Support Effects in the Gold-Catalyzed Preferential Oxidation of CO

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The study of support effects on the gold-catalyzed preferential oxidation of carbon monoxide in the presence of hydrogen (PROX reaction) is possible only with careful control of the gold particle size, which is facilitated by the application of the direct anionic exchange method. Catalytic evaluation of thermally stable gold nanoparticles, with an average size of around 3 nm on a variety of supports (alumina, titania, zirconia, or ceria), clearly shows that the influence of the support on the CO oxidation rate is of primary importance under CO+O₂ con-

ditions and that this influence becomes secondary in the presence of hydrogen. The impact of the support surface structure on the oxidation rates, catalyst selectivity, and catalyst activation/deactivation is investigated in terms of oxygen vacancies, oxygen mobility, OH groups, and surface area on the oxidation rates, catalyst selectivity and catalyst activation/deactivation. It allows the identification of key morphological and structural features of the support to ensure high activity and selectivity in the gold-catalyzed PROX reaction.

Introduction

The selective oxidation of carbon monoxide in the presence of hydrogen, also called preferential oxidation (PROX), is a key step in the hydrogen purification process in promising polymer electrolyte fuel cell (PE-FC) technology, which has been afforded increasing scientific interest in the recent years.^[1] The catalysts have to operate downstream water–gas shift reactors and allow oxidation of the residual carbon monoxide fractions without consumption of the hydrogen fuel. In this way, the CO concentration, which causes poisoning of the electrocatalysts used to convert hydrogen to electricity, can be lowered to acceptable levels and the overall fuel cell efficiency is improved. PROX catalysts need to be effective in the range of operating temperature of the PE-FC (80–120 °C), highly selective, and resistant to deactivation, particularly when water and carbon dioxide are present in the effluent gas.^[2]

The study of the PROX reaction is strongly related to oxidation catalysis, which explains why the first studied catalyst for this reaction was Pt/Al₂O₃.^[3] Other alumina- or silica-supported metal catalysts have since been studied, such as Pt, Rh, Pd, Ru, Co–Cu, Ni–Co–Fe, Ag, Cr, Fe, Mn,^[4] and, more recently, alloy catalysts.^[5] However, none of these materials are as active at the temperature of interest for a PE-FC application as supported gold nanoparticles. The great oxidation potential of gold systems was revealed by the pilot study of Haruta et al.^[6] on the low-temperature oxidation of carbon monoxide. Since then, numerous studies have highlighted the unique performances of gold catalysts in mild oxidation reactions, in particular the PROX reaction, in which a high selectivity towards CO₂ can be achieved due to the higher oxidation rate of CO, as compared to H₂, at low temperature.^[7] Although Au/MnO_x was initially thought to be the best candidate for the PROX reaction,^[8] other mineral oxides, such as TiO₂,^[9] Fe₂O₃,^[10] CeO₂,^[11] and Al₂O₃,^[12] have since been used as supports for gold nanoparticles in this reaction.

To date, the support effect in the gold-catalyzed PROX reaction is not clear. Some groups^[13] have reported a significant effect of the support on the catalytic performances, with one order of magnitude difference between the most active material, Au/Fe₂O₃, and the least active, Au/Al₂O₃. By contrast, Rossignol et al.^[14] reported similar CO oxidation rates for Au/TiO₂, Au/ZrO₂, and Au/Al₂O₃-catalyzed PROX reactions. Hence, significant improvement of these PROX catalysts can be expected through a deeper understanding of the role of the support in the reaction.

However, there is still a general consensus in the scientific community on the importance of the gold particle size^[15] and structure,^[16] which are functions of the preparation method and the support chemical nature, for oxidation reactions. Hence a rigorous study of the support effect requires the use of catalysts with similar particle size distributions on all supports considered. Such catalysts can be obtained by laser vaporization^[17] or colloidal deposition.^[18] These methods rely

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on the deposition of pre-formed gold clusters or sols on the support via physical adsorption. They have proven successful in comparing alumina-, titania-, zirconia-, and zinc oxide-supported gold catalysts in H_2 -free CO oxidation. However, these catalysts are generally much less active than those prepared from surface reduction of chemically grafted species.^[14] We have designed a chemical method that gives reproducible catalysts, in terms of gold particle size and loadings, on alumina, titania, zirconia, and also on ceria,^[19] which differs from the other supports by its enhanced oxygen storage capacity and mobility features. This “surface bottom-up” methodology is based on the control of the nature of the anchored gold species on each support, which act as nucleation centers upon reduction and formation of the supported gold nanoparticles. By this approach, an enhanced metal–support interaction can be engineered by mild thermal treatments, as evidenced by the increased thermal stability of these supported particles.^[20]

In this context, the aim of this work was to determine the effect of the support in the gold-catalyzed PROX reaction, by using “inert” (Au/Al_2O_3), “active” (Au/TiO_2 , Au/ZrO_2)^[13] and reducible (Au/CeO_2) gold catalysts prepared by direct anionic exchange, which all contain gold particles with a stabilized average size of about 3 nm in close interaction with the support. For this purpose, each material was systematically evaluated in the PROX reaction, in H_2 -free CO oxidation, and in CO-free H_2 oxidation. We will show how the nature of the support affects the CO and H_2 oxidation rates in each reaction, the effect of hydrogen on CO oxidation and the effect of CO on H_2 oxidation, as well as how it influences catalyst selectivity and catalyst activation and deactivation. From a combined study of these effects, we will identify some key morphological and structural features of the support that control the efficiency of gold catalysts in the PROX reaction.

Results and Discussion

Full descriptions and characterizations of the catalysts employed herein are provided elsewhere.^[21] In brief, the four materials 1.50 wt% $Au/\gamma-Al_2O_3$, 1.34 wt% Au/ZrO_2 , 1.50 wt% Au/TiO_2 , and 1.95 wt% Au/CeO_2 were prepared by the direct anionic exchange method with a target gold loading of 2 wt%. The lower gold contents obtained are attributed to the ammonia treatment, upon which some gold is lost, but which is critical to keep the chlorine content of each catalyst below the detection limit of the inductively coupled plasma atomic emission spectroscopy (ICP-AES) method (<150 ppm). Only Au/ZrO_2 contained a relatively large amount of chlorine (329 ppm), which is attributed to the high affinity of the support for the chlorine itself.^[22] In any case, the ammonia treatment limits reduction phenomena and hence growth of gold particles. In this way, after calcination at $300^\circ C$, the average particle size of gold was kept at 3.0 ± 0.2 nm, according to transmission electron microscopy (TEM),^[21] on Al_2O_3 , ZrO_2 , and TiO_2 supports, instead of 16 nm on Al_2O_3 in the absence of ammonia treatment.^[23] Although the contrast between ceria and gold was rather low in TEM, the sizes of the (less numerous) gold crystallites detected were however consistent with those

on the other supports. For an average gold particle size of 3 nm, gold dispersions of 43% were calculated for all catalysts by using the average particle size and the mathematical model for cuboctahedral particles proposed by Polisset.^[24] This particle shape is consistent with that found in high-resolution TEM (HRTEM) studies,^[21b] it is similar for gold supported on Al_2O_3 , ZrO_2 , and TiO_2 , and the accepted particle shape for the catalyst with ceria. X-ray photoelectron spectroscopy (XPS) studies also showed that gold is essentially in a metallic state with binding energies (BE) for Au $4f_{7/2}$ at 83.3 eV on ZrO_2 , 83.3 eV on TiO_2 , and 83.9 eV on Al_2O_3 , as compared with 84.0 eV in a Au^0 foil. No evidence for the presence of oxidized gold was detected on these supports. The presence of oxidized gold was detected on CeO_2 after calcination but these species were easily reduced. An XPS spectrum of Au/CeO_2 calcined at $300^\circ C$ and then reduced at $120^\circ C$ indeed shows that the well-defined Au ($4f_{7/2}$, $4f_{5/2}$) doublet can be fitted with a single component, characteristic of gold in metallic state with a BE of 83.0 eV for Au $4f_{7/2}$.^[25]

As the particle size and shape and oxidation state of gold are almost identical for all of the samples, these are excluded from the parameters that are able to influence the reactivity.^[26] It can thus be presumed that the differences in catalytic behavior will only be caused by direct support effects, in terms of oxygen activation^[13] and metal–support interactions and interfaces.^[27]

As mentioned above, the catalysts were employed in three oxidation reactions performed one after the other, starting with the oxidation of CO in the absence of hydrogen, followed by the PROX reaction, and finally hydrogen oxidation in the absence of CO. For every reaction, four steps were carried out—heating and cooling as the 1st and 2nd steps, and a second cycle of heating and cooling as the 3rd and 4th steps.

In the oxidation of CO (Figure 1), the activities of the catalysts were generally different in the first heating step than in the subsequent ones. The activities then stabilized and the catalysts displayed similar activities in the 2nd, 3rd, and 4th steps. Both ceria- and alumina-supported catalysts were deactivated during step 1. The high-surface-area ceria support, with a high number of defects, is known to be prone to surface carbonate formation,^[28] from reaction between the ceria/gold surface and the reaction products upon heating under $CO+O_2$. These species are known to inhibit CO oxidation,^[29] which could account for the lower activity observed in the subsequent steps. In the case of Au/Al_2O_3 , the high CO conversion up to $150^\circ C$ in the first heating step is attributed to the high amount of surface hydroxy groups on the alumina surface combined with the beneficial effect of water vapor. Hydroxy groups have indeed been reported to be part of the active site and trigger oxygen activation on gold catalysts supported on “inert” oxides, such as alumina^[30] and silica.^[31] Loss of these groups above $150^\circ C$, due to dehydroxylation of the support (thermogravimetric studies^[20b]), causes thermal deactivation.^[30a] The CO conversion thus increased less rapidly with temperature above $150^\circ C$. Furthermore, the activity of the alumina-supported catalyst below $150^\circ C$ can be promoted by water produced from thermal dehydration of the support and released in the $CO+O_2$ gas-phase

Figure 1. CO oxidation on different catalysts as a function of temperature during the 1st heating ($\triangle$), 1st cooling ($\blacktriangle$), 2nd heating ($\triangle$), and 2nd cooling ($\blacktriangle$) steps.

mixture.^[32] However, reconstruction of the gold particles under reaction conditions can not be fully ruled out.^[33] However, since the amounts of water liberated and hydroxy groups lost directly depended on the specific surface area of the alumina support, and since this reactivity pattern is specific to high-surface-area alumina-supported gold catalysts^[12] and was not detected in the activity patterns of gold nanoparticles supported on low-surface-area alumina,^[20b] the involvement of OH and H₂O is likely. Conversely, both the titania- and zirconia-supported catalysts were activated under reaction conditions upon heating to 280 °C, despite the likely formation of poisonous surface carbonate species under these conditions.^[34] The titania support (P25), which is a mixture of anatase and rutile phases, showed particularly high sensitivity towards the test conditions, which can be attributed to a modification of its texture and the formation during the first heating step of a favorable contact between gold and titania.^[27] Nevertheless, the CO conversion pattern was similar in the cooling steps for all of the samples; data from the first cooling step (step 2) were thus used to compare the stabilized activity of the catalysts. Table 1 contains the stabilized specific rates at 80 °C for all oxidation reac-

tions as a function of the support. Based on these data, the following order of reactivity was determined for the oxidation of CO under CO+O₂ conditions:

with a ratio of 40:1 for the reaction rates obtained over the most active and the least active catalyst at 80 °C (Table 1). As the average gold particle size is close to 3 nm for all samples, the comparison of the activities of the catalysts based on turnover frequencies (TOFs) is identical and TOFs (Table 1) are only given for information and comparison with literature data. As mentioned before, given the similarities in size and shape of the gold particles, these differences in activities are likely to have arisen essentially from differences in the nature of the supports, and in particular their surface chemistry and

Table 1. Stabilized reaction rates and turnover frequencies calculated at 80 °C in the first cooling step (step 2) for the oxidation of CO in the absence [CO(ox)] and in the presence [CO(PROX)] of hydrogen and for the oxidation of hydrogen in the absence [H₂(ox)] and in the presence [H₂(PROX)] of CO.

Sample ^[a]	Reaction rate [mmol g _{Au} ⁻¹ s ⁻¹]				TOF [mol _{COconv} mol _{surface Au} ⁻¹ s ⁻¹]	
	CO(ox)	CO(PROX)	H ₂ (PROX)	H ₂ (ox)	CO(ox)	CO(PROX)
1.50 % Au/Al ₂ O ₃	0.07	2.40	1.37	1.71	0.03	1.10
1.34 % Au/ZrO ₂	0.28	2.67	1.04	2.86	0.13	1.22
1.50 % Au/TiO ₂	2.85	3.89	1.67	2.68	1.31	1.78
1.95 % Au/CeO ₂	0.84	0.92	0.36	0.86	0.38	0.42

[a] Average particle size of gold deduced by TEM was 3 nm in all cases.

reactivity towards the various reactants and products, as will be discussed later.

Interestingly, the order of reactivity found by comparison of CO conversions in the first heating step, that is, before any modification of the catalyst during heating under reaction conditions, is somewhat different: $\text{Au/CeO}_2 \gg \text{Au/Al}_2\text{O}_3 \approx \text{Au/TiO}_2 \approx \text{Au/ZrO}_2$. It is, however, similar to that found previously by testing these catalysts under steady-state CO oxidation conditions (1.5 % v/v CO, 5 % v/v O₂ in He, total flow rate of 50 cm³ min⁻¹) at 25 °C.^[21a] The superiority of Au/CeO₂, for which reaction rate of 2.8 mmol_{CO} g_{Au}⁻¹ s⁻¹ at 80 °C in step 1 is identical to the stabilized reaction rate for Au/TiO₂, confirms the critical importance of oxygen mobility during the reaction. The numerous oxygen vacancies on the ceria support have been proposed to ensure oxygen activation and reaction under CO+O₂, probably via peroxide and superoxide species.^[26b] High-surface-area ceria-supported gold catalysts have already been reported to be more active than the Au/TiO₂ reference catalyst^[35] for CO oxidation.^[36] Nevertheless, Au/TiO₂ became as active, in step 2, as Au/CeO₂ in step 1, probably due to the formation of an intimate contact surface between gold and titania, suggesting that Au/TiO₂ was truly activated not by the oxygen treatment (calcination in air at 300 °C for 4 h) but by a more reductive treatment (presence of CO and O₂ in the first heating step). Reducing atmospheres have indeed already proven superior to oxidizing treatments in obtaining highly active Au/TiO₂ catalysts.^[37] Conversely, the efficiency towards low-temperature oxygen activation of the OH groups in the alumina catalyst

(CO oxidation rate of 0.28 mmol_{CO} g_{Au}⁻¹ s⁻¹ at 80 °C in step 1) was similar to that of the conditioned Au/ZrO₂ catalyst (stabilized reaction rate of 0.28 mmol_{CO} g_{Au}⁻¹ s⁻¹ at 80 °C).

In the oxidation of hydrogen in the absence of CO, neither activation/deactivation of the catalyst upon heating under reaction conditions, nor hysteresis in the reactivity pattern, were detected. All catalysts seemed perfectly stable under these reaction conditions, after they were conditioned in the CO oxidation and PROX reactions. The maximum H₂ conversion achieved was 8.3%, corresponding to the relative fractions of O₂ and H₂ (2 and 48 vol.%) in the feed. Only slight variations in the light-off temperatures were observed, ranging from 100 °C for Au/ZrO₂ to 110 °C for Au/CeO₂. One can conclude that the support effect is not as critical in this case as it is for CO oxidation, since the most active catalyst, Au/ZrO₂, displays an H₂ oxidation rate only 3.3 times higher than the poorest catalyst, Au/CeO₂, at 80 °C (Table 1). However, the following trend can be written:

In the presence of both CO and H₂ in the reactant feed (Figure 2), the profile for H₂ oxidation was basically unchanged, with no hysteresis, activation, or deactivation with heating upon time-on-stream. Concerning the stability of the materials towards CO oxidation under PROX conditions, the peculiar behavior of Au/Al₂O₃, which was observed in hydrogen-free CO oxidation, had disappeared. However, all catalysts still displayed a different reactivity towards CO oxidation in the first

Figure 2. Oxygen consumption in CO (triangles) and hydrogen (rectangles) oxidations under PROX conditions on different catalysts as a function of temperature during the 1st heating ($\triangle$), 1st cooling ($\blacktriangle$), 2nd heating ($\triangle$), and 2nd cooling ($\blacktriangle$) steps. Note: Due to the relative CO/O₂ fraction in the feed (2 vol. %:2 vol. %) and the stoichiometry of the $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$ reaction, the values for CO conversion are two times higher than those represented by triangles on the graph (O₂ consumption by CO oxidation).

heating step and stabilized only after they had been heated to 280 °C under CO+O₂+H₂ conditions. Au/Al₂O₃, Au/TiO₂, and Au/ZrO₂ were activated whereas Au/CeO₂, as under CO+O₂ conditions, was deactivated upon heating under PROX conditions. In any case, the data from step 2, corresponding to stabilized activity, are used herein for discussion, unless otherwise stated.

In comparison to the CO-free hydrogen oxidation, the light-off temperatures for the oxidation of hydrogen under PROX conditions were only slightly shifted, by 10–20 °C towards higher temperatures. In contrast, the light-off temperatures for CO oxidation were significantly shifted towards lower temperatures when hydrogen was present in the feed, except over Au/CeO₂, whereupon the shift was rather small. Actually, the whole CO conversion profiles had changed. Indeed, the CO conversion first increased with temperature up to 110–150 °C, at which point it then decreased as the temperature was further raised to 280 °C. This effect is attributed to competitive adsorption between CO and H₂ on the same catalytic sites^[10a,9,38] and competitive reaction with the limited amount of oxygen (2%) present in the feed.^[7a] As the apparent activation energy for H₂ oxidation is superior to that for CO oxidation,^[7a,10a] hydrogen oxidation is favored at high temperature and causes inhibition of the oxidation of CO. This phenomenon was general for all catalysts. However, the decrease in CO conversion at $T > 150$ °C was limited on Au/CeO₂; the residual activity for CO oxidation at $T > 300$ °C was high (ca. 70%) as compared with that on the other catalysts (5–15%). This can be attributed to the activity of Au/CeO₂ for the water–gas shift (WGS) reaction (CO+H₂O⇌CO₂+H₂).^[39] Indeed, the presence of water, formed from the oxidation of H₂, at temperatures at which gold catalyzed-WGS can proceed, provides CO with an additional path for conversion to CO₂, which may also account for the full CO conversion achieved over this catalyst at 150 °C.^[29b]

It can be concluded that, for all four catalysts, regardless of the support, the effect of the presence of hydrogen on the oxidation of CO is beneficial at low temperature and detrimental at higher temperature. In contrast, the presence of CO apparently has less impact on the oxidation of hydrogen; the hydrogen oxidation is only slightly inhibited by the presence of carbon monoxide, whatever the type of support used, with decreases in H₂ oxidation rates (Table 1) ranging from 20% on Au/Al₂O₃ to 64% on Au/ZrO₂.

As the PROX reaction is intended to be carried out at low temperature (ca. 80 °C), the relative activities of the catalysts at 80 °C were taken into account. The following trend was established, based on the stabilized specific CO oxidation rates (Table 1):

The differences in the order of CO oxidation activity were far more subtle when H₂ was present in the stream, as the activity ratio between the most efficient and least efficient catalyst was one order of magnitude lower for PROX than for H₂-free CO oxidation (4.2:1 vs 40:1). Thus, the promoting effect of hydro-

gen on the low-temperature CO oxidation rate depends on the type of support used.

The biggest effect of hydrogen presence was observed for Au/Al₂O₃, with a decrease in light-off temperature from 130 °C to less than 20 °C in the presence of hydrogen, and a 34-fold increase in the CO oxidation rate, as compared to CO oxidation in a CO+O₂ mixture. The same effect, but less pronounced, was observed for Au/ZrO₂, for which the CO oxidation rate was 10 times higher in the presence of hydrogen. For the catalysts supported on titania and ceria, which were the most active in the absence of hydrogen, the addition of hydrogen increased the low-temperature CO oxidation rate by only 36% and 10%, respectively.

To understand these results, we need to return to literature data, in which regeneration of a Au/TiO₂ catalyst upon adding hydrogen to a CO+O₂ feed is reported.^[40] This effect has been attributed to the decomposition by H₂ of the formate/carbonate species, formed on the catalyst surface during H₂-free CO oxidation and responsible for catalyst deactivation. The formation of these poisoning species is also inhibited under PROX conditions, due to their immediate decomposition by reaction with H₂O, which is formed in the process by H₂ oxidation.^[9] Hence deactivation of the catalyst is prevented. The presence of hydrogen in the stream thus allowed the titania-supported catalyst to reach maximum and stable activity. This optimum activity, which is 36% higher than the stabilized activity under CO+O₂ conditions (Figure 1), was achieved only after a whole heating step under CO+O₂+H₂ (Figure 2). This result is consistent with modification of the Au/TiO₂ catalyst surface upon step 1 of PROX, in which the activity was similar, at low temperature, to that obtained under CO+O₂ (Table 1), with a CO oxidation rate of 2.92 mmol_{CO} g_{Au}⁻¹ s⁻¹ at 80 °C. The presence of hydrogen also enhances gold reduction, that is, it lowers the number of oxidized species present at the gold particle perimeter/interface with the TiO₂ support.^[41] The higher CO conversion achieved under PROX conditions on fully reduced gold catalysts thus confirms that metallic gold is active for the oxidation of CO.

The exceptional H₂-induced promotion of the Au/Al₂O₃-catalyzed, low temperature CO oxidation rate is attributed to a combination of full Au reduction and, through water formation, removal of poisoning species, increase in the number of active –OH species, and direct water promotion. Water, produced at higher temperatures upon hydrogen oxidation under PROX conditions (Figure 2), is known to allow decomposition of formate and carbonate species and regeneration of Au/Al₂O₃ catalysts.^[30a,32a] Water vapor also regenerates the fully hydroxylated state of the alumina surface. The number of hydroxy groups close to gold nanoparticles, which have been proposed to participate in the oxidation of CO through hydroxycarbonyl intermediates,^[30b] is thus maximized on the high-surface-area catalyst surface.^[9,42] The presence of water in the CO+O₂ feed is also known to directly promote the CO oxidation activity of an alumina-supported gold catalyst, a lot more significantly than that of Au/TiO₂,^[32b] potentially by hydroxylation of the high-surface-area material. Enhancement in the low-temperature CO oxidation rate over alumina-support-

ed gold catalysts in PROX has also been attributed to the weakening of CO adsorption on gold with hydrogen in the feed.^[12] However, the promotion was maximal only after a whole heating step under PROX conditions, which suggests that there is more than just an effect of H₂ on the gas and adsorbed phases. This behavior is consistent with modification of the active surface by thermal conditioning of the catalyst under CO+O₂+H₂. Furthermore, Au/Al₂O₃ displayed the lowest selectivity to CO₂ (Figure 3). It is thus the most active for H₂ oxidation, and hence water formation, under PROX conditions and the contribution of water to the enhanced stabilized CO oxidation activity is expected to be significant.

Figure 3. Selectivity to CO₂ over Au/Al₂O₃ (x), Au/ZrO₂ (■), Au/TiO₂ (●), and Au/CeO₂ (◆), as a function of CO conversion under PROX conditions in step 2.

Conversely, Au/CeO₂, with the lowest amount of hydroxy groups of all the catalysts (due to ololation and oxolation reactions upon dehydroxylation of ceria), also exhibited the lowest activity for H₂ oxidation, whether under CO-free or PROX conditions (Table 1). The positive effect of H₂, related to water formation, is thus expected to be weak on the ceria-supported gold catalyst. In particular, the extent of the removal of poisoning species by water should be small. The species formed on this peculiar, highly oxygen-deficient, reducible support actually behave differently to those present on the alumina and titania supports upon introduction of hydrogen. Formation of thermally stable, poisoning monodentate carbonates has been reported for Au/CeO₂ catalysts under CO₂/H₂ atmospheres and WGS conditions.^[29a] It is enhanced by the presence of CO₂ in the reaction gas, for example, at high CO conversions, whereas the presence of H₂ leads to the transformation of these species into bidentate and bridging formate species, which are less reactive than the bidentate formate species proposed to act as reaction intermediates in H₂-free atmospheres.^[29a] These phenomena can account for both the negligible promotion (10%) of Au/CeO₂ oxidation activity by H₂ and the deactivation of the catalyst during heating step 1 under CO+O₂ (Figure 1) and CO+O₂+H₂ (Figure 2).

The effect of water is also expected to be minimal on the low-surface-area ZrO₂-supported catalyst, which, like CeO₂ and

P25-TiO₂, and unlike alumina, is a poorly hydroxylated solid. Indeed, full Au reduction and removal of poisoning species induced only a moderate promoting effect on low-surface-area materials, as on Au/TiO₂. However, the CO oxidation rate promotion was significant over Au/ZrO₂. The fact that this catalyst was the most active for hydrogen oxidation in H₂+O₂ mixtures (Table 1) and that it displayed the highest decrease in the H₂ oxidation rate when CO is introduced to the feed (PROX conditions) suggests that intermediate species in the formation of water are used as additional or alternative oxidizing species for CO oxidation, instead of carrying out hydrogen oxidation,^[7a] and that hydrogen is involved in the direct activation of O₂, regardless of the formation of water, as recently proposed for Au/Al₂O₃.^[43]

Hence, under PROX conditions, Au/Al₂O₃ is a viable catalyst for CO oxidation. Indeed, Au/Al₂O₃ became more active than Au/CeO₂ and comparable to the most active catalysts for CO oxidation (Table 1). However, it remained less selective than the other catalysts studied herein (Figure 3), with an average selectivity to CO₂ of 65% at conversions of up to 50%. Au/TiO₂ was the most selective catalyst at low temperature (90%). It also maintained its superior selectivity over a wide range of CO conversions (40–85%), in particular up to the highest conversion. Despite its enhanced oxygen storage capacity and mobility features, which facilitate oxygen activation in CO+O₂ mixtures, ceria was not the best support for low-temperature PROX gold catalysts, due to its poisoning under reaction conditions and the presence of alternative oxygen activation pathways on other materials in the presence of hydrogen. However, Au/CeO₂ is the catalyst of choice to retain high selectivity towards CO₂ at high temperature, due to its activity in the water–gas shift reaction or, in other words, the alternative CO conversion pathway it can follow.

Conclusions

By carefully controlling the gold particle size, we have shown that the critical influence of the support on the gold-catalyzed CO oxidation rate under CO+O₂ conditions is significantly reduced when hydrogen is added to the feed. The presence of hydrogen indeed promoted the low-temperature CO oxidation rate to an extent that is a function of the type of support used. From this study, it appears that high activity in PROX was ensured by a combination of three key parameters:

- 1) The fully reduced state of gold achieved under PROX conditions.
- 2) The impact of water formation (from reaction between O₂ and H₂) on the chemical composition of the catalyst surface: Increase in the relative number of active sites/promoting species through enhanced hydroxylation and minimization of poisonous species formation (not for ceria).
- 3) The impact of O₂ and H₂ on providing additional reaction paths for CO conversion: Direct reaction of CO with water, at high temperature, through the water–gas shift (on Au/CeO₂) or

reaction of CO with H_2O species, intermediate to the formation of water, at low temperature, on Au/ZrO₂.

However, to be an efficient support for gold PROX catalysts, that is, to achieve high selectivity at high CO conversion, the oxide should preferably exhibit a low surface area and a low density of surface OH groups, so that formation of carbonate-type species, which inhibit the oxidation of CO, and consumption of oxygen in unselective water formation can be minimized. Au/TiO₂ thus remains the best catalyst for CO oxidation in the presence of hydrogen, whereas Au/CeO₂ is the catalyst of choice to retain high selectivity towards CO₂ at high temperature, due to its activity in the water–gas shift reaction.

Experimental Section

All materials were prepared according to a chemical method developed in Strasbourg, based upon the direct anionic exchange (DAE) of the gold species with the hydroxy groups of the support, followed by ammonia treatment, as extensively described in previous publications.^[19,21] In brief, aqueous solutions (900 mL) of HAuCl_4 ($10^{-4} \text{ mol L}^{-1}$; pH 3.5) were prepared and heated to 70 °C. Commercially available powder support $\gamma\text{-Al}_2\text{O}_3$ (Rhône Poulenc GCO 64, $200 \text{ m}^2 \text{ g}^{-1}$), CeO₂ (Rhône Poulenc Actalys HSA 5, $240 \text{ m}^2 \text{ g}^{-1}$), TiO₂ (Degussa P25, $60 \text{ m}^2 \text{ g}^{-1}$), or ZrO₂ (Degussa IRC, $45 \text{ m}^2 \text{ g}^{-1}$) were added in appropriate amounts (1 g) to aim for a final Au loading of 2 wt%. The slurries were then treated with aqueous solutions of ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$; concentrations, given later, were dependent on the support), to remove chlorine residues from the solution, from adsorbed gold chlorohydroxy complexes, and from the support. This procedure is strictly necessary in order to prevent gold particle size from increasing during the thermal treatments.^[23] Two different ammonia treatments were applied, based on a study reported in ref. [21], in order to aim for the same gold particle size on all supports: the Au/TiO₂, Au/ZrO₂ and Au/CeO₂ samples were submitted to a short in situ treatment, in which a concentrated ammonia solution (18 mol L^{-1} , 50 mL) was added to the suspension after 20 min and left to react for 20 min, while the slurry was allowed to slowly cool to room temperature. The Au/Al₂O₃ sample was submitted to a slow ex situ treatment, in which the powder was recovered by filtration after 1 h and redispersed for 1 h at 25 °C in a dilute ammonia solution (3 mol L^{-1}). The samples were then filtered, washed with distilled water, dried in air at 120 °C for 12 h, and calcined in air at 300 °C for 4 h.

Caution/safety note

Exposing the gold-containing solutions to ammonia could lead to the formation of gold–ammonia complexes, which are potentially explosive.^[44] Therefore, the use of this procedure is only safe if all of the gold is chemically bonded to the support as a result of the DAE, that is, none of the gold precursor is present in the solution during the ammonia treatment.

The materials were tested in a typical continuous-flow fixed-bed reactor operating at atmospheric pressure in the three reactions—the oxidation of CO, the selective oxidation of CO in the presence of H₂, and the oxidation of H₂—according to the same protocol. Only the incoming gas mixture was changed from one reaction to the next: 2% CO+2% O₂+96% He for the oxidation of CO; 2% CO+2% O₂+48% H₂+48% He for the preferential oxidation of CO (PROX); 48% H₂+2% O₂+50% He for the oxidation of H₂, using high-purity (>99.995%) gases from Air Liquide. Accurate and re-

producible CO/O₂/He, H₂/O₂/He and CO/O₂/H₂/He mixtures could be generated at a typical flow rate of 50 mL min^{-1} , using calibrated mass-flow controllers (Brooks). Product analysis was carried out on-line with a Varian-Micro GC (CP2003) equipped with a TCD detector and two columns, operated at 50 °C: a Molsieve 5 A column (Ar as carrier gas) to quantify O₂ and CO, and a PORAPLOT Q column (He as carrier gas) to quantify CO₂. Calibration of the GC was done with the unreacted gas mixture and a mixture containing 3% CO, 3% CO₂ and 6% O₂ in N₂ for CO₂. The gas mixture was then sent through the quartz tube reactor located in a ceramic furnace, which contained the catalytic powder. The catalyst was diluted in γ -alumina (Condea Puralox SCFa215, $215 \text{ m}^2 \text{ g}^{-1}$), which was inert under all reaction conditions used, to ensure similar gold content (0.16 mg in total) in the catalytic beds, similar bed lengths (13 mm) and similar gas hourly space velocities (GHSV) of approximately 3000 h^{-1} . The reactor was heated from 25 °C to 280 °C at a rate of $1^\circ \text{C min}^{-1}$ and then cooled down at the same rate. The reaction temperature was controlled by a thermocouple located inside the catalytic bed. Two reaction cycles (heating up to 280 °C and cooling to RT) were performed in order to evaluate the stability of the catalyst under reaction conditions.

Mass-specific reaction rates ($r \text{ mmol g}_{\text{Au}}^{-1} \text{ s}^{-1}$) were calculated for each reactant (CO, H₂, O₂) as follows:

$$r_{\text{reactant}} = y_{\text{reactant, in}} \times X_{\text{reactant}} \times \frac{V_{\text{gas}}}{m_{\text{Au}}}$$

where $y_{\text{reactant, in}}$ is the mole fraction of the reactant in the inlet gas mixture, X_{reactant} is the conversion of the reactant; V_{gas} is the total molar flow rate ($=50/60/22.4=3.72 \times 10^{-2} \text{ mmol s}^{-1}$), and m_{Au} is the mass of Au in the catalytic bed in g.

Consumption of oxygen in the oxidations of CO ($X_{\text{O}_2, \text{CO}}$) and H₂ ($X_{\text{O}_2, \text{H}_2}$) in PROX are calculated as follows:

$$X_{\text{O}_2, \text{CO}} = 1/2 X_{\text{CO}}$$

and

$$X_{\text{O}_2, \text{H}_2} = X_{\text{O}_2} - X_{\text{O}_2, \text{CO}}$$

where X_{O_2} is the total conversion of O₂.

Turnover frequencies (s^{-1}) are defined as the number of mole of reactant (CO, H₂) converted per number of mole of surface gold atom per second; they are determined as follows:

$$\text{TOF} = \frac{r_{\text{reactant}}}{1000} \times \frac{\text{MW}_{\text{Au}}}{d}$$

where MW_{Au} is the molar weight of gold ($196.95 \text{ g mol}^{-1}$); d is the dispersion of the gold particles (0.43 for all catalysts). Gold dispersions of 43% were obtained for all catalysts based on the average particle size determined by TEM (3 nm) and the mathematical model for cuboctahedral particles proposed by Polisset.^[24]

Selectivity to CO₂ under PROX conditions is defined as $1/2 \cdot \frac{r_{\text{CO}}}{r_{\text{O}_2}}$.

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Keywords: gold • hydrogen • nanoparticles • oxidation • supported catalysts

[1] E. D. Park, D. Lee, H. C. Lee, *Catal. Today* **2009**, 139, 280–290.

[2] A. F. Ghenciu, *Curr. Opin. Solid State Mater. Sci.* **2002**, 6, 389–399.

- [3] M. L. Brown Jr., A. W. Green, G. Cohn, H. C. Andersen, *Ind. Eng. Chem.* **1960**, 52, 841–844.
- [4] S. H. Oh, R. M. Sinkevitch, *J. Catal.* **1993**, 142, 254–262.
- [5] a) M. M. Schubert, M. J. Kahlich, G. Feldmeyer, M. Hüttner, S. Hackenberg, H. A. Gasteiger, R. J. Behm, *Phys. Chem. Chem. Phys.* **2001**, 3, 1123–1131; b) S. Alayoglu, A. U. Nilekar, M. Mavrikakis, B. Eichhorn, *Nat. Mater.* **2008**, 7, 333–338.
- [6] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* **1987**, 405–408.
- [7] a) E. Quinet, F. Morfin, F. Diehl, P. Avenier, V. Caps, J.-L. Rousset, *Appl. Catal. B* **2008**, 80, 195–201; b) C. W. Corti, R. J. Holliday, D. T. Thompson, *Top. Catal.* **2007**, 44, 331–343.
- [8] a) R. M. Torres Sanchez, A. Ueda, K. Tanaka, M. Haruta, *J. Catal.* **1997**, 168, 125–127; b) R. Grisel, K.-J. Weststrate, A. Gluhoi, B. E. Nieuwenhuys, *Gold Bull.* **2002**, 35, 39–45; c) A. Luengnaruemitchai, D. T. K. Thoa, S. Osuwan, E. Gulari, *Int. J. Hydrogen Energy* **2005**, 30, 981–987.
- [9] B. Schumacher, Y. Denkwitz, V. Plzak, M. Kinne, R. J. Behm, *J. Catal.* **2004**, 224, 449–462.
- [10] a) M. J. Kahlich, H. A. Gasteiger, R. J. Behm, *J. Catal.* **1999**, 182, 430–440; b) M. M. Schubert, A. Venugopal, M. J. Kahlich, V. Plzak, R. J. Behm, *J. Catal.* **2004**, 222, 32–40; c) P. Landon, J. Ferguson, B. E. Solsona, T. Garcia, S. Al-Sayari, A. F. Carley, A. A. Herzing, C. J. Kiely, M. Makkee, J. A. Moulijn, A. Overweg, S. E. Golunski, G. J. Hutchings, *J. Mater. Chem.* **2006**, 16, 199–208.
- [11] a) F. Arena, P. Famulari, G. Trunfio, G. Bonura, F. Frusteri, L. Spadaro, *Appl. Catal. B* **2006**, 66, 81–91; b) L.-H. Chang, N. Sasirekha, Y.-W. Chen, W.-J. Wang, *Ind. Eng. Chem. Res.* **2006**, 45, 4927–4935.
- [12] D. Gavril, A. Georgaka, V. Loukopoulos, G. Karaiskakis, B. E. Nieuwenhuys, *Gold Bull.* **2006**, 39, 192–199.
- [13] M. M. Schubert, V. Plzak, J. Garche, R. J. Behm, *Catal. Lett.* **2001**, 76, 143–150.
- [14] C. Rossignol, S. Arrii, F. Morfin, L. Piccolo, V. Caps, J.-L. Rousset, *J. Catal.* **2005**, 230, 476–483.
- [15] M. Haruta, *Gold Bull.* **2004**, 37, 27–36.
- [16] A. A. Herzing, C. J. Kiely, A. F. Carley, P. Landon, G. J. Hutchings, *Science* **2008**, 321, 1331–1335.
- [17] S. Arrii, F. Morfin, A. J. Renouprez, J. L. Rousset, *J. Am. Chem. Soc.* **2004**, 126, 1199–1205.
- [18] M. Comotti, W.-C. Li, B. Spliethoff, F. Schüth, *J. Am. Chem. Soc.* **2006**, 128, 917–924.
- [19] S. Ivanova, C. Petit, V. Pitchon, *Appl. Catal. A* **2004**, 267, 191–201.
- [20] a) S. Ivanova, C. Petit, V. Pitchon, *Gold Bull.* **2006**, 39, 3–9; b) E. Quinet, PhD thesis, University of Lyon I, **2008**.
- [21] a) S. Ivanova, V. Pitchon, C. Petit, *J. Mol. Catal. A* **2006**, 256, 278–283; b) S. Ivanova, PhD thesis, University of Strasbourg 1, **2004**.
- [22] M. E. Manriquez, T. López, R. Gómez, J. Navarrete, *J. Mol. Catal. A* **2004**, 220, 229–237.
- [23] S. Ivanova, V. Pitchon, Y. Zimmermann, C. Petit, *Appl. Catal. A* **2006**, 298, 57–64.
- [24] M. Polisset, Ph. D. Thesis, University of Paris VI, **1990**.
- [25] B. Campo, M. Volpe, S. Ivanova, R. Touroude, *J. Catal.* **2006**, 242, 162–171.
- [26] a) T. V. W. Janssens, A. Carlsson, A. Puig-Molina, B. S. Clausen, *J. Catal.* **2006**, 240, 108–113; b) J. Guzman, S. Carrettin, A. Corma, *J. Am. Chem. Soc.* **2005**, 127, 3286–3287.
- [27] E. D. Park, J. S. Lee, *J. Catal.* **1999**, 186, 1–11.
- [28] C. Li, Y. Sakata, T. Arai, K. Domen, K.-I. Maruya and T. Onishi, *J. Chem. Soc. Faraday Trans. 1* **1989**, 85, 929–943.
- [29] a) Y. Denkwitz, A. Karpenko, V. Plzak, R. Leppelt, B. Schumacher, R. J. Behm, *J. Catal.* **2007**, 246, 74–90; b) R. Burch, *Phys. Chem. Chem. Phys.* **2006**, 8, 5483–5500.
- [30] a) C. K. Costello, M. C. Kung, H.-S. Oh, Y. Wang, H. H. Kung, *Appl. Catal. A* **2002**, 232, 159–168; b) C. K. Costello, J. H. Yang, H. Y. Law, Y. Wang, J.-N. Lin, L. D. Marks, M. C. Kung, H. H. Kung, *Appl. Catal. A* **2003**, 243, 15–24.
- [31] D. Gajan, K. Guillois, P. Delichère, J.-M. Basset, J.-P. Candy, V. Caps, C. Co-péret, A. Lesage, L. Emsley, *J. Am. Chem. Soc.* **2009**, 131, 14667–14669.
- [32] a) X.-H. Zou, S.-X. Qi, Z.-H. Suo, L.-D. An, F. Li, *Catal. Commun.* **2007**, 8, 784–788; b) M. Daté, M. Okumura, S. Tsubota, M. Haruta, *Angew. Chem.* **2004**, 116, 2181–2184; *Angew. Chem. Int. Ed.* **2004**, 43, 2129–2132.
- [33] E. Roze, E. Quinet, V. Caps, D. Bianchi, *J. Phys. Chem. C* **2009**, 113, 8194–8200.
- [34] P. Konova, A. Naydenov, T. Tabakova, D. Mehandjiev, *Catal. Commun.* **2004**, 5, 537–542.
- [35] Gold reference catalysts, *Gold Bull.* **2003**, 36, 24.
- [36] S. Carrettin, P. Concepción, A. Corma, J. M. López Nieto, V. F. Puentes, *Angew. Chem.* **2004**, 116, 2592; *Angew. Chem. Int. Ed.* **2004**, 43, 2538–2540.
- [37] N. Weiher, E. Bus, L. Delannoy, C. Louis, D. E. Ramaker, J. T. Miller, J. A. van Bokhoven, *J. Catal.* **2006**, 240, 100–107.
- [38] R. J. H. Grisel, B. E. Nieuwenhuys, *J. Catal.* **2001**, 199, 48–59.
- [39] D. Tibiletti, A. Amieiro-Fonseca, R. Burch, Y. Chen, J. M. Fisher, A. Goguet, C. Hardacre, P. Hu, D. Thompson, *J. Phys. Chem. B* **2005**, 109, 22553–22559.
- [40] M. Azar, V. Caps, F. Morfin, J.-L. Rousset, A. Piednoir, J.-C. Bertolini, L. Piccolo, *J. Catal.* **2006**, 239, 307–312.
- [41] J. H. Yang, J. D. Henao, M. C. Raphulu, Y. Wang, T. Caputo, A. J. Groszek, M. C. Kung, M. S. Scurrell, J. T. Miller, H. H. Kung, *J. Phys. Chem. B* **2005**, 109, 10319–10326.
- [42] H. H. Kung, M. C. Kung, C. K. Costello, *J. Catal.* **2003**, 216, 425–432.
- [43] E. Quinet, L. Piccolo, F. Morfin, P. Avenier, F. Diehl, V. Caps, J.-L. Rousset, *J. Catal.* **2009**, 268, 384–389.
- [44] a) J. M. Fisher, *Gold Bull.* **2003**, 36, 155; b) G. A. Cusumano, *Nature* **1974**, 247, 456.

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