape of the cluster [41].

The effect of the particle size is also evident in the present study. When the size decreases, the specific activity is higher. Many authors propose that the key factor of the activity in Au catalysts is the presence of under-coordinated gold atoms [42,43] which adsorb CO and oxygen more strongly, making the reaction possible.

The fact that both the support and the particle size influences on the reaction rate is in agreement with theories proposing the existence of several reaction pathways occurring simultaneously with reducible supports [44,45]. One pathway implies only the gold nanoparticles. In that case the particle size plays a critical role, as smaller particles have a higher number of under-coordinated sites. The other pathway involves the participation of the support, where the oxygen can be activated more easily, either on the support itself or in the gold-support perimeter. This last reaction pathway has found to be more important when the temperature increases, maybe because the adsorption of oxygen on gold nanoparticles is weaker at high temperatures. On silicon oxide, as non-reducible support, only the first mechanism operates, explaining its less activity at high temperatures.

3.3. Planar model catalysts preparation and characterization

Selected gold nanoparticles with 2 and 3.7 nm sharp size distribution were deposited on titania and silica thin films using the

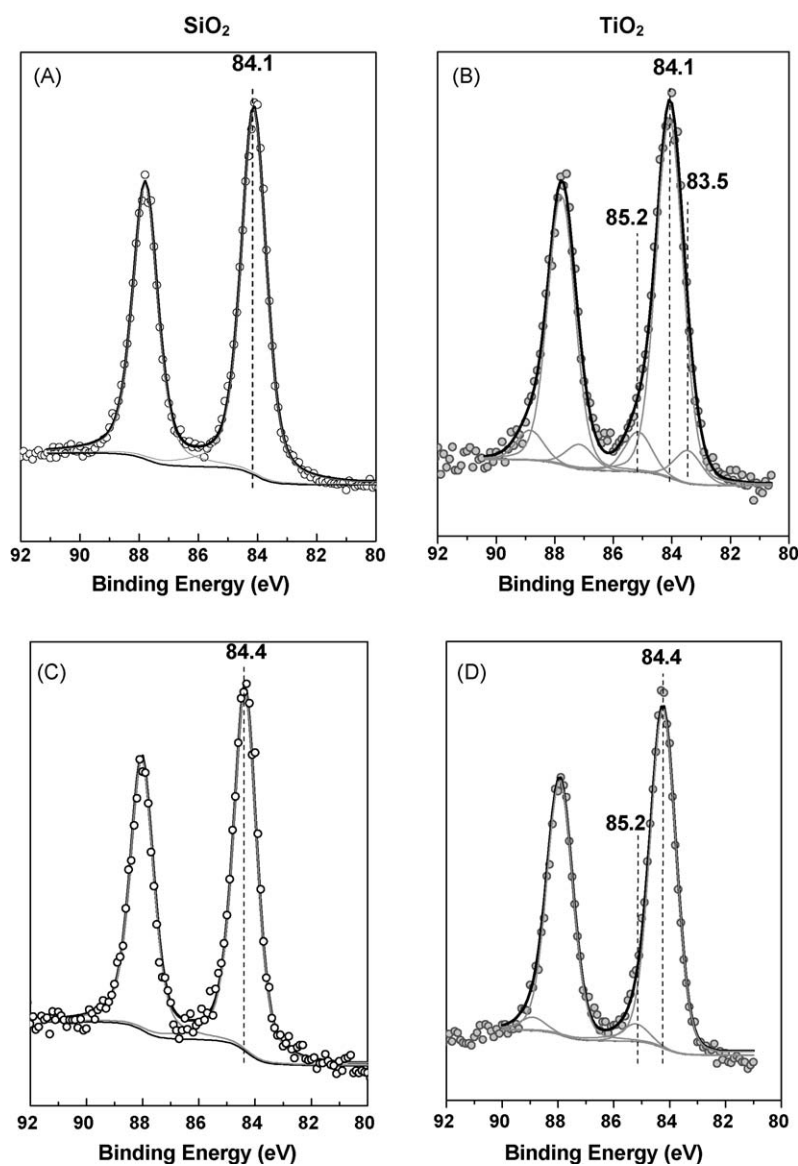


Fig. 9. Au 4f region of 2 nm gold nanoparticles in planar samples measured by APPS in vacuum after cleaning with oxygen at 130 °C (A and B) and during reaction conditions: 150 °C and 0.1 Torr of CO and 0.1 Torr of O₂ (C and D). (A and C) Corresponds with SiO₂ support and (B and D) with TiO₂.

Langmuir–Blodgett technique. In order to remove the surfactant and thiols, the samples were cleaned with ozone. Fig. 8 shows high resolution scanning electron micrographs of the samples after cleaning. The gold nanoparticles are spread over the support with a loading of 0.4–0.7 monolayer and even after the cleaning treatment they keep their shape and size with no agglomeration.

XPS analysis of the freshly prepared samples reveals Au in the metallic state and traces of sulphur due to the thiols used as stabilizers. After cleaning, the sulphur disappears, the ratio Au/C increases while the gold remains in the metallic state (Au $4f_{7/2}$ at 83.9–84.1 eV).

3.4. Ambient pressure photoelectron spectroscopy

In situ XPS experiments were performed with the gold nanoparticles supported over silica and titania thin films. Before the experiments, the samples were treated in oxygen (50 mTorr) at 130 °C to reduce the amount of hydrocarbons adsorbed on the surface. The oxygen was removed while the temperature was still high and the samples were allowed to cool in vacuum to ensure that no species were adsorbed on the surface. Fig. 9A and B shows the XPS spectra of the Au $4f$ region of the 2 nm sample over SiO $_2$ and TiO $_2$ in vacuum (the results are similar for the 3.7 nm sample). When gold is supported on silicon oxide, metallic Au, with a binding energy of 84.1 eV, is exclusively observed. In the case of titania, two additional small contributions can be seen at 83.5 eV (Au δ^-) and 85.3 eV (Au δ^+). The Au δ^- species can originate from the interaction of gold with titanium. It is known that TiO $_2$ presents oxygen vacancies, with Ti $^{3+}$ atoms in the lattice. Gold is more electronegative than titanium. Therefore, Ti can donate electron density to gold in order to compensate the oxygen vacancies, creating thus negatively charged gold species.

Under reaction conditions (150 °C, 0.1 torr of CO and 0.1 Torr of O $_2$) the Au $4f$ peaks are shifted 0.3 eV to higher binding energies in both supports (TiO $_2$ and SiO $_2$). This shift could be due to the effect

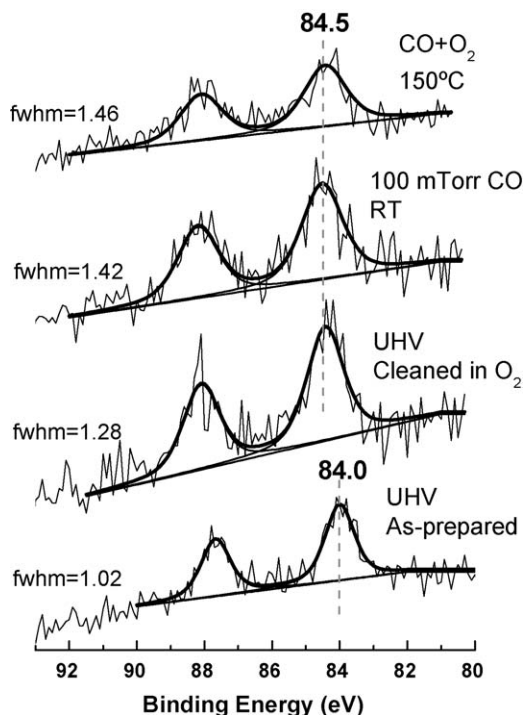


Fig. 10. Au $4f$ region of 2 nm gold nanoparticles supported over powder titanium dioxide measured by APPS during exposure to CO (0.1 Torr) and reaction conditions (150 °C and 0.1 Torr of CO and 0.1 torr of O $_2$).

of the adsorbed CO, which withdraws electron density from the gold nanoparticles (Fig. 9C and D). When the Au/SiO $_2$ samples were exposed to the reactant gases at room temperature, the XPS spectra did not change when compared to those acquired in vacuum, i.e., the gold atoms remain in the metallic state. However, for the Au/TiO $_2$ samples, there was a significant broadening of the XPS peaks corresponding to Au species.

The same experiment was performed with gold nanoparticles supported on powder TiO $_2$ (Fig. 10). In vacuum the gold is in the metallic state and a 0.4 eV shift to higher binding energies is observed when exposed to reactant gases. Also, the gold peaks became broader in the presence of gases. The only work published until now using APPEs with powder Au/TiO $_2$ catalysts prepared by deposition-precipitation also describes the shifting and broadening of the gold peaks (using Ti $3p$ from the support as a reference). The authors attributed the shift and broadening to the oxidation of gold nanoparticles by the reactant gases [32]. Another possible explanation could be charging effects. This can be caused by charge transfer from the titanium to gold, which also transfers electron density to the antibonding states of the gas molecules [38]. This phenomenon could be the reason why titanium oxide support enhances the reactivity of Au in the CO oxidation [46], although more experimental evidence is needed to confirm these results.

4. Conclusions

Metallic gold nanoparticles prepared by colloidal chemistry with a sharp size distribution and deposited over SiO $_2$ (non-reducible) and TiO $_2$ (reducible) supports were used to elucidate the influence of the particle size and the support in the carbon monoxide oxidation reaction. Catalytic tests studies combined with characterization techniques demonstrate the key role of the particle size and the support in the reactivity of gold. On one hand, the activity increases as the gold particle size is decreased. On the other, the presence of a reducible support increases the activity when the temperature is higher than 50 °C. *In situ* ambient pressure photoelectron spectroscopy with powders and with model planar samples (using the same nanoparticles) demonstrated that under reaction conditions the gold remains in the metallic state with a slight shift to higher binding energies (~0.3–0.4 eV) due to the gases adsorbed. The promoting effect of titanium dioxide could be due to the enhancement of the charge transfer between the gold and the antibonding states of the oxygen molecule, being activated in this way. However, more experimental evidence is necessary to clarify this point.

Acknowledgments

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