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Support Effect in High Activity Gold Catalysts for CO Oxidation

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Abstract: In this work, we present a detailed study concerning the evaluation of the metal−support interaction in high activity gold catalysts for CO oxidation. Using the colloidal deposition method, model catalysts were prepared, which allow the isolation of the effect of the support on the catalytic activity. Prefabricated gold particles were thus deposited on different support materials. Since the deposition process did not change the particle sizes of the gold particles, only the influence of the support could be studied. TiO_2, Al_2O_3, ZrO_2, and ZnO were used as support materials. Catalytic tests and high resolution transmission electron microscopy clearly show that the support contributes to the activity. However, our results are not in line with the distinction between active and passive supports based on the semiconducting properties of the oxidic material. The most active catalysts were obtained with TiO_2 and Al_2O_3, while ZnO and ZrO_2 gave substantially less active catalysts. Furthermore, the effect of other important parameters on the catalytic activity (i.e., particles size distribution, calcination temperature, and aging time for a Au/TiO_2 catalyst) has also been studied. Using this preparation route, the catalysts show high-temperature stability, size dependent activity, and a very good long-term stability.

Introduction

Gold had long been disregarded for catalytic applications, due to its inert nature in the bulk state. However, when it is very highly dispersed on different supports, it exhibits a surprisingly high activity for several reactions, both in the liquid and in the gas phase. Thus, since Haruta discovered a remarkable activity of supported gold nanoparticles in CO oxidation, different methods to prepare high activity gold catalysts have been developed, and several potential application fields have been explored.[1−8]

The availability of efficient gold catalysts was then the driving force of many publications devoted to the analysis of the different factors controlling the activity. Unfortunately, despite numerous studies published on supported gold catalysts, there is still no clear picture with respect to the origin of the catalytic activity, and often, the results reported in the literature concerning gold catalysis are contradictory. The role of the support is still under discussion, and recent reports have also demonstrated that unsupported gold particles can exhibit a comparable activity to the supported ones in the aerobic glucose oxidation.[9] In the CO oxidation reaction, highly controversial are the mechanisms for oxygen adsorption and activation, which are required to explain the high activity of gold nanoparticles and that contrast the inhibited oxygen dissociation on single crystals.[10] Several models have been proposed to resolve this discrepancy. In the probably most widely accepted of them, oxygen adsorption is believed to occur on the support or at the metal support interface, possibly in oxygen vacancies that should be present on semiconductor materials (e.g., TiO_2 and ZnO) as a consequence of the Schottky junction at the metal−support interface. Consequently, the different activities observed for different catalysts were attributed to the different conducting properties of the material used as support.[11]

To gain further insight in this controversial issue, and to also obtain a complete picture on how a good gold catalyst should be prepared, pretreatment and preparation conditions, reaction conditions, and many other physicochemical parameters have been investigated.[12−16] Among them, the most relevant seem to be particle size, oxidation state of the gold species, nature of

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the support, and preparation method.[17−21] However, the majority of the studies on gold catalyzed systems have been carried out using catalysts prepared via the deposition−precipitation method. Because of the complexity of the synthetic method and the influence of the large number of parameters affecting the properties of the resulting catalysts, this method often does not allow a clear distinction and evaluation of the aforementioned effects. Even reproducibility of the synthesis is not always guaranteed.[22] We have therefore recently reported a standard procedure that allows the preparation of reproducible catalysts via deposition−precipitation and impregnation methods.[23]

To overcome the complexity related to the standard preparation methods so far employed, the colloidal deposition method is an interesting alternative. Using this route, it is possible to obtain model catalysts in which the effect of support on the catalytic activity can be isolated from other factors. This is due to the fact that the colloidal gold metal particles are generated before they are deposited on the support. Influence of the support on the formation of the gold particles is therefore eliminated. This special feature allows the creation of identical gold particles for different types of supports, independent of the support used. This route should therefore allow the evaluation of support effects on the catalyst activity. To achieve satisfactory activity for CO oxidation, the gold particles must be small (below 10 nm), and obviously the very well-known citrate synthesis method for the generation of colloidal gold particles cannot be used.[24] Smaller particle sizes, in the range of 1−7 nm, can today be obtained with different methods.[25,26] With this aim, Grunwaldt et.al. have already studied the low-temperature CO oxidation using tetrakis(hydroxymethyl)phosphonium chloride as a reducing agent and a limited number of supports (TiO_2 and ZrO_2).[27]

Here, we report the preparation of gold catalysts, using different commercial supports, via the deposition of metallic sols, using organic molecules as protecting agents and sodium borohydride as reducing agents for the metal species. The metal oxide supports used in this study were chosen to discriminate between active (TiO_2, ZnO) and passive (Al_2O_3, ZrO_2) materials and also to evaluate the influence of the point of zero charge on this preparation route. Transmission electron microscopy analysis of the metal dispersions before and after deposition has been used to ascertain that the particles sizes of the gold particles are not changed during the deposition, so that the metal−support interaction can indeed be studied.

Experimental Procedures

Catalyst Preparation. The colloidal deposition method used here has been extensively described elsewhere.[28,29] The colloidal gold solutions were prepared using two different protecting agents (poly(vinyl alcohol), M_W 10 000 from Aldrich, 80% hydrolyzed or glucose monohydrate, purity grade ≥99.7% from Fluka) to achieve two different particle size distributions. In a typical preparation, the protecting agent was added (Au/PVA = 1.5:1 mg mg^{-1}; Au/glucose = 1:300 mg mg^{-1}) to a 100 mg L^{-1} aqueous gold solution (as $HAuCl_4$ Alfa-Aesar, 99.99%) at room temperature under vigorous stirring. The obtained solution was then left under stirring for 10 min. A following rapid injection of an aqueous solution of $NaBH_4$ 0.1 N from Aldrich, 97% purity (Au/$NaBH_4$ = 1:5 mol mol^{-1}), led to formation of a dark orange−brown solution, indicating the formation of the gold sol. The support was then added to the colloidal gold solution under stirring and kept in contact until total adsorption (1 wt % of gold on the support) occurred, indicated by decoloration of the solution. All steps previously described were carried out under exclusion of light by covering all containers with a layer of aluminum foil. When glucose was used as protecting agent, operations were in addition carried out under inert atmosphere. The solids were collected by vacuum filtration followed by washing the solid with 2 L of doubly distilled water to remove all the dissolved species (e.g., Na^+, Cl^-). Finally, the solids were dried under a vacuum of 10^{-2} mbar in a desiccator where P_2O_5 (Aldrich 97% purity grade) as a drying agent was scattered on the bottom. All supports (TiO_2 P25 from Degussa, ZnO AC-45 from Brüggemann Chemicals and γ-Al_2O_3 PURALOX SBa-200 from Sasol) were used as received except in the case of ZrO_2. Zirconium oxide was synthesized from $Zr(OH)_4$ (MEL Chemicals) by calcination at 350 °C for 4 h, using a heating rate of 3 °C min^{-1}. The obtained support was analyzed by X-ray diffraction revealing the monoclinic phase. Reproducibility (or better, the lack of reproducibility) can be a severe problem in gold catalysis. Catalysts prepared via the methods described previously were typically found to have a reproducible performance in CO-oxidation, with the exception of the Au/Al_2O_3 system for which some scatter of the activity was observed for samples from different batches. More detailed results on the reproducibility of the catalysts will be discussed for all systems at the end of this paper.

Catalyst Characterization. Microscopy Experiments. The morphological characterization of the supported and unsupported gold particles was performed with a Hitachi HF2000 microscope equipped with a cold field emission gun at a beam energy of 200 kV and a Si-(Li) EDX spectrometer from Noran Instruments for point resolved elemental analysis. To obtain suitable samples for TEM characterization, the samples were treated as follows: solid catalysts were finely powdered and then deposited onto a holey copper carbon grid in the native form. Colloidal solutions were first diluted with water (10 mg L^{-1}). A drop of solution was then deposited on a thin film carbon grid and left to dry under pure N_2 or Ar flow. Particle sizes and particle size distributions were determined from the TEMs by measuring the sizes of typically 200 particles. The gold content of the catalysts including possible contaminations of chloride ions were determined by energy-dispersive X-ray analysis (EDX), which was performed on a Hitachi S-3500N scanning electron microscope equipped with an OXFORD EDX system.

X-ray Photoelectron Spectroscopy (XPS). XPS measurements were performed with a Kratos HSi spectrometer with a hemispherical analyzer. The monochromatized Al Kα X-ray source (E = 1486.6 eV) was operated at 15 kV and 15 mA. For the narrow scans, an analyzer pass energy of 40 eV was applied. The hybrid mode was used as a lens mode. The base pressure in the analysis chamber was 4×10^{-9} Torr. The binding energy scale was corrected for surface charging by taking the C 1s peak of contaminant carbon as a reference at 285.0 eV.[12,30] This technique was used to ascertain that in the case of fresh catalysts, gold was in the metallic state. Furthermore, to obtain closer insight in the interaction of gold particles and support, and to observe possible events occurring during reaction, selected samples were analyzed before and after reaction.

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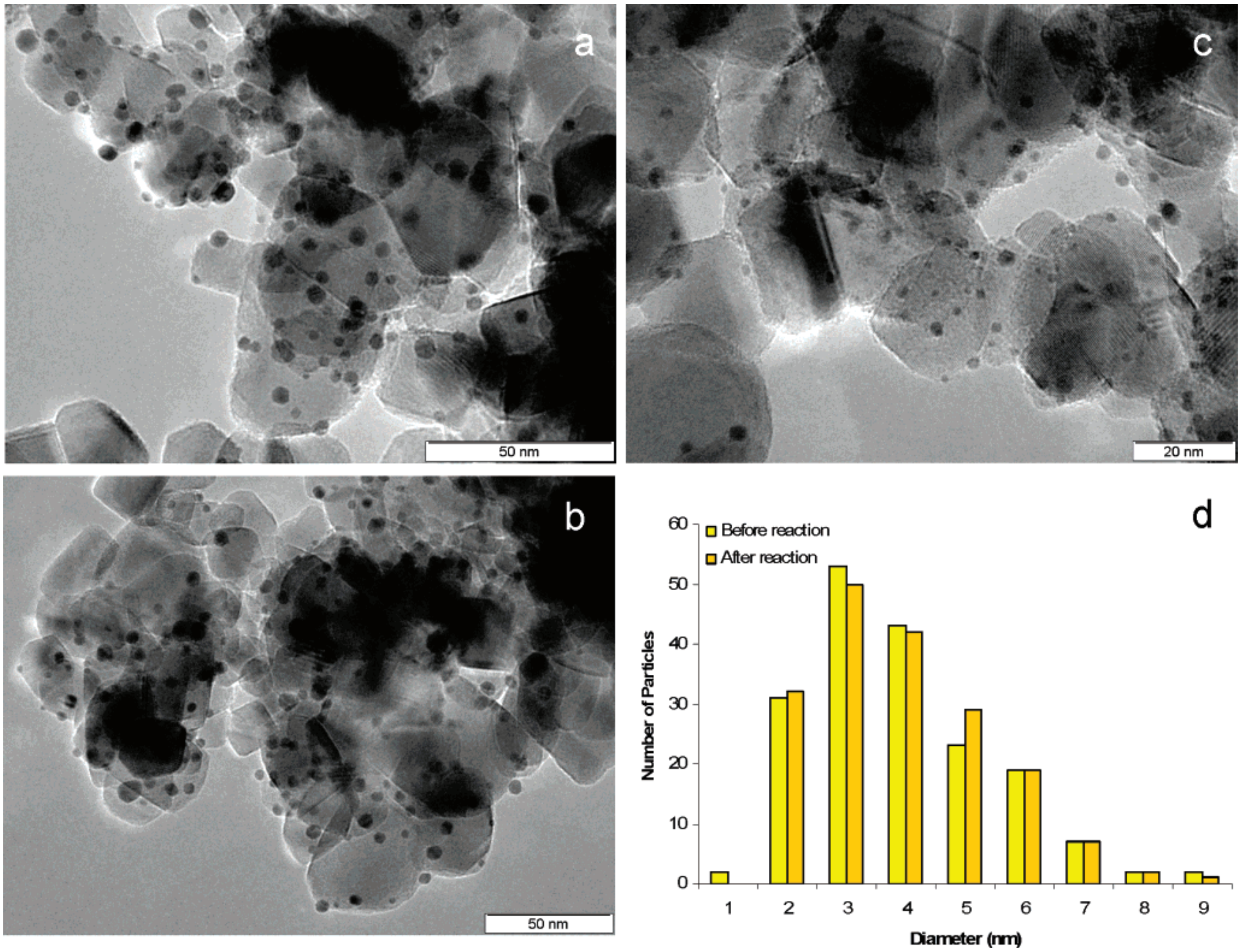

Figure 1. Au/TiO_2 catalysts. (a) TEM of the glucose protected sample before reaction. (b) TEM of the glucose protected sample after reaction. (c) TEM of the PVA protected sample before reaction. (d) Particle size distributions for the glucose protected catalyst before and after reaction.

X-ray Diffraction Experiments. XRD measurements were carried out on a Stoe STADI P reflection diffractometer using Cu Kα radiation.

Catalytic Test: CO Oxidation. The activities of the catalysts for CO oxidation were measured in a plug flow reactor using 50 mg of sieved catalyst (250−500 μm) in a gas mixture of 1% CO in air (from AIR LIQUIDE, 99.997% purity) at a flow rate of 67 mL/min, corresponding to a space velocity of 80 000 mL/h g_{cat}. The operation temperature was controlled with a thermocouple and could be adjusted in the range of −100 to 300 °C. Temperature data in the catalytic test are always referred to the value measured with a second thermocouple placed in the inlet immediately before the catalyst bed. To avoid internal and external mass transfer limitation, the necessary tests have been carried out as described in the work of Perego et al.[31] With this aim, the kinetic regime was checked by varying the flow rate and mass of catalyst in the same proportion to keep constant the contact time (exclusion of film diffusion) and by varying the size of the catalyst grains at a constant flow rate (exclusion of pore diffusion). According to the results of these tests, mass transfer limitations can be excluded. The experiments for all the materials studied were carried out both under steady state and under temperature gradient conditions. In a typical run, in which the temperature was ramped, the reactor was cooled to −40 °C prior to each experiment under a flow of nitrogen (from AIR LIQUIDE, 99.999% purity), which was then replaced by the gas mixture, after the base temperature had been reached. Then, the temperature was ramped with a rate of 2 °C/min to the final temperature. In typical steady-state experiments, the system was adjusted to the desired temperature value under N_2 flow, which was then replaced by the reagent mixture. Kinetic data were taken during 20 min after at least 1 h time on stream. Generally, very good agreement was observed between steady-state and gradient conditions, with the exception of the Au/ZnO material. This special case will be separately discussed in the next section. The concentrations of CO_2 and CO were analyzed at the outlet of the reactor with nondispersive IR spectroscopy, using two URAS 3E (Hartmann and Braun). The system was calibrated with a gas mixture of 1% CO_2 in N_2 (AIR LIQUIDE 99.9995% purity). Temperature for 50% conversion ($T_{50\%}$) as an index was used to evaluate the activity of the catalysts.

Results and Discussion

Au/TiO_2 is the most intensively studied gold based catalyst for CO oxidation. This system was therefore chosen as the starting point for our investigations. Particle size distribution, calcination, aging, and stability of the Au/TiO_2 catalysts were studied and related to the activity results.

The two different protecting agents used, glucose and PVA, resulted in the formation of gold colloids with different particle sizes, which were also maintained after deposition of the gold particles on the titania support, as can be seen in Figure 1a,c.

The mean diameter (number weighted average) for a typical PVA protected catalyst was 3.0 ± 1.3 nm, while it was 3.8 ±

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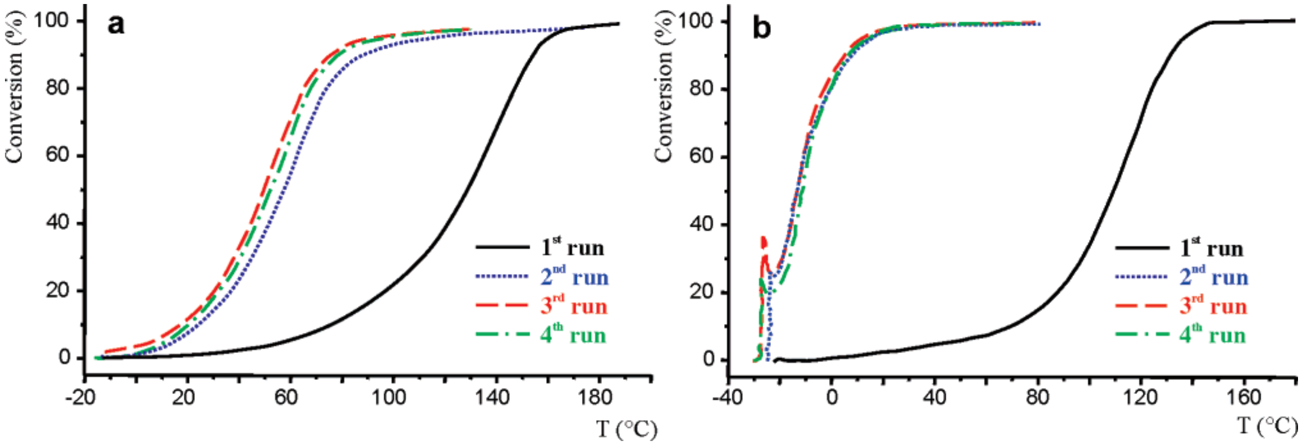

Figure 2. Activity results for Au/TiO_2 catalysts. (a) Glucose protected and (b) PVA protected.

1.6 for the glucose protected one. These catalysts have been then tested in CO oxidation, giving the results reported in Figure 2a,b. As expected, the catalysts with different particle size distributions have different activities. For the catalysts protected with PVA, the temperature of half conversion ($T_{1/2}$) was −12 °C, while it is as high as 50 °C for the glucose protected ones. For both samples, the results of the first run were substantially different from the results for subsequent temperature cycles.

The catalysts seem to require a thermal activation, probably due to the inhibitory effect of the protecting agent that is present on the catalyst after preparation, although this had not been detected in the EDX and XPS measurements. To understand the origin of this phenomenon, samples were calcined in air at 250 °C for 4 h, to combust the organic species. The catalysts thus treated did not show any difference between the first and the following runs, which supports the assignment of the activation to the presence of organic matter on the surface of the catalysts. The activity of these samples was identical to the one of the uncalcined ones after activation. This result is a first indication of a good thermostability of these systems. To further confirm the origin of the activation phenomenon, a sample was prepared without protecting agent, using a similar procedure as reported in the work of Mallick et al.[32] A gold colloid was prepared from an aqueous solution of gold (as $HAuCl_4$, [Au] $= 50$ mg L^{-1}) via direct reduction with sodium borohydride ($Au/NaBH_4 = 1{:}5$ mol mol^{-1}). The 1 wt % Au/TiO_2 was then obtained by direct addition of the support (TiO_2, P25 from Degussa) to the vigorously stirred colloidal solution. The subsequent treatment was identical to the one applied to all the catalysts and reported in the Experimental Procedures. The as-made catalysts was tested in CO oxidation, and also for this system, no difference between the first and the following runs was observed, confirming the inhibitory effect related to the presence of the organic protector on the catalysts surface of the as-made protected materials. The temperature of half conversion for this catalyst was 31 °C for all runs.

To check for possible other changes of the catalysts during reaction, TEM and XPS measurements have been performed on the glucose protected Au/TiO_2 material before and after reaction. The mean diameter and the particle size distribution were 3.8 ± 1.6 before and 3.9 ± 1.5 after reaction, as also shown in Figure 1a,b,d, confirming that no significant change occurs during reaction. Also, XPS measurements have been performed on this catalyst before reaction, after the first catalytic run, and after completion of the catalytic evaluation. The binding energies for the Au $4f_{7/2}$ peak were 83.8, 83.7, and 83.7 eV, respectively. This indicates that the oxidation state does not change during reaction. The binding energy is characteristic for zerovalent gold, no peaks corresponding to oxidized species, which would be located around 85.5 and 86.3 eV,[30] have been detected. Furthermore, the binding energies are close to the ones observed for bulk metallic gold (84.0 eV). XPS analysis has been performed for the 250 °C calcined sample as well, and also in this case, a similar binding energy was measured (83.7 eV). These results do not agree with the results reported in a recent paper of Arrii and co-workers, who claim that a negative shift in the Au $4f_{7/2}$ binding energy peak before and after reaction (83.4 and 82.9 eV, respectively) for a Au/TiO_2 catalyst with respect to bulk gold occurred, and which has been attributed to the metal support interaction.[33]

As a consequence of the promising result obtained from the preliminary calcination test described previously, the thermostability of the most active Au/TiO_2 system (PVA protected) was studied in more detail. A sample was calcined at 350, 450, and 550 °C for 4 h and then catalytically tested. The results are shown in comparison with the as-made catalyst in Figure 3. Up to 350 °C, the catalyst activity remains unchanged, and even after calcination at 550 °C, the activity loss is not severe. The drop of activity is related to a growth of the particles as shown in Figure 4, and in particular, an increase of particles size from 3.0 nm (for the as-made sample) to 4.9 nm was observed after calcinations at 550 °C.

This is remarkable, especially considering the low thermal stability observed for systems prepared with the same support (TiO_2 P25 Degussa) via deposition−precipitation or impregnation in our previous work.[23] In fact, for these systems, an increase of $T_{1/2}$ from −6 to 50 °C and from 21 to 67 °C has been observed for catalysts prepared via DP method and impregnation, respectively, after calcinations at 300 °C. Furthermore, it seems to be possible to obtain much more stable catalysts by expanding the colloidal deposition method to different supports for which it has recently been claimed that thermally highly stable catalysts can be obtained using the DP method. In particular, Yan and co-workers have shown that

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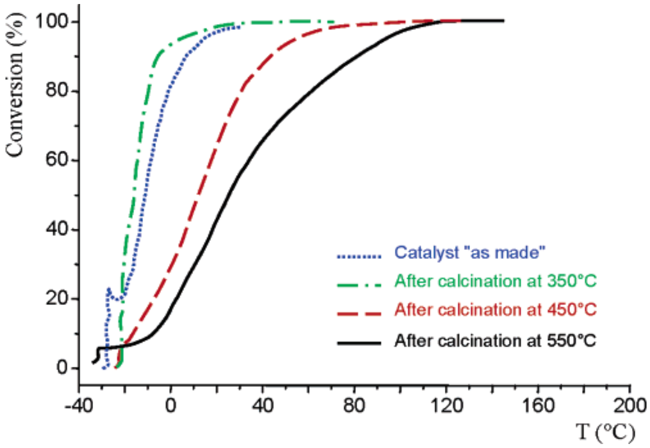

Figure 3. CO conversion as a function of temperature for Au/TiO_2 (PVA protected) catalysts calcined at different temperatures.

ultrastable gold catalysts can be obtained using Brookite and surface- modified TiO_2 as supports. For these catalysts, the loss of activity was limited even after calcinations at 500 °C.[34,35]

As already mentioned, a good gold catalyst should be active at low temperature, be thermally stable, and also have long-term stability under reaction conditions and upon storage. To check if there is any loss of activity for both our Au/TiO_2 systems, these catalysts have been stored in a vial in the dark under ambient atmosphere for 6 months at room temperature and subsequently catalytically evaluated again. The catalytic activity was found to be unchanged as compared to the original sample for the glucose protected catalysts. A slight increase of the temperature of half conversion ($T_{1/2}$) from −13 to −3.5 °C was found for the PVA protected one. This increase of conversion temperature is not very large but outside the error margin. Stability tests under reaction conditions have been carried out during temperature cycling. The catalytic activity has been evaluated during 20 consecutive runs, which corresponds to altogether 30 h time on stream. No deactivation occurred during our measurements for both the systems.

After completion of the investigation on the titania based systems, the study was extended to other supports to isolate the support effect. In addition to the titania, one other active oxide (i.e., ZnO) and two passive (i.e., γ-Al_2O_3, ZrO_2) supports have been chosen. These supports also markedly differ in their point of zero charge (p.z.c: $TiO_2 = 6-7$; $ZrO_2 = 6-7$; γ-$Al_2O_3 = 9$; and ZnO = 11).

Since the PVA route gave the more active catalysts for the titania support, this route was chosen for the other supports as well, and consequently, all the catalysts were prepared using this protecting agent. The first goal was to obtain samples with similar gold particle size distributions, independent of the support used. This proved to be possible for all supports studied. Typical size distributions for our catalysts are shown in Figure 5.

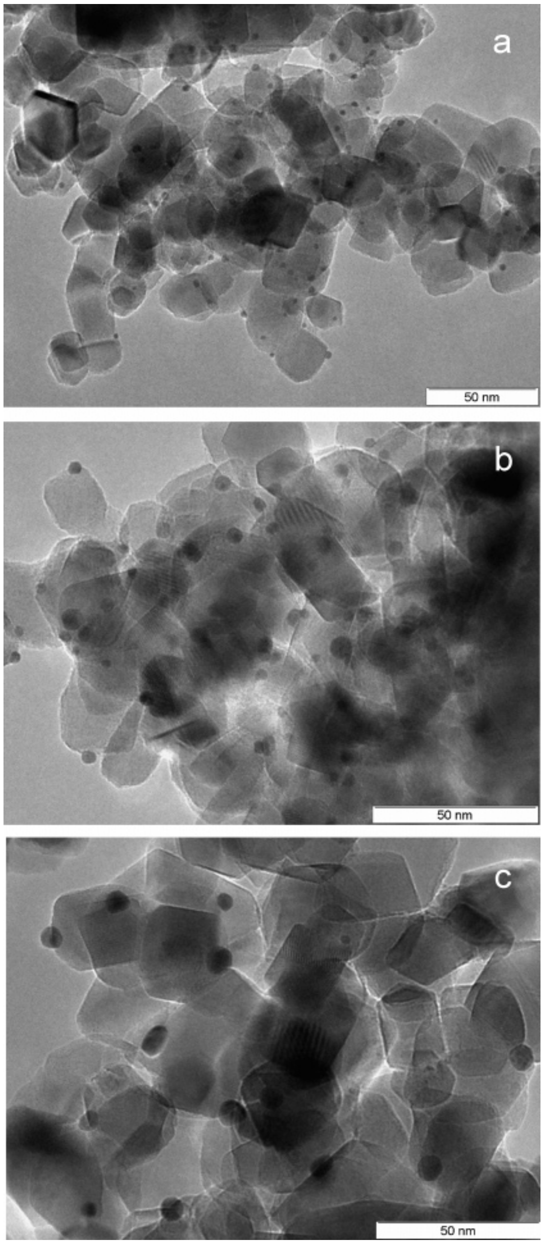

Figure 4. TEM images of Au/TiO_2 catalyst (PVA protected) calcined at different temperatures. (a) 350 °C, (b) 450 °C, and (c) 550 °C.

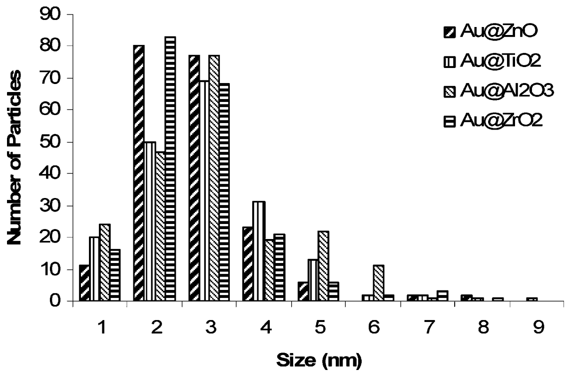

Figure 5. Size distribution histogram of gold clusters.

As one can see, particle size distributions are almost identical for all the materials prepared. Average particle sizes and standard deviations were 2.8 ± 1.1 (Au/ZnO), 3.0 ± 1.3 (Au/TiO_2), 3.1 ± 1.3 (Au/γ-Al_2O_3), and 2.8 ± 1.2 nm (Au/ZrO_2). This was expected because the gold clusters had been produced before deposition, and the deposition process should not alter the particle sizes and distributions. Complete adsorption of the colloid (1 wt % of Au) on the support was achieved, as described

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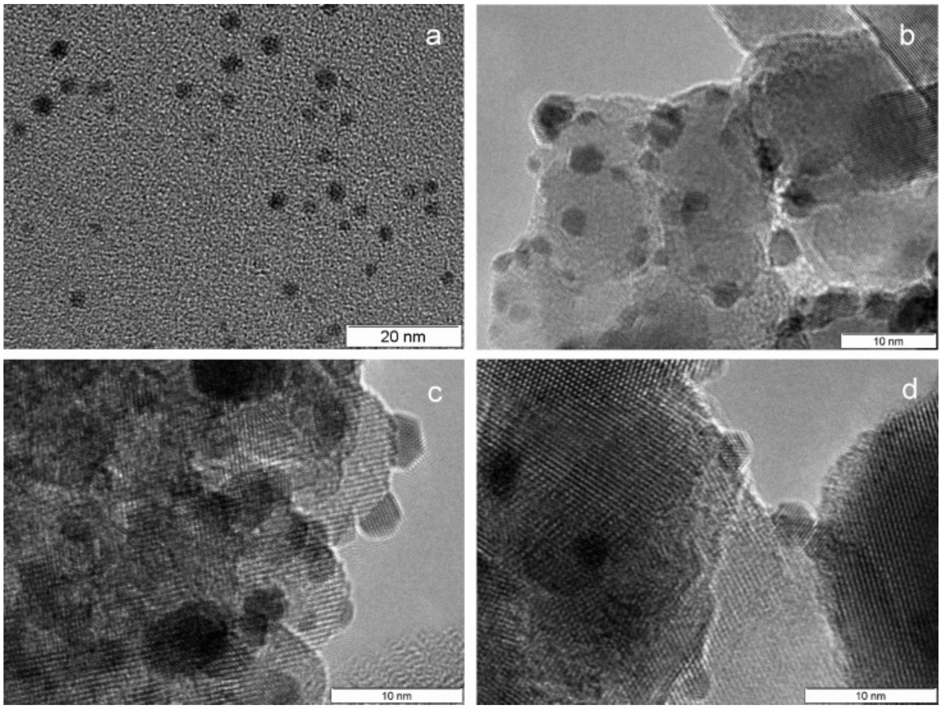

Figure 6. HRTEM images of (a) gold colloid before deposition, (b) Au/ZnO, (c) Au/ ZrO_2, and (d) Au/TiO_2.

in the Experimental Procedures, by leaving the colloidal solution in contact with the support for a sufficient period of time. The time needed for complete adsorption is dependent on the type of support used. Deposition times varied from 30 min for TiO_2 and ZnO up to 24 h in the case of γ-Al_2O_3. The deposition time is clearly not dependent on the point of zero charge (p.z.c) of the support, which may have been expected. TiO_2 and ZnO adsorbed the colloid in a similar period of time, although they have strongly different p.z.c. (i.e., 6−7 and 11, respectively), while ZrO_2 with a p.z.c. close to that of TiO_2 adsorbed the gold appreciably more slowly.

The independence on p.z.c. may be due to the nature of the protecting agent used with its negative charges, which may shield the charges of the support and the gold clusters under the conditions of the deposition (pH ∼ 7−8). However, the differences between the supports with respect to the adsorption rate of the colloids can presently not be explained, and this effect is presently under study in our laboratory.

The TEM images of the catalysts in comparison to the native gold colloidal solution are shown in Figure 6. As one can see, the gold clusters in the native solution are almost spherical and are characterized by the same particle size distributions observed for the supported ones. However, adsorption on the oxide does seem to change the shape of these clusters for all the supports employed in this study. The particles clearly appear to be faceted if adsorbed on the support materials. There are no strong obvious differences in the shapes for the different supports, and various geometries seem to be possible on each of the supports. This change of geometries could lead to defect formation on the gold clusters. This latter aspect may be of importance because previous reports in the literature claim such defects as active sites on which the reaction could take place.[36−39] Possible differences between the activities of the catalysts supported on the four oxides may thus be attributed to different extents of defect formation.

The differently supported catalysts were tested in the catalytic CO oxidation, and the results are plotted in Figure 7 and Figure 2b (for the titania system already discussed). As for titania as a support, the performance in the first run is rather bad since the protecting shell of the gold particles first has to be removed. After this activation, the catalytic activity remains constant and well-reproducible for the following runs. Catalysis results for Au/TiO_2 and Au/ZrO_2 (Figure 2b and 7a, respectively) are in good agreement with the ones reported in the work of Grunwaldt et al.,[27] although gold loading and reaction conditions were slightly different. In particular, gold on titania was much superior to gold on zirconia, with a $T_{1/2}$ equal to − 13 and 74 °C, respectively.

Unexpected were the results obtained using Au/γ-Al_2O_3 and Au/ZnO (Figure 7b,c). Gold on alumina catalysts was very active and characterized by a $T_{1/2}$ close to the ones achieved using gold on titania. Low activity was observed for the Au/ZnO system.

Furthermore, this latter system showed an unusual behavior in the experiments where a temperature gradient was used during the activity measurements (Figure 7c), while regular temperature versus conversion curves were measured under steady-state conditions for each data point.

This deviation is marked at low temperature (from −40 to 20 °C) and decreases raising the temperature. For high-temperature isothermal and gradient conditions, the results were in agreement. One possibility for such behavior could be the adsorption of carbonate at low temperatures, which would desorb at higher temperatures. However, this can be excluded here since the outlet gas concentrations were monitored both

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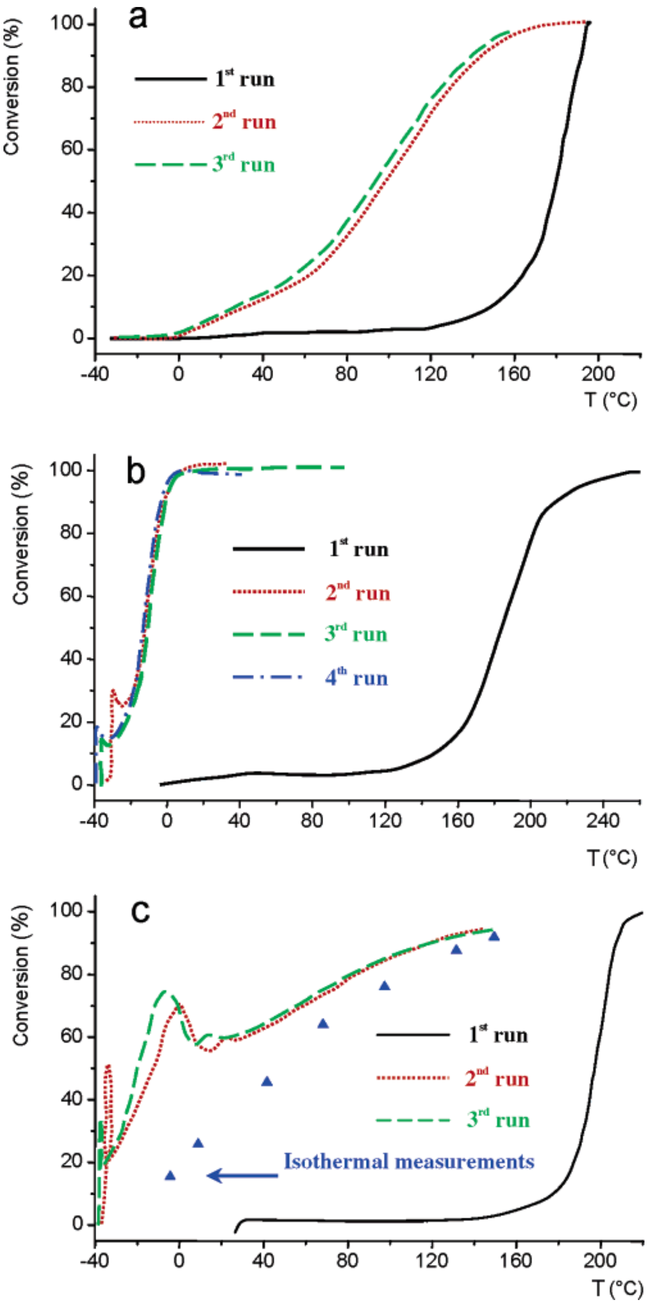

Figure 7. CO conversion as a function of temperature for supported gold catalysts (a) Au/ZrO_2, (b) Au/γ-Al_2O_3, and (c) Au/ZnO.

for CO and CO_2, and mass balances close to 1.0 (± 0.03) were measured at any temperature during the runs both in gradient and in isothermal conditions.

At low temperature, this catalyst seems to be in a highly dynamic state, having high activity initially, which is, however, transient, as demonstrated by the isothermal test results that give the regular activity curve with temperature as for the other catalysts.

To check whether this was a reproducible phenomenon or a spurious effect, different catalysts were prepared, and different ramping rates were applied. However, for all of these experiments, the unusual low-temperature behavior was confirmed. So far, we have no explanation for this phenomenon that is still under study in our laboratory.

Table 1. Reproducibility Results (given as $T_{1/2}$) of All the Catalysts Investigated

	Au/TiO_2		Au/ZnO	Au/Al_2O_3	Au/ZrO_2
	PVA	glucose	PVA	PVA	PVA
entry no.	$T_{1/2}$ (°C)	$T_{1/2}$ (°C)	$T_{1/2}$ (°C)	$T_{1/2}$ (°C)	$T_{1/2}$ (°C)
1	−13.7	54.9	50.1	−11.6	74.3
2	−11.2	55.1	43.6	29.5	100.6
3	−11.7	50.6	44.2	−10.5	92.1
4	−19.5	53.3		45.6	89.4

γ-Alumina is very difficult to reduce and has a low ability to adsorb or store oxygen, while ZnO has just the opposite properties. Considering the almost identical gold particles size in both the materials and the fact that the alumina based catalyst is much more active than the ZnO based system, our results are in disagreement with the classification of supports for gold catalysts proposed by Schubert et al.[11] The results presented here suggest that the metal−support interaction concept should be revised. The reducibility of the support and its ability to activate oxygen does not seem to be the decisive factor. In a comparative study, Lopez and co-workers found that differences in activity between reducible or unreducible supports for the same gold particle size were at most a factor of 2−4, suggesting that the reducibility was not a key factor.[21] For most synthesis methods with the exception of cluster deposition used here, the support certainly influences the size of the gold particles formed during the synthesis, and this is the major factor contributing to the activity of the catalysts. However, beyond this influence on the particle size, there must be additional effects affecting the activity since our results show a clearly different activity with essentially the same Au particle size on different support materials. Our results suggest that the support interacts with gold clusters, leading to a change in the shape of the particles. As a consequence, the different activities registered in the CO oxidation reaction may be attributed to this phenomenon. A direct correlation is so far not possible, but work is in progress on a more detailed statistical analysis of the particle shapes.

Finally, since reproducibility of the gold catalysts is often a difficult issue, this point has been checked for the catalyst in this study. A number of different batches has been prepared for each system using the same procedure on different days. All samples were then tested in CO oxidation, with the results reported in Table 1.

The temperatures of half-conversion shown are always referred to the third catalytic run for each sample, but as shown previously, run to run reproducibility was very good, and this therefore does not affect the results. As can be seen from the table, very good reproducibility has been achieved for Au/TiO_2 (for both protecting agents employed), Au/ZnO and, to a somewhat lesser degree, for Au/ZrO_2, although reproducibility can also be considered as satisfactory for this system. This is not the case for the Au/Al_2O_3 catalysts. Differences of more than 50 °C are observed for catalysts from different batches, and so far, the reason for this low degree of reproducibility could not be elucidated. However, it is clear from the data that highly active catalysts for CO oxidation can be prepared for alumina as support.

Conclusions

We have shown that via colloidal deposition, a series of very active and reproducible gold catalysts for low-temperature CO oxidation can be synthesized. A detailed study has been carried out for the Au/TiO_2 catalysts, which shows very good activity, reproducibility, and thermal stability. This material is also characterized by high long-term stability upon storage and very good stability under reaction conditions. Using different protecting agents, different gold particle size distributions were obtained on the same support. These catalysts have been catalytically evaluated, and the data confirm the widely spread notion in the literature, that the activity for CO oxidation is strongly dependent on the gold particle size. The most important finding of this study is the fact that almost identical gold particle size distributions on different supports result in different activities for CO oxidation. This clearly demonstrates that the metal support interaction strongly influences the catalytic properties of the final materials. However, this influence does not follow the reducibility and oxygen activation ability of the supports. Active catalysts were prepared based on titania (supposedly active) and alumina (supposedly inactive), while much less active samples were synthesized with ZnO (supposedly active) and zirconia (supposedly inactive). However, although the gold particle sizes are not changed by deposition, the support influences the shape of the deposited particles, leading to faceting and possibly creating defect sites. The exact mechanism of how the different supports influence the activity is still unclear, but different faceting may be related to the catalyst activity. However, even if a full understanding of the systems is still lacking, the synthetic method described here and the analysis of the samples provide the basis for decoupling the influence of the support on the synthesis of the gold particles and the influence of the support on the reactant activation during the catalytic reaction.

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