

Dynamic observations of Au catalysts by environmental electron microscopy

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Abstract

Au clusters in the size range (1-8 nm), supported on MgO and TiO₂, are studied at the atomic scale by High Resolution Transmission Electron Microscopy (HRTEM), in standard conditions and during cycles of gas treatments by environmental HRTEM. Their morphology, the structure of the interface with the substrate and their adhesion energy are deduced from top and profile views, according to the preparation techniques, by atomic deposition in ultra high vacuum or by deposition precipitation in wet conditions.

Under hydrogen atmosphere the gold clusters exhibit a truncated octahedron shape while under oxygen they show a rounding of the shape. These evolution are reversible in hydrogen / oxygen cycles. In the case of the CO oxidation by Au clusters supported on TiO₂, the formation of CO₂ in the microscope sample holder is evidenced by a differentially pumped mass spectrometer connected to the environmental sample holder, at the same time as the rounding of the clusters. The implication of the shape evolution in CO oxidation is discussed.

Introduction

M. Haruta and co-workers [1] have shown that nanometer sized gold clusters on several oxide surfaces were very active for CO oxidation at low temperature whereas gold in the bulk state is catalytically inactive [2]. An explosion of papers has appeared in recent years. The catalytic aspect of these studies [3-5] as well the surface science aspect [6] are well described in some recent reviews [3-6].

It turns out that Au particles supported on several oxides such as TiO₂, MgO, Fe₂O₃, CoOx, NiO, in the size range 1-5 nm, have important catalytic activities. It is generally observed that by decreasing particle size below 4 nm the rate of the catalytic oxidation of CO increases and that if the Au clusters are supported on more reducible oxides the activity is also higher. However it is difficult to disentangle between the support and size effects because, depending on the preparation method and on the nature of the support, particles with different sizes are obtained. To overcome this problem S. Aii et al [7] have deposited size selected gold clusters prepared by laser vaporization with a mean size of 2.6 to 2.9 nm, determined by TEM, on alumina, zirconia and titania oxide powders. They clearly found that gold particles are a little more active on titania than on zirconia and much more active on these two supports than on alumina. These results clearly evidence a support effect.

An intimate contact between the Au deposit and the oxide surface increases the catalytic activity [8]. The active interfacial gold atoms could be cationic [9, 10].

As concerning the increase of activity by decreasing clusters size it has been shown that 8 atoms gold clusters deposited on MgO films are active for CO oxidation at room temperature (RT) [11]. However it not yet known if these few atoms clusters are more active than 2-4 nm clusters generally used in catalysis by gold. Another important factor in catalysis is the morphology of the metal clusters [12]. The shape of gold particles prepared by vacuum evaporation on MgO substrates, at a temperature of at least 300°C, has been studied by *ex situ* HRTEM [13,14] and by *in situ* AFM [12, 15]. They present a truncated octahedron shape exposing smooth (111) and (100) facets. A molecular beam study of the CO oxidation on gold clusters grown under UHV on MgO (100) single crystals has shown that no activity was detectable for particles larger than 4 nm and that 1.5 nm clusters were very active at RT (reaction probability of 50%) [16]. The sample with 1.5 nm particles were prepared at RT and the particles presented faceted fcc shapes, multiple twins with fivefold symmetry and for a large number unidentified shapes. As concerning gold clusters prepared by wet chemical methods it has been shown, by HRTEM observation, that for gold particles prepared by deposition precipitation on TiO₂ powder, the particles with a well faceted truncated octahedron shape were less active than those with a more rounded shape [17].

The origin of the catalytic properties in the case of nanometer sized clusters is attributed to different factors, as the existence of low coordination sites (edges, corners) [18] or interface sites [19], charge transfer between the oxide and

the metal [11,20], and quantum size effects [21]. If the origin of the catalytic activity of gold nanoclusters is not completely understood it seems that low coordinated sites and interface sites play a prominent role, the former sites playing a major role [22].

Furthermore, recent works have shown that the best gold catalysts supported on TiO₂ were prepared on TiO₂ with the anatase structure [23].

However beside the intrinsic properties of the catalyst the environment during the catalytic reaction can play also a crucial role. It has been established that presence of water, at moderate concentration can increase significantly the catalytic activity for CO oxidation [24]. The presence of adsorbates can change the particle shape by modification of surface energies [25], it has also been shown that the presence of oxygen can induce coalescence of tiny gold clusters [26]. Thus, it is important to study *in situ*, during the reaction, the structure and the morphology of the gold clusters. This goal can be reached now by using environmental HRTEM [27].

In this paper, different samples of Au supported on MgO and TiO₂ are studied by HRTEM to determine the influence of the preparation techniques on the adhesion energy between Au clusters and the oxides substrates. Then, in order to improve the knowledge on the CO oxidation on Au clusters, *in situ* studies of the same clusters during cycles of gas treatments are performed by using the technique of environmental electron microscopy in high resolution, under high pressure of gas (2 mbar) at the level of the sample.

2 Equilibrium shape of Au clusters supported on MgO and TiO₂

2.1 Au/MgO

In the case of large fcc metal particles, the equilibrium shape is a truncated octahedron limited by small (100) and (111) faces and the extension of the facets is determined by the Wulff construction [12]. However, when the particle size decreases, the proportion between the edges, corners and external facets varies rapidly and their shape can deviate from the Wulff construction [28]. This prediction has been verified on Pd clusters supported on MgO [29].

Au clusters were prepared by UHV condensation on MgO micro-cubes *in situ* synthesized by burning a Mg ribbon in a mixture of pure gases (N₂ + O₂) in the vacuum chamber [13]. The Au nanoparticles were *in situ* capped by a carbon layer to avoid contamination during transfer through air. They were observed in top and profile views in HRTEM for varying sizes between 1 and 6 nm.

Fig. 1 presents a small cluster (2 nm) on a MgO (001) crystal face in profile view along a [100] axis. The shape is a perfect pyramid, limited by four (111) faces, sitting on one (001) face, in epitaxial orientation (001) Au // (001) MgO, [100]Au // [100] MgO. Fig. 2 shows a larger Au cluster (3 nm), on MgO with the same orientation and shape as in fig. 1. The

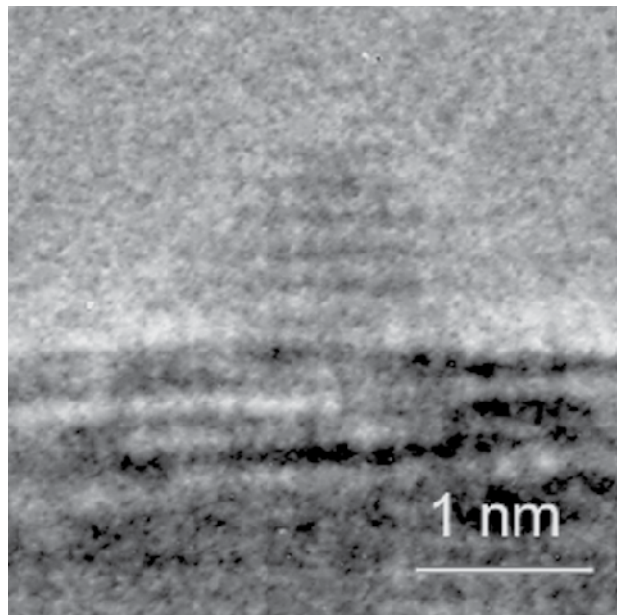


Figure 1
Small Au cluster (2 nm) in profile view, oriented (001) on MgO (001)

interface is completely accommodated to the substrate leading to a dilatation of the Au lattice by 3% at the interface.

In these conditions, no re-entrant angles are seen at the interface and the adhesion energy (β) can be expressed in terms of the height to width (h/w) of the particle and of the anisotropy ratio $g = \sigma_{100} / \sigma_{111}$ between the surface energies [30], then

$$\beta = 2 - (\div 3/2)(h/w) g.$$

If the top (100) facet does not exist (in the case of a sharp pyramid), the adhesion energy would be larger than σ_{100} .

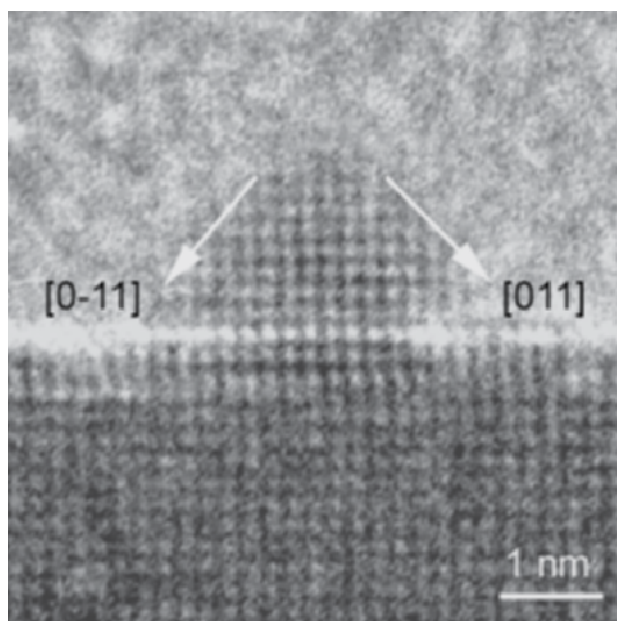


Figure 2
Au cluster (3.5 nm) with the same half pyramidal shape and orientation as in 1a

From fig. 2, the 3 nm particle is too sharp to determined accurately the adhesion energy. We can just tell that it is nearly equal or larger than σ_{100} .

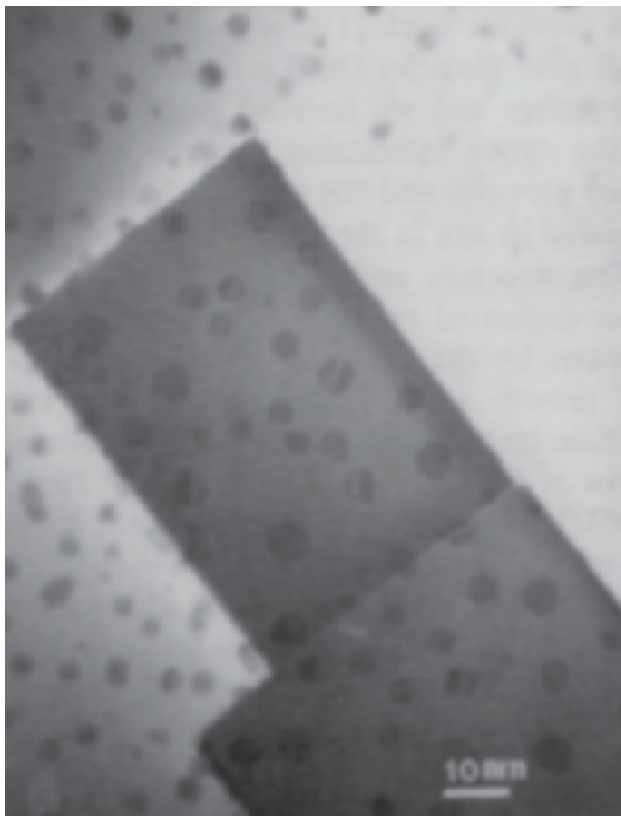


Figure 3
Overview of large Au clusters oriented (111) on MgO cubes

In the case of Au clusters of larger sizes (>5 nm), (100) and (111) epitaxial orientations are observed on MgO (001). Fig. 3 is an overview of Au clusters on MgO micro cubes. Their outline shape is limited by 6 edges with angles corresponding to the (111) orientation in top view. In profile view, a cluster oriented (111) on MgO (001) is seen parallel to its [110] direction, so that it is observed along (111) and (001) limiting faces. It is truncated asymmetrically at the top and at the interface by (111) faces, then its adhesion energy with the substrate can be deduced from the Wulff-Kaishev equation [12]:

$$\beta = \sigma_1 \cdot (h_1 - h_s) / h_1.$$

The central distances of the (111) faces are indicated on fig. 4. Taking the value $\sigma_{111} = 1.04 \text{ J.m}^{-2}$ [31], the adhesion energy is estimated to 0.45 J.m^{-2} that is in good agreement with theoretical calculations which gives 0.52 J.m^{-2} [32]. The gold lattice is relaxed in the particles.

2.2 Au/TiO₂

Au clusters were also prepared by UHV condensation on TiO₂ micro spheres and *in situ* capping with carbon [33]. With micro-crystals of anatase structure, the clusters are found in (111) epitaxy on the (111) surface of TiO₂ and in (110) epitaxy

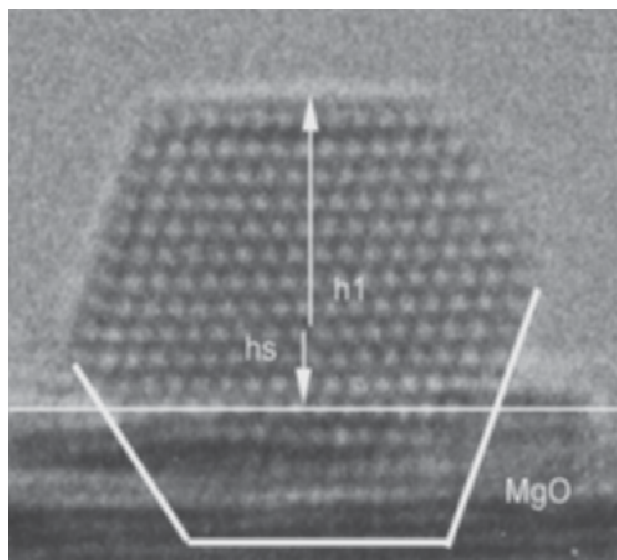


Figure 4
HRTEM image of a large Au cluster seen along its [110] direction, oriented (111) in MgO (001) with the drawing of the central distance from the (111) truncation at the top

on TiO₂ (110). A 2-D layer of gold can be observed at the periphery of the 3-D clusters, the Au atoms are located in front of the Ti atoms at the interface Au/ TiO₂. The adhesion energy deduced from the profile view images is estimated to about 0.98 J.m^{-2} .

In the case of Au clusters prepared in wet conditions by deposition precipitation on TiO₂ micro crystals [17, 34], the samples were directly deposited in the air on a TEM grid previously covered with a carbon film and sometimes protected by another carbon film on the surface. Au clusters were observed on a rutile (110) TiO₂ surface, in epitaxial

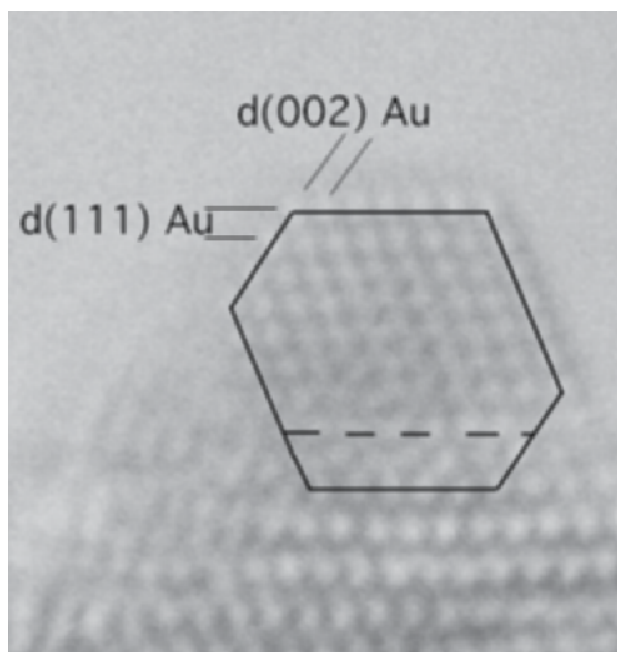


Figure 5
Profile view of a Au cluster prepared by deposition precipitation, (111) oriented on a (110) face of TiO₂ rutile

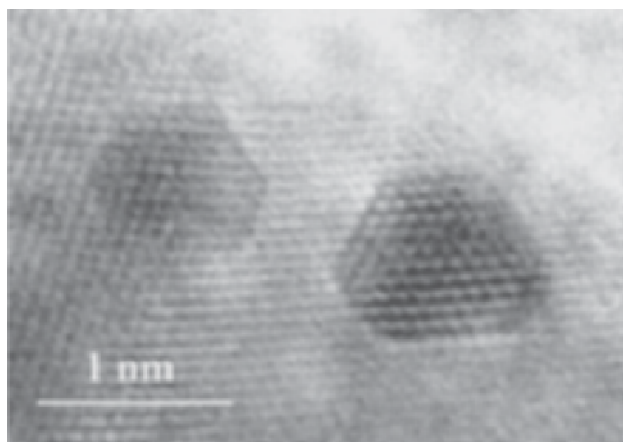


Figure 6
Perfectly faceted Au clusters after annealing at 400°C

orientation (111) Au // (110) TiO₂. From profile view images as in fig. 5, the adhesion energy drops to 0.3 J.m⁻². This drop can be attributed to the effect of the presence of contaminants at the interface, during the wet chemical preparation.

The effect of calcination on the reactivity of the samples towards CO oxidation has been studied in a temperature range between 100° and 400°C [17]. After calcination of Au clusters supported on TiO₂, the reactivity of the clusters increases with a maximal value of the TOF (TOF = 0.16) for 200°C, then it decreases for higher temperatures (TOF = 0.08 at 400°C). This drop is attributed to the change of morphology. Indeed, a strong faceting of the clusters is observed as in fig. 6, with less low coordinated sites like corners and steps.

However, even in the case of perfectly homogeneous preparations, in size, shape and density, all the observations by HRTEM are performed on different clusters to study the effect of annealing or to study the effect of the gas adsorption on the morphology. In order to study the modifications of the shape due to the adsorption of gas at varying temperatures and at the atomic scale, *in situ* observations must be performed by environmental electron microscopy. Furthermore, due to the non-perfect homogeneous collections of particles, these observations must be done on the same cluster during cycles of different gas treatments.

3 Environmental high resolution electron microscopy

Pioneer works in the technique of environmental electron microscopy at the atomic resolution, for applications in catalysis, were initiated by P. Gai and E. Boyes [35]. In this system, the gas is injected at the level of the sample with a multi stage differential pumping on each side of the pole piece of the objective lens.

Then, the system was improved and commercialized by FEI and developed by 3 groups from Arizona State University, Dupont and Haldor Topsoe companies [36-42].

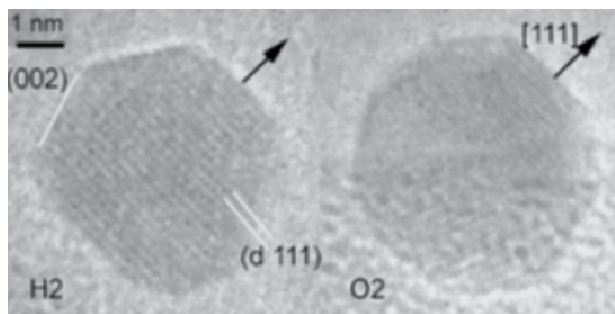


Figure 7
In situ reversible cycle of gas treatments of the same Au cluster in H₂, then O₂, at the pressure of 2 mbar, room temperature, by environmental electron microscopy

Despite the possibilities offered by this type of instrument, the circulation of pure O₂ is forbidden due to the residual partial pressure near the electron source.

Another type of environmental microscope, constructed by JEOL, uses a TEM sample holder that encloses both sample and gas in a cell closed with two electron transparent carbon windows. This sample holder (E-CELL) can be used with a standard microscope [27]. The samples are directly placed in the air between both carbon windows before closing the E-CELL.

With this equipment, atomic resolution can be achieved down to 0.21 nm in samples sandwiched between 2 carbon films windows, stuck on copper disks pierced with holes. Two different E-CELL(s) are used. The first one works at room temperature up to a gas pressure of 30 mbar and the sample directly lies on the bottom carbon window. The other one contains a heating wire able to operate between RT and 350°C, the sample is directly deposited on the heating wire, the maximal gas pressure is 10 mbar.

Au clusters were prepared by ultra high vacuum condensation of metal on amorphous carbon covering a copper disk pierced with small holes to be directly inserted in the sample holder of the microscope. Other samples were prepared by deposition precipitation on TiO₂ micro spheres (Degussa P25 with BET surface area = 45 m² g⁻¹, nonporous, 70% anatase and 30% rutile, purity > 99.5%), annealed at 400°C, then deposited on the carbon layer on the copper disk.

After the sealing of the sample holder with another copper disk covered with a carbon film, the samples were observed at room temperature in vacuum, then during cycles of reduction in H₂ and oxidation in O₂. The gas circulates between the 2 carbon films so that the catalysts are directly in the gas flow.

Fig. 7 a,b show the same Au cluster supported on carbon, in H₂ (left image), then in O₂ (right image), at the pressure 2 mbar. In both gases, the cluster keeps its original size. It is clearly faceted, limited by (111) and (001) faces in an H₂ environment, with an anisotropy ratio between the surface free energies $\sigma_{100}/\sigma_{111} = 1.15$ and more rounded in O₂, but (111) faces are still visible.

Similar experiments have been performed on Au clusters supported on TiO_2 . Fig. 8 a, b, c, d, e show the same Au cluster supported on TiO_2 , in vacuum just after the transfer to the microscope (left image 8a), then during H_2 circulation at 2 mbar (8b and c), and finally 10 sec after O_2 circulation at the same pressure (2 mbar), in fig. 8d, e. The same behaviour as with Au clusters supported on amorphous carbon is observed with this Au cluster supported on TiO_2 . H_2 induces faceting by (001) and (111) planes that corresponds to the Wulff shape, while O_2 induces rounding of the shape which can be interpreted by a strong interaction with oxygen.

From fig. 8c, the anisotropy ratio between the surface free energies is still estimated to be around 1.15, and the adhesion energy with the substrate to about 0.28 J.m^{-2} , whereas in fig. 8e, the formation of many facets with high order index is observed and the adhesion energy drops to 0.09 J.m^{-2} . The rounding of the shape observed in the case of an Au cluster supported on TiO_2 is more pronounced than in the case of Au supported on amorphous carbon.

As it is assumed that oxygen is chemisorbed on the edges, corners and defects of Au clusters and has little interaction with low index facets [3-6,18], this result needs comments. The same type of oxido-reduction cycles with environmental electron microscopy were performed with pure Pd particles supported on TiO_2 . In this case, the effect of oxygen was shown to flatten the particle shape, extend the (001) faces,

decrease the extension of the (111) faces and decrease the adhesion energy between the metal and the oxide support by a factor 2 or 3 [27]. These *in situ* results agree with the *ex situ* measurements previously performed after annealing of the Pd clusters in pure O_2 , then transfer to the microscope [25]. All these observations are in agreement with the flattening of the shape and the reduction of the adhesion energy, but no rounding was observed for Pd particles under oxygen. In both cases, with Au or Pd, the oxido reduction cycles have a reversible effect on the particles shapes.

A mass spectrometer was connected to the outlet of the sample holder of the microscope in order to analyse the reaction products at the exit of the chamber and get quantitative measurements of the reactivity of the samples. The volume of the E-CELL used for RT observations is of about 0.7 mm^3 , which is small enough to give indications on the catalytic activity of the samples.

In the case of Au/ TiO_2 catalysts, loaded in weight by 8% Au, with 0.5 mg of sample in the E-CELL, a mixture of CO, and O_2 diluted in N_2 at a total pressure of 4 mbar was used. From the measured quantity of produced CO_2 in the gas flow at the outlet of the E-CELL a conversion factor of about 1% was estimated. The calculated TOF (turnover frequency) is comparable to those measured in a conventional flow reactor for 3 nm Au clusters prepared by deposition precipitation on TiO_2 powders [17].

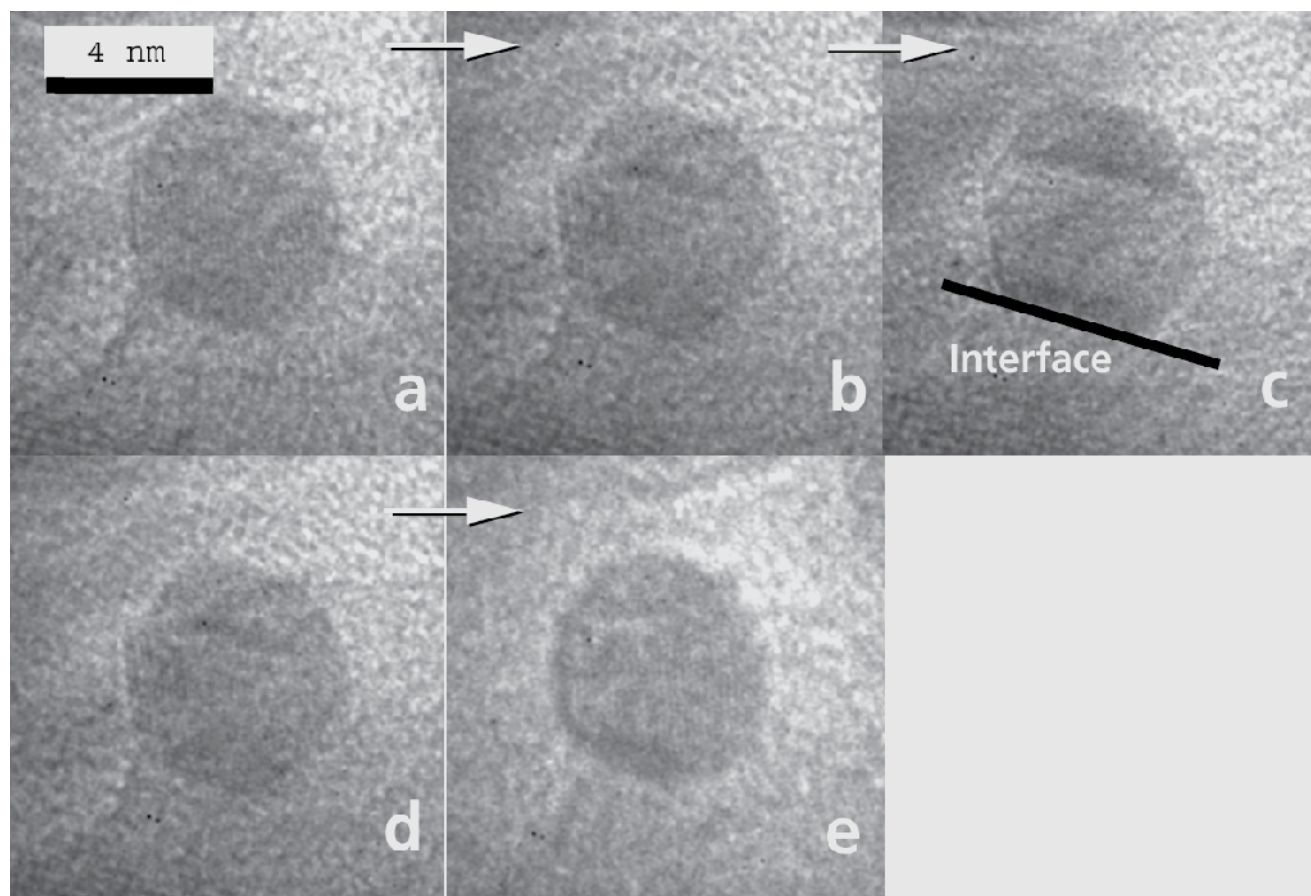


Figure 8

In situ gas treatments of the same Au cluster supported on TiO_2 , in vacuum (a), during circulation of H_2 (b, c) then during circulation of O_2 (d, e) at the pressure of 2 mbar, room temperature, by environmental electron microscopy. Time elapsed between each image: 10 sec

During the gas circulation, the shape variations observed are also the rounding of the Au clusters.

4 Discussion

The aim of this paper was to study by HRTEM the morphology and the adhesion of gold supported nanoparticles and also the influence of the particle morphology on the catalytic activity in the CO oxidation reaction. Previous work on *ex situ* HRTEM were reviewed and new results of *in situ* HRTEM (environmental TEM) were presented.

Au clusters grown in clean conditions (vacuum deposition) have a 3D shape on MgO microcubes. They present both (100) and (111) epitaxy in agreement with growth studies on extended MgO (100) surfaces obtained by cleavage under UHV [12]. This result is in contrast with the observation that Pd clusters grow exclusively in the (100) epitaxy [12, 25] and reflects the relatively weak adhesion energy of Au on MgO (0.5 J/m²) relatively to Pd on MgO (0.91 J.m⁻² [25]).

Au clusters grown in clean conditions on TiO₂ have a much stronger adhesion than on MgO. On TiO₂ - anatase an adhesion energy of 0.98 J.m⁻² is measured which is in agreement with the growth of Au on a TiO₂ -rutile (110) extended surface under UHV which results in an adhesion energy of around 0.9 J.m⁻² measured by Cosandey and Madey [43]. This large adhesion energy explains also the possibility to grow 2D gold clusters at low coverage [33, 43]. For Au clusters prepared by wet chemistry (deposition-precipitation method) a weaker adhesion energy was measured (around 0.3 J.m⁻²) which could be explained by the contamination of the substrate during the wet chemistry preparation.

By using the environmental cell (E-CELL) in the HRTEM it has been possible to observe the morphology of the same gold clusters during cycles of H₂ and O₂ gas treatments. Gold clusters deposited on amorphous carbon or TiO₂ exhibit under hydrogen (2 mbar) a truncated octahedron shape, which corresponds to the expected Wulff shape for a fcc crystal. Furthermore, the fact that the surface energy anisotropy $\sigma_{100}/\sigma_{111}$ is equal to 1.15 implies that a negligible quantity of hydrogen is adsorbed on the cluster. In presence of oxygen (2 mbar) the cluster shape rapidly becomes rounded and simultaneously the adhesion energy decreases. The later fact is in agreement with the dewetting of gold observed on Au/TiO₂ during treatment under oxygen [44]. The fact that the Au particles tend to become round under oxygen means that the oxygen interacts with the outer surface and not only on some low coordinated sites like edges and steps. Indeed calculations have shown that oxygen can be adsorbed on those low coordinated sites and not on the flat terraces [22]. However on small gold clusters it has been calculated by Monte Carlo methods that at RT there is a non-negligible fraction of adatoms on the facets (0.1 and 10⁻⁴ on {100} and on {111} facets, respectively) [45]. This result means that oxygen can also be chemisorbed on the facets of the gold clusters. It is possible that the chemisorption process

itself produces more adatoms then, more adsorbed oxygen and progressively the gold particles would become more and more rounded. The same hypothesis can also explain the time delay observed in the reactivity of small (1.5 nm) Au clusters on an extended MgO(100) surface [16]. Molecular beam experiments showed that on clean Au clusters, prepared under UHV, the activity is very small and after an induction period the activity increased up to a conversion factor of 50% then it stayed constant [16]. Thus, during the induction period, in the presence of an oxygen pressure, the Au clusters would become round and then more active for CO oxidation. In the present experiments with the environmental HRTEM, we have seen that circulating O₂, CO and N₂ in the E-CELL, the catalyst was active since CO₂ was produced and in the same time the gold clusters were also rounded.

In a previous study on the effect of calcination temperature on Au/TiO₂ catalysts prepared by deposition precipitation, it was shown by HRTEM that well faceted Au clusters were less active for CO oxidation than clusters with a rough outer shape [17]. This was explained by the presence of a high density of low coordinated sites on the later clusters [17].

In conclusion, the main result of this study is that the shape of supported Au clusters evolves under oxygen or during CO oxidation to become rounded. Under hydrogen the gold particles retrieve the faceted shape close to the Wulff polyhedron. We believe that this shape evolution in reaction condition is a key factor in the CO oxidation on nm-sized supported Au clusters. About the nature of the support, it has been shown that the adhesion of gold clusters is larger on TiO₂ than on MgO. In further studies we will compare the activity of these two systems in the same conditions.

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