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Oxidation of CO on Gold Supported Catalysts Prepared by Laser Vaporization: Direct Evidence of Support Contribution

S. Arrii, F. Morfin, A. J. Renouprez, and J. L. Rousset*

Contribution from the Institut de Recherches sur la Catalyse, 2 Av. A. Einstein, 69626 Villeurbanne Cedex

Received May 27, 2003; E-mail: rousset@catalyse.univ-lyon1.fr

Abstract: γ-Al_2O_3, ZrO_2, and TiO_2 gold supported model catalysts have been synthesized by laser vaporization. Structural characterization using Transmission Electron Microscopy and X-ray Photoelectron Spectroscopy experiments have shown that the gold clusters deposited on the different supports have similar distribution of size centered around 3 nm and are in the metallic state. However, X-ray photoemission measurements also indicate lower binding energies than the usual Au $4f_{7/2}$ at 84.0 eV for both alumina and titania supported catalysts, indicating a modification of the electronic structure of the metal. One has taken benefit of these features to study the influence of the nature of the support toward CO oxidation activities without being hindered by particle size or gold oxidic species effects. By comparing the activities of the different catalysts, it is concluded that the nature of the support directly affects the activity of gold. The following tendency is observed: titania and zirconia are superior to alumina as supports, titania being slightly better than zirconia. From XPS and activity results we can conclude that the existence of negatively charged clusters is not the key point to explain the high activity observed for Au/ZrO_2 and Au/TiO_2 catalysts and also that metallic Au is the major catalytically active phase. Hence, due to their very nature, titania and to a less extent zirconia should participate to the catalytic process.

Introduction

Gold has often been used as a component introduced in alloys to increase or modify the catalytic properties of an active metal. For example, in the hydroconversion of methylcyclopentane, Riahi et al.[1] have shown that the addition of gold to palladium or platinum enhances the activity of the pure metals, whereas the selectivity toward products resulting from ring expansion increases. Schmidt et al.[2] have also shown that $Pd_{0.8}Au_{0.2}$/Vulcan represents the most CO-tolerant catalyst in the potential range of interest for practical fuel cell application. Oxidation measurements have even shown the superior activity of PdAu at fuel-cell anode compared with a state-of-the-art PtRu catalyst.

Molenbroek et al.[3] have presented a detailed study of Ni–Au catalysts which in the steam reforming reaction have been proved to be more resistant toward carbon formation than pure Ni catalyst. Blocking highly reactive Ni edge and kink sites by Au atoms was assumed to be the reason for the increased robustness of the Ni–Au catalyst.

Nevertheless, the genuine catalytic properties of pure gold have been almost ignored until the pioneering work of Haruta et al.[4] which demonstrated the high activity of gold for CO oxidation at low temperatures. Other reactions such as Water Gas Shift reaction, propylene epoxidation, benzene total oxidation have also been shown to be catalyzed by gold.[5]

The discovery of gold efficiency in catalysis was at the origin of many publications devoted to the analysis of the different factors controlling the activity of gold based catalysts. Among them the most relevant appear to be the particle size, the nature of the support[6] and the preparation methods.[7,8] Depending on the pretreatment or preparation conditions, different oxidized or hydroxidized gold species have been detected on the surface of catalysts prepared by chemical methods.[8,9] These different oxidation states of gold have been claimed to be important for CO oxidation. Clearly, a distinction between support, size, and oxidation state effects on the reactivity is not straightforward. Indeed, the calcination step often needed to synthesize supported catalysts on different supports leads to different gold species and particle size showing that gold phases, support and particle size are interdependent. To circumvent this problem, Grunwaldt et al.[10] have used a colloidal route to prepare "size controlled" gold particles whose particle size is established before deposit on the oxide supports.

In the present study, we report for the first time on the activity of gold supported catalysts obtained by low energy cluster beam

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Table 1. Metal Loading and Mean Diameters of Fresh and Used Supported Catalysts Deduced Respectively from Chemical Analysis and TEM Experiments

sample	gold metal content (weight %)	mean diameter fresh catalysts (nm)[a]	mean diameter used catalysts (nm)[a]
$Au/\gamma\text{-}Al_2O_3$	0.08	2.6 (1.6)	3.1 (1.6)
Au/ZrO_2	0.05	2.9 (1.7)	3.8 (1.9)
Au/TiO_2	0.02	2.9 (1.7)	3.2 (1.3)

[a] The standard deviations are indicated in parentheses.

deposition onto high surface area oxides. The aim of this work is to determine the influence of the nature of the support toward CO oxidation without being hindered by particle size or oxidized gold species effects. Actually, these parameters strongly complicate the interpretation of the catalytic results and attempts to elucidate whether the activity is solely due to the gold nanoparticles or to the gold-support interface.

Experimental Section

Catalyst Preparation using Low-Energy Cluster Beam Deposition. The laser vaporization cluster source has been extensively described elsewhere.[11,12] The second harmonic of a Nd:YAG pulsed laser is used to vaporize the metal from the rod which creates a plasma. Cluster nucleation and growth occur when a continuous flux of inert gas (a mixture of He and Ar) is introduced into the vacuum chamber. Differential pumping extraction of the clusters through a skimmer yields a cluster beam which carries neutral and ionized species. The ionized clusters can be analyzed by time-of-flight mass spectrometry (TOFMS). After removal of the ionized clusters by electrostatic deflection, the neutral clusters are deposited on the substrates. Typical deposition rates (equivalent thickness) of about 10 nm/min are obtained with neutral clusters of various materials. The deposition rates were monitored using a quartz microbalance. To deposit the clusters on the supports, which in the present case are alumina, titania and zirconia powders, a device was developed which stirs the powder in front of the cluster beam. This device is expected to favor homogeneous cluster deposition on most of the powder grains. After deposition, the samples are air transferred, characterized, and/or used in catalytic reactions. For these experiments, a gold rod of 99.99% purity from Goodfellow was used. Approximately five grams of each alumina (Condea Puralox ScFa-215, 221 m^2/g), titania (Hombikat T100 20-S20 Type, anatase 60 m^2/g) and zirconia (MEL chemical, 79 m^2/g) supported catalyst were prepared. The metal content of each catalyst measured by chemical analysis (ICP or ICP−MS) is reported in Table 1.

Catalyst Characterization. Microscopy Experiments. The morphologic characterization of the supported clusters was performed with a JEOL JEM 2010-F Transmission Electron Microscope (TEM) operating at 200 kV. To obtain suitable samples for TEM characterization, the powders were dispersed in ethanol by ultrasonication. A drop of the solution was then deposited onto a thin holey-carbon film supported on a copper microscopy grid (200 mesh, 3.05 mm) and left to dry. The grains of powder containing the metallic particles are well separated and may thus be characterized by TEM to determine the size of the clusters and their distribution over the support. Because the size is an important parameter in the reactivity of gold we performed extractive replicas for each samples. Extractive replicas are needed whenever supports are not enough transparent to electrons and even if the support is thin enough, they enable a better contrast allowing to observe the smallest particles. In the present case, the catalysts are ultrasonically dispersed in a liquid and a drop of the suspension is deposited on freshly cleaved mica. After drying, the dispersed powder

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is covered by a carbon film. The mica sheet is then plunged into a solution containing a mixture of water (89%), acetone (10%) and hydrofluoric acid (1%). The acid concentration is chosen to dissolve the support without dissolving the metal particles.

X-ray Photoemission Spectroscopy. The XPS experiments were carried out in an ESCALAB 200R machine from Fisons Instruments, including a hemispherical analyzer and working at a pressure lower than 3×10^{-10} mbar. The metal loading of our catalysts are so low that the measurement of Au 4f core level binding energies were not possible with enough accuracy. To overcome this difficulty, small cluster deposits have been performed (equivalent deposited thickness, 0.4 nm) on self-supported disks obtained by pressing, without any additives, the three different oxide powders. XPS measurements were performed using the $Al_{k\alpha}$ line of the dual anode and a pass energy of 50 eV. In this case, the resolution of the spectrometer was better than 0.1 eV.

Catalytic Activity Measurements: Carbon Monoxide Oxidation. Activity measurements were carried out at atmospheric pressure in a continuous flow fixed bed reactor. The gas mixture consisted in 2% CO, 2% O_2 balanced in helium. For calibration, a gas mixture containing 3% CO, 3% CO_2, 6% O_2 in N_2 was used.

Gases were mixed with mass flow controllers (Brooks) calibrated for the above gases with a soap-bubble flow-meter. In this way, accurate and reproducible CO/O_2/He mixtures could be generated at a flow rate of typically 50 Nml/min. The gas mixture could then either be sent through the reactor or directly to the gas chromatograph for analysis.

The reactor consisted of a quartz tube located in a ceramic furnace. The reaction was temperature programmed between 30 and 420 °C with a heating (and cooling) rate of 1°/min. Several reaction cycles, each consisting of a heating and a cooling period, were recorded to monitor possible hysteresis, deactivation or activation. The weight of the catalyst bed ranged from 800 to 1200 mg, which resulted in a length of ~15 mm. Product analysis were carried out on-line with a VARIAN−Micro GC (CP2003) equipped with a TCD detector. Two columns were used in parallel: a Molsieve 5A column (Ar as carrier gas) to quantify O_2 and CO, and a poraPLOT Q column (He as carrier gas) to quantify CO_2. Both columns were operated at 50 °C. The usual procedure was used to verify that the activity was measured in the kinetic regime by varying the flow rates and the mass of catalyst in the same proportions to provide a constant contact time, and consequently a constant space velocity. The conversion does not vary as the mass flow is changed, indicating that the measured rate is not limited by external transfers (film diffusion).

Results

Transmission Electron Microscopy Experiments. Electron Microscopy experiments have been performed on each catalyst before and after reaction.

The photographs at both stages are displayed respectively in Figure 1 for Au/Al_2O_3, Au/ZrO_2, and Au/TiO_2 catalysts. Since the size is an important parameter to determine the activity of gold we have performed extractive replicas for ZrO_2 and TiO_2 supports which are not transparent enough to electrons to visualize precisely the smallest particles.

The size histograms, deduced from these images are respectively shown in Figures 2 and 3 before and after reaction.

The mean particle diameters d_m were calculated from size histograms with the following formula

$$d_m = \frac{\sum_i (x_i \cdot d_i)}{\sum_i x_i}$$

where x_i is the number of particles with diameter d_i.
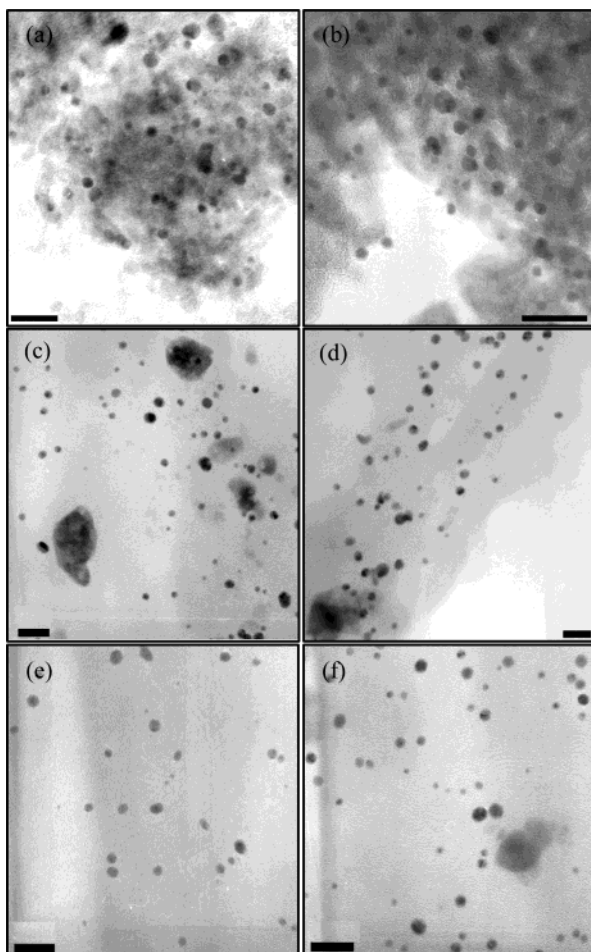
Figure 1. TEM images of (a) Au/γ-Al₂O₃, (c) Au/ZrO₂, and (e) Au/TiO₂ fresh catalysts and after reaction (right side). The scale bars are 20 nm.
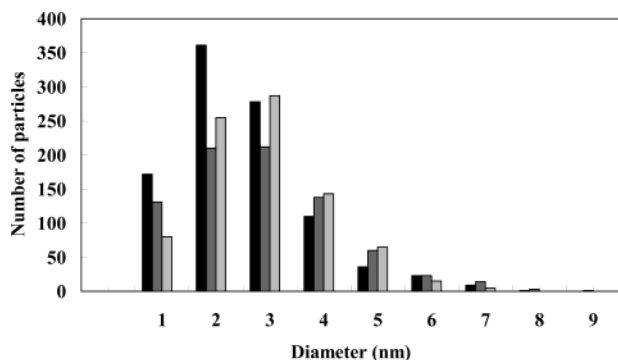

Figure 2. Size distribution histograms of gold clusters before reaction. Au/γ-Al₂O₃ (black), Au/ZrO₂ (dark gray) and Au/TiO₂ (light gray).

The corresponding standard deviation σ was calculated using the following equation

$$\sigma = \sqrt{\dfrac{\sum_i (x_i \cdot (d_m - d_i)^2)}{\sum_i x_i - 1}}$$

For the fresh samples (before reaction), the mean particle sizes and standard deviation were found to be nearly identical within 10% (Table 1). This indicates that the vaporization source produces clusters of the same size whatever the support.
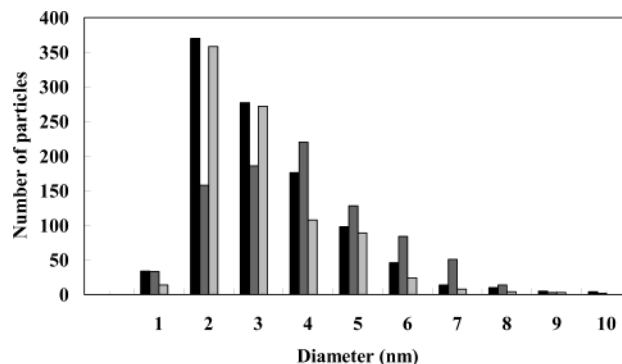

Figure 3. Size distribution histograms of gold clusters after reaction. Au/γ-Al₂O₃ (black), Au/ZrO₂ (dark gray) and Au/TiO₂ (light gray).
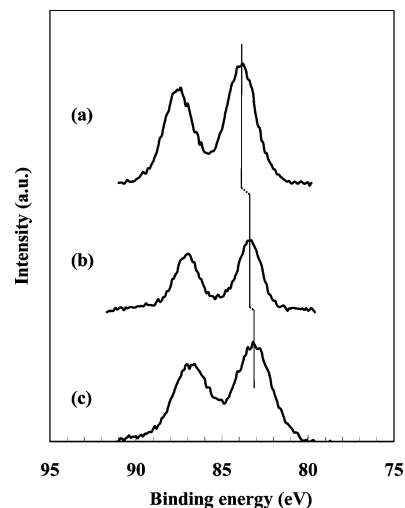

Figure 4. XPS spectra of Au 4f of fresh Au/ZrO₂ (a), Au/TiO₂ (b), and Au/γ-Al₂O₃ (c) catalysts.

This was, of course, expected because the clusters are produced before deposit. After reaction, TEM showed that the crystallites have a mean diameter slightly larger than that of the fresh catalysts (Table 1) and also that the sintering depends only slightly on the nature of the support.

As the catalytic properties vary appreciably only between the first and second catalytic cycle, one can deduce that the observed increase of the mean particle size has already occurred during the first annealing treatment and not during the following reaction cycles. Later on, the structure of the catalysts does not undergo any further change.

These results clearly demonstrate that the laser vaporization source constitutes a precious tool to investigate the effect of the support on the reactivity with only limited size effects.

X-ray Photoemission Analysis: Influence of the Nature of the Support and of Reaction Conditions. To get a closer insight into the interaction between gold particles and their supports, the characteristics of the Au 4f XPS peaks before and after reaction were compared. For this purpose, the three pellets (see the Experimental Section) were characterized either for "fresh catalyst" or after having been submitted to the conditions of the reaction. The Au 4f XPS spectra of the catalysts before and after reaction are shown in Figures 4 and 5.

The binding energy scale was corrected for surface charging by taking the C1s peak of contaminant carbon as a reference at 285.0 eV.[8,9] Table 2 indicates the binding energies obtained on all the investigated samples.
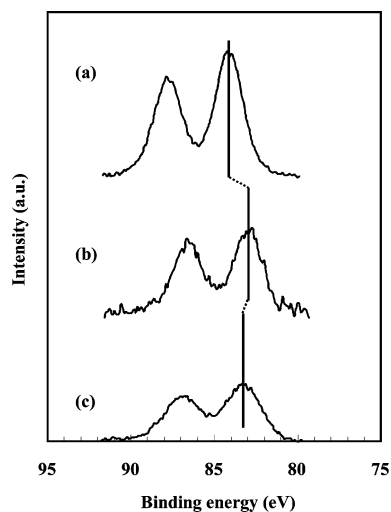
Figure 5. XPS spectra of Au 4f for used Au/ZrO$_2$ (a), Au/TiO$_2$ (b), and Au/γ-Al$_2$O$_3$ (c) catalysts.

Table 2. Au 4f$_{7/2}$ Binding Energies of Supported Particles Also with Al 2p$_{3/2}$, Zr 3d$_{5/2}$, and Ti 2p$_{3/2}$ Binding Energies from the Supports

	sample	Au 4f$_{7/2}$ BE (eV)	Al 2p$_{3/2}$ (eV)	Zr 3d$_{5/2}$ (eV)	Ti 2p$_{3/2}$ (eV)
Au/Al$_2$O$_3$	fresh	83.1	74.5		
	after reaction	83.3	74.3		
Au/ZrO$_2$	fresh	83.9		182.4	
	after reaction	84.1		182.5	
Au/TiO$_2$	fresh	83.4			458.8
	after reaction	82.9			459.2

We first note that for the fresh catalysts, the correction for surface charging effects leads to Al 2p, Ti 2p, and Zr 3d binding energies very close to those generally observed for pure Al$_2$O$_3$, TiO$_2$, and ZrO$_2$ oxides. This gives confidence in our charge correction procedure. Interestingly, important shifts of the binding energy toward lower values are observed for titania and alumina gold supported particles. On the contrary, no shift was observed for gold particles deposited on zirconia. One should note that for both zirconia and titania supports, our results agree quantitatively well with those of Claus et al.[13,14] Afterward, the influence of the reactive conditions (heating under reactive atmosphere) on the Au spectra of the different samples were studied. No significant modifications were detected for either alumina or zirconia supported catalysts.

Conversely, on titania, an additional shift of 0.5 eV to lower binding energy of the Au 4f peak is observed resulting in a binding energy of Au 4f at 82.9 eV, together with a positive shift of 0.4 eV of the Ti 2p.

Catalytic Activity of Al$_2$O$_3$, ZrO$_2$, and TiO$_2$ Gold Supported Catalysts. Most gold catalysts prepared by chemical ways are generally stabilized and/or activated in oxygen or air at temperatures up to 700 K. In the present case, no calcination or reduction steps are needed since the deposited clusters are assumed to be ligand free. Hence, all the catalytic tests have been performed on the fresh catalysts without any pretreatment.

Figures 6 and 7 display the catalytic activities for CO oxidation as a function of the temperature up to 420 °C. This
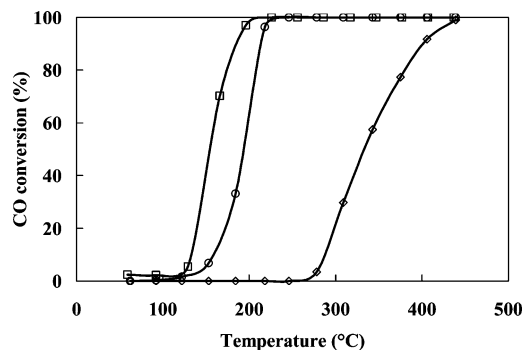
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Figure 6. Temperature effects on CO oxidation on the fresh gold catalysts for the first heating. Au/γ-Al$_2$O$_3$ ($\diamond$), Au/ZrO$_2$ ($\circ$) and Au/TiO$_2$ ($\square$).
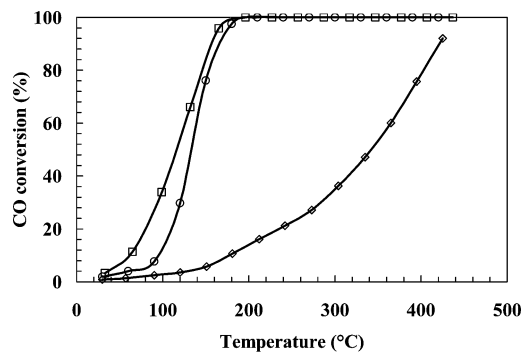
Figure 7. Temperature effects on CO oxidation over gold catalysts for the second heating. Au/γ-Al$_2$O$_3$ ($\diamond$), Au/ZrO$_2$ ($\circ$) and Au/TiO$_2$ ($\square$).

rather high temperature is needed to achieve, under the same reaction conditions, a 100% conversion with the Au/γ-Al$_2$O$_3$ sample. The same heating and cooling cycles were applied to the different catalysts. Figure 6 shows the effect of temperature during the first heating of the fresh catalysts. Marked differences in activities between titania, zirconia, and alumina supported catalysts are already observed.

Indeed, the temperatures for half CO conversion, $T_{1/2}$, are 140, 190, and 330 °C for Au deposited on TiO$_2$, ZrO$_2$, and Al$_2$O$_3$ respectively. As mentioned above, several reaction cycles, each consisting of a heating and a cooling period, were performed to evidence possible hysteresis, deactivation, or activation. Actually, an activation is observed between the first and second cycles. Later on, no modification of the catalytic activity was observed for further cycles, indicating a stabilization of the catalysts. The results corresponding to the second cycle are displayed in Figure 7. The half conversion temperatures are now slightly lower for all the catalysts, 120, 130, and 300 °C respectively for gold deposited on titania, zirconia, and alumina support.

To check for a possible deactivation, the effect of time on stream was measured on the most active catalyst, Au/TiO$_2$, in two different ways. First, immediately after three heating and cooling cycles, the temperature was increased up to 120 °C under the reactive mixture and then kept constant during 70 h. Figure 8 shows that no deactivation occurs. Second, the fresh sample has been heated to 160 °C under reactive atmosphere and then kept in steady-state conditions.

As shown in Figure 8, after a brief activation period, similar to that already observed between the first and second cycle, the conversion reaches 98% and the sample never deactivates during time on stream.
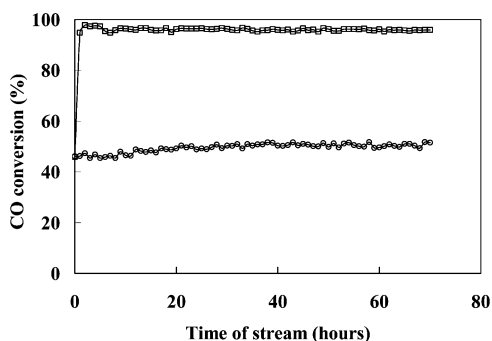
Figure 8. CO conversion as a function of time on steam for the fresh Au/TiO$_2$ catalyst at 160 °C (□) and for the used Au/TiO$_2$ (○) catalyst (after three heating and cooling cycles) at 120 °C.

Discussion

The physical properties and reactivity of gold nanoparticles deposited on γ-Al$_2$O$_3$, ZrO$_2$, and TiO$_2$, synthesized with this physical method can be compared with those of catalysts obtained by chemical preparations such as CVD, impregnation or deposition precipitation. Because the gold particles are produced before deposits, the particle size distributions are similar on the different supports. Moreover, XPS analysis has shown that gold is in a metallic state because no peaks corresponding to oxidized species, located around 85.5 and 86.3 eV,[9] have been detected. However, surprisingly, XPS shows significant shifts of the Au 4f$_{7/2}$ peaks toward lower binding energies, with respect to the value of 84.0 eV for bulk metallic gold, for both particles deposited on γ-Al$_2$O$_3$ and TiO$_2$ supports. On the contrary, only a slight shift was observed with the ZrO$_2$ support. The results concerning Au/TiO$_2$ and Au/ZrO$_2$ agree *quantitatively* well with recent results of Radnik et al.[13] and of Schimpf et al.[14] They have observed a clear dependence of the Au 4f$_{7/2}$ binding energies on the kind of the support. The lowest Au 4f$_{7/2}$ electron binding energy levels have actually been found for SiO$_2$ (83.2 eV) and TiO$_2$ (83.0 eV) supported catalysts. In contrast, for gold particles deposited on ZrO$_2$, a binding energy close to that of bulk metallic gold was measured.

It is well-known that the Au 4f$_{7/2}$ electrons of surface Au atoms have a binding energy lower than that of bulk atoms and these values should decrease for decreasing coordination number. Indeed, the Au 4f$_{7/2}$ surface core level shift (SCLS) has been studied experimentally and values of −0.35, −0.35, and −0.38 eV have been reported[15] for the Au(111), (110)−(2 × 1), and (100) surface orientations respectively. Coordination numbers as small as 7 to 9 are thus required to observe such a negative SCLS in the particles. This can only be achieved either by the presence of ultra small clusters (<1 nm) or for flat, unidimensional particles. Both possibilities were discarded by electron microscopy: it has indeed been shown that the particle diameter is well above 1 nm whatever the support and that they have an isotropic shape.

Alternatively, because the SCLS even for open surfaces are roughly only equal to −0.4 eV, it seems that electron transfer from the substrate to the particle should significantly contribute to the observed shift, this latter effect leading also to a shift to lower core level binding energies. Actually, electronic structure differences between the supports can play a role in the gold

support interaction. Looking at the literature data for TiO$_2$ based systems, it appears that a small concentration of electrically active donor-type defects arises from randomly distributed oxygen vacancies.[16] These intrinsic defects lead to the appearance of occupied electronic states located just below (0.3 eV) the bottom of the conduction band.[17] From earlier studies, it is fairly well established that these filled band gap surface defect states correspond to Ti^{3+}.[18] Moreover a value of 3.9 eV for the electron affinity (i.e. the gap energy between the vacuum level and the bottom of the conduction band) of TiO$_2$ has been reported by Konenkamp.[19] The above arguments lead to a typical work function value of about 4.2 eV for surface defective TiO$_2$, whereas the work function of 3 nm gold nanoparticles is 5.0 eV.[20] According to simple work function arguments, an electron transfer from Ti^{3+} to Au clusters is thus expected to occur. Zwijenburg et al.[21] have determined the binding energies of the Au 4f$_{7/2}$ level and the Auger parameter of gold clusters supported on TiO$_2$. Using Auger parameter and binding energy values, the initial and final state contributions to the Au 4f$_{7/2}$ binding energy shift have be separated. The initial-state effect observed in their experiment was found to be −0.90 eV i.e., much larger than the expected value for SCLS (−0.4 eV), whereas the change of the final-state relaxation energy was only −0.14 eV indicating that the gold particles are almost metallic. Moreover, the TEM experiments show that the particle diameter is about 5 nm i.e., with approximately 20% of the atoms located at the surface. This allows to conclude that the initial state effect they observed cannot be solely due to surface effects. Alternatively, a charge transfer from the substrate to the Au particles would better explain the sign and the magnitude of the initial state effect.

Concerning the zirconia support, recent calculations performed by Foster et al.[22,23] provide quantitative energy level values of oxygen vacancies in neutral, singly or doubly charged states. These neutral (V^0) or singly (V^+) and doubly (V^{2+}) charged vacancy levels were found at respectively at 3.2, 3.33, and 3.54 eV below the bottom of the conduction band, itself located at 1.8 eV below the vacuum level.[24] Hence, V^0, V^+, and V^{2+} energy levels are located respectively at 5.0, 5.1, and 5.3 eV below the level of vacuum. These values are very close to the work function of the gold particles and could only lead to a very small electron transfer *from the particles to the support*.

Zafeiratos et al.[25] have determined experimentally the binding energy of the Au 4f$_{7/2}$ level and the Auger parameter on very small particles on ZrO$_2$ (obtained by the evaporation of 0.25 monolayer (ML) of gold). For such particles, most of the atoms are located at the surface i.e., with a mean coordination number close to 7. The initial state effect observed in their experiment

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was equal to −0.49 eV i.e., very close to the value (−0.4 eV) of the SCLS. Hence, the initial state shifts measured on these small clusters were interpreted as surface core level shifts reflecting the reduced average coordination number of Au atoms. This result corroborates our conclusion that no charge transfer occurs between ZrO_2 and gold particles.

Hence, the above arguments provide possible explanations for the observed Au $4f_{7/2}$ binding energies of both Au/TiO_2 and Au/ZrO_2 catalysts.

γ-Al_2O_3 is a basically irreducible large band gap insulator. Thus, electronic interactions with gold nanoparticles could not easily be due to oxygen vacancies and related electronic states. Nevertheless, strong metal substrate interactions between different metals and alumina have been already reported.[26−28] The observed initial state shift was in each case associated with electron transfer in the substrate to cluster direction. In the study by Ealet and Gillet,[28] a correlation between the charge transfer and electronegativity of the deposited metals has been shown. For metal which has an electronegativity close to that of oxygen and higher than that of aluminum ions of the support oxide (this is the case of gold), the interface phenomena involve an electronic interaction between metal atoms and the cation of the surface. This is due to the fact that metal atoms (gold in this case) act as electron-acceptors with respect to aluminum ions and thus compete with oxygen atoms on the surface. Hence, an electron transfer from alumina to gold particles could explain the large Au $4f_{7/2}$ binding energy shift observed in our XPS experiments.

The infrared study of CO adsorption is widely used as a probe for electronic structure modifications of the substrate. Indeed, a negative charge on the clusters should induce a significant shift of the CO band stretching frequencies to lower wavenumbers. This phenomenon is related to the metal back-donation into the $2\pi^*$ orbitals of the adsorbed CO. Such an effect has been observed by Boccuzzi et al.,[29] who carried out an infrared study of CO adsorbed on gold nanoparticles supported on titania. These authors have observed on reduced samples a new band in the 2050 to 1900 cm^{-1} frequency range assigned to CO linearly and bridge bonded on negatively charged small gold clusters. This band is located at lower frequency than the band centered around 2100 cm^{-1} generally assigned to CO molecules adsorbed in on top position on three-dimensional gold metallic particles.

To our knowledge, only few results mention low-frequency bands for CO molecules adsorbed on Au/γ-Al_2O_3 supports. Pestryakov et al.[30] have reported results of IR spectroscopy of CO on 5 wt % Au/γ-Al_2O_3. After a reducing treatment of the sample with hydrogen, they have observed an intense band at 2118 cm^{-1} and a double band at 2050−2060 cm^{-1} assigned by the authors to surface carbonyls of metallic (Au^0) gold. So, a clear evidence of negatively charged gold particles on alumina support has not yet been provided by IR spectroscopy with CO molecule as a probe.

One can wonder about the effect of charge on the O_2 activation or dissociation since this activation is a critical step

of the reaction. Only ultra small clusters have been experimentally and theoretically studied for this purpose.[20,31−34] It has been shown that the binding of O_2 to Au_n clusters is different (lower) from that on Au_n^-, suggesting that charging a supported cluster increases its reactivity with respect to oxygen.

More precisely, activation of O_2 on gold clusters is a consequence of the charge transfer from Au to the antibonding π^* orbital of O_2. The binding energy of oxygen to Au_n or Au_n^- actually depends on the parity of the number of electrons in the cluster. This binding is strong when the number of electrons is odd. A plausible explanation[34] is that the clusters with an odd number of electrons have a smaller ionization potential, promoting the availability of the electrons of the HOMO. Measurements performed in the gas phase by Salisbury et al.[20] on Au_n^- anions ($n = 2...22$) show a similar behavior also explained by a correlation between a low electron affinity of the cluster and its high reactivity with oxygen. Of course, the addition of one electron to a small cluster with discrete and well-separated energy level could affect drastically the energy level of the HOMO. On the contrary, for larger clusters, with thousands of atoms, the average spacing of the level around the Fermi level E_f is approaching a continuum,[35] and additional electrons should not, in principle, modify appreciably their Fermi level at least for transition metals with d states at E_f. However, gold is a noble metal with a small density of states at E_f. Hence, contrary to transition metals, a charge transfer could lead to a rather significant energy shift of E_f and a somewhat better reactivity toward O_2 molecules.

Comparing the activities of the different catalysts, it immediately appears that the nature of the support directly affects the activity of gold. The following tendency is observed: titania and zirconia are superior to alumina as a support, titania being slightly better than zirconia. After the first heating and cooling cycle which slightly activates and stabilizes the catalysts, the different turnover frequencies (TOF) of Au/TiO_2 and Au/ZrO_2 can be easily compared. The TOF based on surface gold atoms (assuming a spherical shape) were deduced from size histograms obtained after reaction and activity measurements. At 393 K, the TOF of Au/TiO_2 reaches 1.1 s^{-1}, i.e., 4 times that of the TOF calculated for Au/ZrO_2 (0.28 s^{-1}). The activity of these low loaded titania and zirconia gold catalysts prepared by a physical method are thus comparable to that of the most active catalysts reported in the literature.[6,36,37] Such a support effect was also reported by Grunwaldt et al.[10] who found the activity of a titania supported gold catalyst to be 1 order of magnitude higher than that of Au/ZrO_2. However, this support effect was also shown to be dependent on the treatment procedure. In the present case, support effects exist but are obviously less pronounced. For Au/γ-Al_2O_3, the TOF is equal to 0.28 s^{-1} at 573 K. The extrapolation of this latter value to 393 K with activation energy E_a comprised between 15 and 30 kJ/mol leads to lower TOF comprised between 6.7 × 10^{-2} s^{-1} and 1.6 ×

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10^{-2} s^{-1}. These results agree entirely with the classification of supports proposed by Schubert et al.[6] into two categories: "inert" and "active" materials. The first category, which includes γ-Al$_2$O$_3$, is characterized by the nonreducibility and their low ability to adsorb or store oxygen. The second one, which includes TiO$_2$ and to a lower extent ZrO$_2$, is composed of reducible oxides.

In any case, the above XPS and activity results show that metal support interactions are present. If metal particles work as the active phase, with the support modifying their electronic structure through electron transfer, we should observe comparable activities for Au/γ-Al$_2$O$_3$ and Au/TiO$_2$ catalysts. This is obviously not the case. Concerning Au/ZrO$_2$, which exhibits a rather high activity, XPS experiments have shown that gold clusters are quasi-neutral indicating that a charged cluster is not necessary to provide high activity,[38] even if charging may also help.[31] Hence, the particle-support perimeter should be the scene of cooperative effects where both the support and the metal participate to the catalytic process.. This implies that the nature of the support itself is much more important, with respect to the activity, than the electronic modifications induced on the gold particles. Moreover, it is unlikely that oxidized Au species would be the main active phases because the activity of the present Au/TiO$_2$ and Au/ZrO$_2$ catalysts, *which only contain metallic gold*, compare well with the most active supported catalysts described in the literature.

Most catalysts are highly efficient during a short period of time and some gold catalysts such as Au/TiO$_2$,[39,8] Au/Fe$_2$O$_3$,[9] Au/ZrO$_2$,[40] and Au/MnO$_x$ rapidly deactivate. Deactivation has been related to sintering or accumulation of carbonate-like species on the catalyst.[35-38] Also the decrease of activity was assigned to the reduction of oxidized gold species which have been claimed to be the most active sites for CO oxidation.[8,9,40]

In our case, stability tests have thus been performed on both the fresh and used Au/TiO$_2$ catalysts (see Figure 8). No deactivation was observed on either systems during 70 h. This result has to be related to the TEM and XPS results. From TEM experiments, one does not notice any significant sintering even after a heat treatment up to 420 °C. The comparison of XPS results on fresh and used sample did not show any modification of the gold oxidation state during the reaction. One has to note that the stability tests were performed at 120 °C and 160 ° C, temperatures at which surface carbonate species should be already desorbed.[45,46]

Conclusion

Gold nanoparticles with diameters of about 3 nm were synthesized by laser vaporization and deposited with low kinetic energy on TiO$_2$, γ-Al$_2$O$_3$, and ZrO$_2$ powder supports. The structural and catalytic properties of the as prepared supported catalysts have been compared. TEM investigations carried out before and after reaction showed only a slight increase of the crystallite size during the reaction with size distributions rather similar whatever the support. As evidenced by XPS, the particles are in a metallic state and metal support interactions exists, especially with alumina and titania. These interactions have been ascribed to a charge transfer in the substrate to cluster direction. The analysis of our activity results clearly shows that the existence of negatively charged clusters is not the key point to explain the high observed activities of Au/ZrO$_2$ and Au/TiO$_2$ catalysts. A synergetic or cooperative effect between the TiO$_2$ and ZrO$_2$ supports and the metal particles is indeed more likely. Moreover, thanks to the joint results of XPS experiments and activity tests, we conclude that oxidic Au species are not the major catalytically active phases because the activities of the present Au/TiO$_2$ and Au/ZrO$_2$ catalysts, which solely contain metallic gold, compare well with the most active supported catalysts.

Finally, the ability of the laser vaporization to produce gold particle with similar sizes on different supports provides a rigorous way to study the effects of the supports on the reactivity. We will soon report on the synergistic effects between titanium oxide and gold observed on supported Au−Ti clusters produced by this laser method.

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