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LETTERS

FTIR, UV−Vis, and HRTEM Study of Au/ZrO_2 Catalyst: Reduced Reactivity in the $CO-O_2$ Reaction of Electron-Deficient Gold Sites Present on the Used Samples

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A Fourier transform infrared (FTIR), UV−vis, and high-resolution transmission electron microscopy (HRTEM) study of fresh and used Au/ZrO_2 catalyst is reported. FTIR data show that on a fresh sample CO is adsorbed on regular gold metallic sites, while on the used sample the adsorption sites are bidimensional gold clusters made positive by interaction with the support. NIR−UV−vis reflectance spectra show that the gold plasmonic peak appears broader and the ZrO_2 absorption edge weaker on the used sample with respect to the fresh one. HRTEM indicates the disappearance of the gold metallic particles in the used catalysts. Moreover, a strong reduction in the CO oxidation activity has been evidenced on the used sample and ascribed to the positivization of gold and/or to the decrease of the number of highly uncoordinated gold sites, consistently with the spreading of gold at the support surface.

1. Introduction

Gold did not attract much attention in heterogeneous catalysis until 10 years ago because of its chemical inertness and because of the difficulty to obtain highly dispersed samples. In the last 10 years, several methods have been described by Haruta et al.[1] for the preparation of small gold particles. The same authors have shown that gold is remarkably active for low-temperature CO oxidation when it is well dispersed on some metal oxides or hydroxides of alkaline earth metals.[2] Gold catalysts are now being studied intensively also for their low-temperature activity in the water gas-shift reaction[3] and for other reactions such as the catalytic combustion of hydrocarbons, NO reduction, hydrogenation of carbon oxides, etc.[4]

As for the CO oxidation mechanism, on the basis of FTIR studies of this reaction on Au/ZnO and Au/TiO_2, it was concluded that the reaction occurs mainly on small gold particles, where oxygen and carbon monoxide are adsorbed in close contact.[5] No clear explanation has been found to date for the different catalytic properties observed in samples containing gold particles of similar size, supported on a variety of supports,[6] or for the deactivation observed on some supports such as ZrO_2.[7,8] The problem is probably that, up to now, there is not enough information at the atomic level on the metal−oxide interfaces, on the electronic character of the metal atoms present at these interfaces, and on how the contact with the oxide interface can be influenced by physical and chemical treatments. Provided that small particles must be considered a priori as out of equilibrium, modifications of the interfacial and surface energies can occur depending on the gas-phase composition and temperature. In this respect, different phenomena have been evidenced such as particle coalescence, migration, spreading, breaking, encapsulation, alloying, and dissolution, depending on the nature of the metal, on the surface stoichiometry of the oxide, and on the gas composition. As for gold samples, since gold is the least reactive and the noblest of all metals, only coalescence phenomena are generally expected. In this work, we report some results that evidence the occurrence of irreversible effects on the properties of an Au/ZrO_2 sample upon

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reduction and oxidation treatments under mild conditions that, quite unexpectedly, give rise to electropositive gold surface sites.

2. Experimental Section

The catalysts were prepared by deposition−precipitation on ZrO_2 obtained by hydrolysis of zirconium oxycloride with ammonia. The support was suspended in an aqueous solution of $HAuCl_4$, followed by neutralization with Na_2CO_3 (pH 7.5) and aging in suspension at 343 K for 2 h. After drying at 383 K, the samples were calcined at 673 K for 2 h. Metal chemical analysis was performed by atomic absorption spectroscopy. Gold loading is 1.72 wt %.

FTIR spectra were recorded with a 1760 Perkin-Elmer FTIR spectrometer at 298 K. The powders were pressed in pellets and subjected, directly in the IR cell, to different thermal and chemical treatments. The sample simply pretreated in oxygen up to 673 K will be termed "fresh", the sample heated first in oxygen at 673 K, contacted with 15 mbar of hydrogen for 30 min and with 15 mbar of oxygen for 30 min at 353 K, and finally treated in oxygen at 673 K, will be termed "used".

HRTEM images were made with a JEOL 2000 EX electron microscope, equipped with a top entry stage and a LaB_6 filament. The powder was ultrasonically dispersed in *n*-heptane, and the suspension was deposited on a copper grid, coated with a porous carbon film. The residual vacuum at the specimen region was approximately 1×10^{-6} mbar.

UV−vis near-infrared (NIR) diffuse reflectance experiments have been performed with a Varian CARY5 spectrometer.

3. Results and Discussion

In Figure 1 the FTIR spectra of CO adsorbed on fresh and used Au/ZrO_2 catalysts are displayed: in part **a** the spectra obtained by interaction with 10 mbar of CO on the two samples are compared, in parts **b** and **c** the evolution of the spectra when the equilibrium CO pressure decreases from 10 to 0.05 mbar on the fresh and used samples is reported, respectively.

Two main bands are evident in both spectra reported in Figure 1a. The first one, at 2193 cm^{-1} on the fresh sample and assigned to the CO adsorbed on Zr^{4+} surface sites, exhibits only a very small frequency shift in the used sample while the other one, at 2108 cm^{-1} on the fresh sample and assigned to CO adsorbed on Au^0 surface sites, is abruptly shifted up to 2140 cm^{-1} on the used one. The large difference in the intensity ratio of the bands at 2193 and 2140 cm^{-1} in the spectra taken under 10 mbar of CO, reported in Figure 1a and 1c can be explained by taking in account that the spectra shown in Figure 1c have been taken at the end of the CO−O_2 interaction, shown below, and that, after this reaction, a large fraction of the surface Zr^{4+} ions is masked by carbonate species.

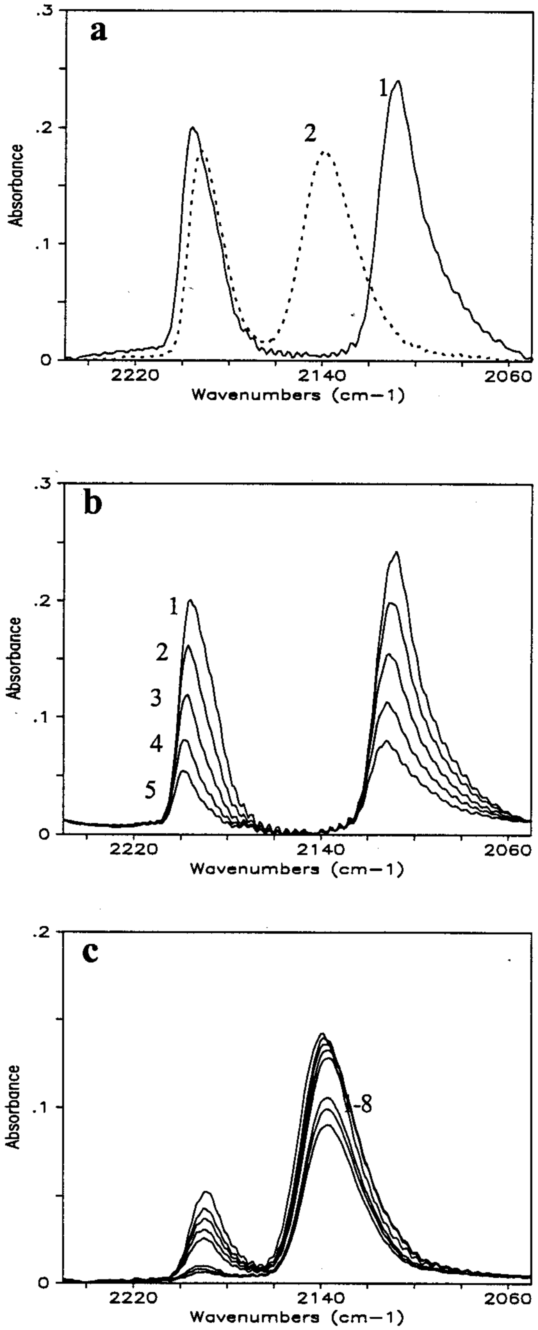

Figure 1. FTIR absorbance spectra of CO adsorbed on fresh and used Au/ZrO_2 samples. (a) Curve 1, 10 mbar on fresh sample; curve 2, 10 mbar on used sample. (b) Spectra of CO adsorbed on the fresh sample taken at decreasing CO equilibrium pressures, from 10 to 0.05 mbar (curves 1−5). (c) Spectra of CO adsorbed on the used sample taken at decreasing CO equilibrium pressures, from 10 to 0.05 mbar (curves 1−8).

Looking at the spectra reported in Figure 1b and 1c another difference can be observed: on the fresh sample (part b) the intensities of both absorptions smoothly decrease in parallel by decreasing the equilibrium pressure and both absorption blue-shift, while on the used sample (part c) the band at 2140 cm^{-1} appears as significantly more resistant to outgassing than the 2108 cm^{-1} one and exhibits, by decreasing the coverage, a red shift. A recent paper[9] concerning the FTIR study of CO adsorbed on the Au (332) surface reported bands in the 2100−2120 cm^{-1} range with blue-shifting due to decreasing coverage, similar to the behavior exhibited by our fresh sample, by some polycrystalline gold films studied by Dumas,[10] and by gold small particles on other supports.[11] These studies clearly show that metallic gold exhibits a behavior similar to that of metallic copper. From the wide literature concerning the CO chemisorption on monocrystalline and dispersed copper samples, it is well known that the IR band of CO adsorbed on oxidized copper sites is usually blue-shifted with respect to that of reduced samples and it is less reversible upon outgassing.[12] Bands significantly blue-shifted with respect to those observed on extended surfaces have been detected also in very small copper clusters or copper ultrathin films deposited on different substrates.[13] They have been interpreted as due to the CO chemisorption on copper sites where there is a charge polarization away from CO. Similar polarization effects occur also when Cu atoms and/or two-dimensional Cu clusters are deposited at the surface of an oxidic support.[14] On this basis it can

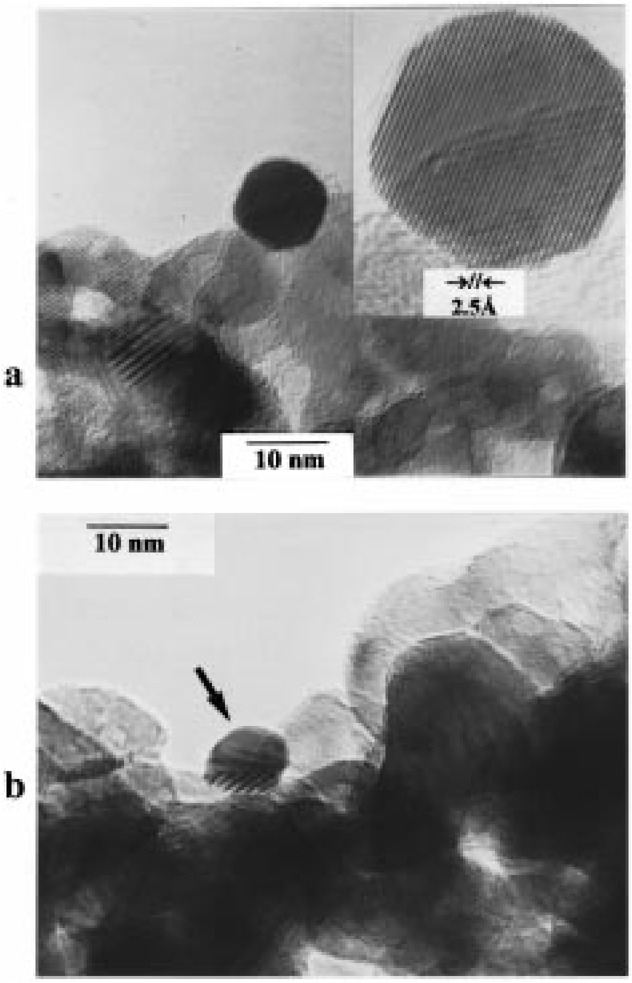

Figure 2. HRTEM micrographs of fresh (a) and used (b) Au/ZrO$_2$ samples.

be hypothesized that the band at 2140 cm^{-1} observed on the used Au/ZrO$_2$ sample is due to CO adsorption on Au bidimensional clusters made positive by interaction with the support.

Recently,[15] a CO absorption band has been detected at a very similar frequency and with a similar resistance to outgassing on a Au/HY sample. This band was assigned to CO adsorbed on Au$^{\delta+}$ sites produced on gold particles by interaction with the acidic protons inside the framework of HY zeolite. For the Au/HY sample, a shoulder at 2110−2120 cm^{-1} is also present, assigned to CO adsorbed on neutral gold sites exposed at the surface of big crystallites, probably located on the external zeolite surface. In our case the 2108 cm^{-1} band is almost completely lacking; however, the surface hydroxyls of the oxidic support do not appear to be involved in the Au$^{\delta+}$ sites formation, in fact, the spectra of both the fresh and the used sample (not shown for sake of brevity) are almost identical.

To find an explanation for these findings, in Figure 2 the electron micrographs of the fresh (Figure 2a) and used (Figure 2b) sample are shown. Figure 2a refers to the Au/ZrO$_2$ fresh catalyst: there is a high incidence of fringe patterns, typical of the ZrO$_2$ monoclinic modification and metallic particles, showing a roundish shape of about 10−15 nm average diameter (the statistics have been made on different images, not reported for sake of brevity). The almost hexagonal particle reported in the inset to Figure 2a, by inspection of the fringes, can be ascribed to a gold particle exposing mainly (111) faces. In Figure 2b a micrograph relative to a used Au/ZrO$_2$ catalyst is reported. On one hand, it can be said that the ZrO$_2$ matrix is not influenced by the chemical treatments: in fact, both shape and average diameter of the support's particles almost coincide with the fresh catalysts. On the other hand, no "as is" Au particles are evident: individual metallic particles, smaller and with less evident lattice fringes, are very seldom detected as that indicated by the arrow in the Figure 2b; this particle shows also a larger contact area with the support. In these conditions it is possible to transfer an electron from the metal to the support. The electron transfer causes usually little effect on the surface properties of the metal particles; however, if the metal particles are very small, an effect could be observed. Moreover, the formation of an intermetallic Au−Zr compound or a solid solution is possible even if the spacing of the lattice fringes of the particle shown in Figure 2b, ≈ 2.9 Å, does not coincide exactly with those reported in the Au−Zr ASTM files.[16]

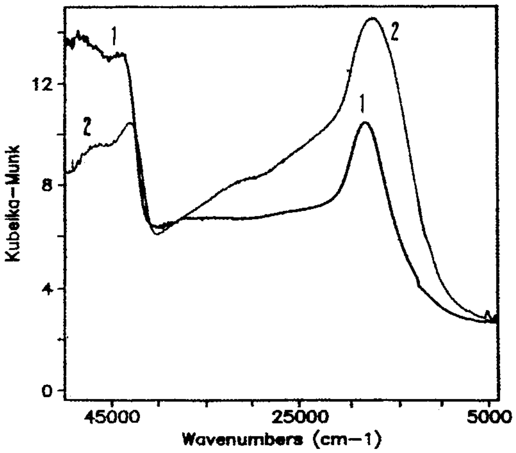

Figure 3. NIR−UV−vis reflectance spectra of fresh (curve 1) and used (curve 2) samples.

Figure 3 shows the NIR−UV−vis reflectance spectra of the fresh and used samples. The first peak at ≈18 000 cm^{-1} can be assigned to the plasmonic oscillation mode of nanosized gold particles, and the edge at ≈42 000 cm^{-1} to the fundamental absorption of ZrO$_2$ microcrystals. Two main effects are evident from the spectra of the used catalysts: the plasmonic peak appears broader and the absorption edge seems to be weaker.

Recently many papers[17] have been published on the optical properties of nanocrystalline gold samples, concerning the effect of the particle size, the shape of the particle, and the effect of the dielectric properties of the surrounding material. It has been shown that by decreasing the particle size a broadening of the plasmonic peak is observed.[18] Also, changes in the shape of the metallic particles, such as a flattening, can produce similar effects on the shape of the plasmonic peak. In our case, it can be hypothesized that these changes may occur as a consequence of alternate treatment in reducing and oxidizing atmosphere. Small particles must be considered as in/out equilibrium condition; this nonequilibrium condition can be modified by changing the gaseous atmospheres.[19] The decrease of the fundamental ZrO$_2$ absorption, associated with the positivization of the gold sites observed on our used samples, could be interpreted as an indication that a spreading of gold occurs at the surface of the support. Gold has a high absorption coefficient; by increasing the spreading of gold a larger fraction of the oxide cannot interact with the radiation.

Finally, we discuss the modification in the catalytic activity of the gold sites in the CO−O$_2$ reaction: in Figure 4 a comparison between CO/O$_2$ experiments made on a fresh and on a used Au/ZrO$_2$ catalyst is presented. The CO/O$_2$ interaction on the fresh sample (Figure 4a) produces, during the first minutes of contact, the shift and the intensification of the band

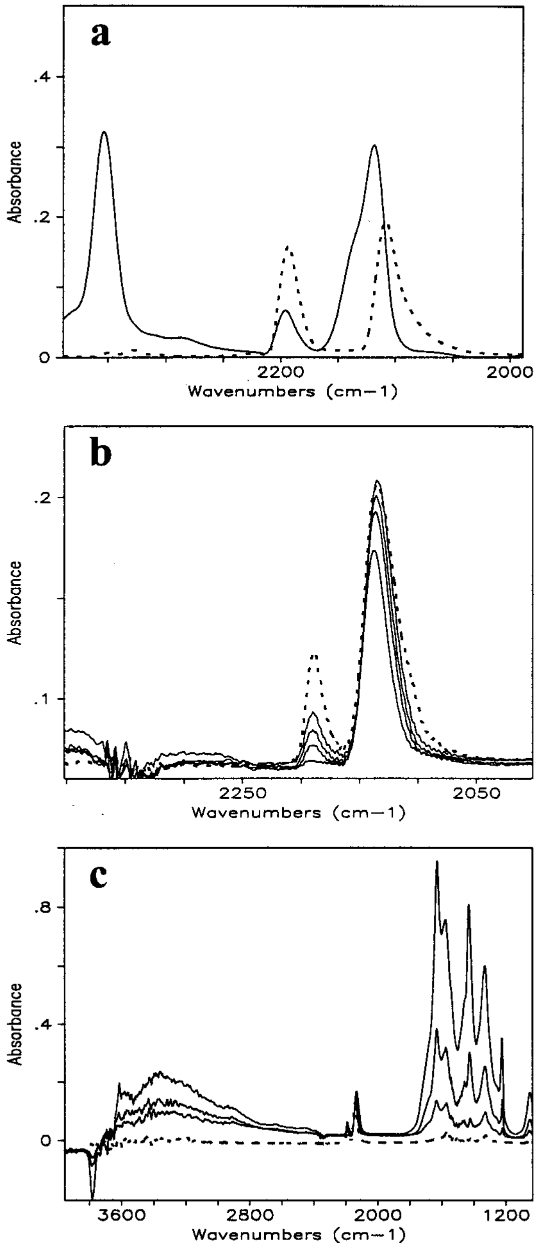

Figure 4. FTIR absorbance spectra of CO−O_2 interactions on Au/ZrO_2 samples. (a) Fresh sample, spectral range 2400−2000 cm^{-1}: dashed curve, 10 mbar of CO; full line, spectrum taken 10 min after the admission of O_2. (b) Used sample, spectral range 2400−2000 cm^{-1}: dashed curve, 10 mbar of CO; full lines,$^{1-4}$ spectra taken at increasing times after the admission of O_2 (2, 6, 8, 10 min). (c) Used sample, spectral range 4000−1000 cm^{-1}: dashed curve, 10 mbar of CO; full lines,$^{1-3}$ spectra taken at increasing contact times (2, 6, 10 min).

initially observed at 2108−2116 cm^{-1}. Many of the observed features are similar to those previously reported for other gold-containing samples;[5] in particular, the shift of the main band and the shoulder at higher frequency were ascribed to the presence of uncoordinated gold sites able to chemisorb oxygen and carbon monoxide at the same time. The intensification of the CO absorption band, not observed on the previously examined samples in similar conditions,[5] can be related to a transient increase in the local CO pressure produced by the oxygen inlet. This effect was not detected on the previously examined samples because of their higher reaction rate due to the smaller size of the gold particles. The band related to CO adsorbed on Zr^{4+} sites decreases in intensity, and molecular CO_2 is detected (band at 2351 cm^{-1}). Moreover, on the fresh sample, very strong bands grow up in the carbonate-like 1700−1000 cm^{-1} range (not shown for sake of brevity). The same interaction in the used sample (Figure 4b) produces quite different effects: immediately an erosion of the main band from the low-frequency side, at ∼2100 cm^{-1}, and a decrease of the band assigned to CO adsorbed on Zr^{4+} sites are observed. At increasing contact times the 2132 cm^{-1} band reduces slightly in intensity. Molecular CO_2 is not detected, and some bands gradually increase with the contact time in the carbonate-like region (Figure 4c) assigned to bidentate carbonate and to bicarbonate species;[20] however, the intensities of these bands are significantly lower than those on the fresh samples. Probably, on the used samples, where positive gold sites are already present before oxygen contact, the oxygen does not activate CO for carbonate-like species formation at the borderline of the bidimensional metallic particles with the support.

From the data discussed it appears evident that on the used sample only a small fraction of the exposed gold sites, those associated with the weak component at ∼2100 cm^{-1}, exhibits the usual reactivity toward oxygen while the electron-deficient two-dimensional metallic islands, which are the vast majority of the exposed gold sites on the used samples, appear significantly less reactive than the neutral gold sites exposed on three-dimensional particles of the new sample. Electronic and/or structural reasons can be at the origin of the observed differences. The positive gold sites give rise to stronger Au−CO bonds, and this fact can cause a reduction of the oxidation activity. The role of the oxidation state and that of the CO on Cu, Cu_2O, and CuO bond strength in the CO oxidation reaction has been discussed by Jernigan and Somorjai.[21] Moreover, the coordinative unsaturation of the surface atoms can play a role. The three-dimensional and almost spherical particles seen by HRTEM on the fresh sample expose a large amount of step and corner sites, where CO and oxygen can be adsorbed in close contact, while flat, bidimensional particles expose mainly highly coordinated sites.

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