Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 230 (2005) 476–483

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Selective oxidation of CO over model gold-based catalysts in the presence of H_2

Cécile Rossignol, Sandrine Arrii, Franck Morfin, Laurent Piccolo, Valérie Caps,
Jean-Luc Rousset [*]

Institut de Recherches sur la Catalyse (CNRS), 2 Avenue Albert Einstein, F-69626 Villeurbanne, France

Received 5 November 2004; revised 17 December 2004; accepted 7 January 2005

Abstract

The model catalysts Au/Al_2O_3, Au/ZrO_2, and Au/TiO_2 were produced by laser vaporization of a metallic gold rod followed by deposition of the formed clusters onto the support powders. This technique allows to obtain a narrow size distribution of highly dispersed gold particles on the support and, most importantly, similar sizes whatever the support. This makes it possible to accurately study of the influence of the support identity on the catalytic reaction. A detailed investigation of the preferential oxidation of CO in the presence of H_2 was undertaken. Catalytic performances in the PROX reaction were compared with those in the oxidation of CO in the temperature range of 25–420 °C. A boost in the conversion of CO was observed in the presence of H_2 at low temperature; the extent of this boost is dependent on the support identity. Hence the reactivity order found for CO oxidation ($Au/Al_2O_3 \ll Au/ZrO_2 < Au/TiO_2$) was changed. In fact, in the presence of H_2, the reaction rates for the oxidation of CO become rather similar on all three systems.

Keywords: Gold catalysis; Model catalyst; Laser vaporization; CO oxidation, PROX

---

1. Introduction

The catalytic potentials of supported gold-based nanoparticles have been considered for a number of useful applications; among these, air-cleaning by oxidation of CO [1–5], hydrogen purification in fuel cell technology via the water–gas shift reaction [6–8] and the selective oxidation of CO in the presence of hydrogen (SELOX or PROX for preferential oxidation) [1,9–11] have received particular attention. The advantage of using gold in these reactions is indeed its catalytic activity at low temperature as compared with the other metals from the platinum group. However, despite extensive efforts in the preparation, characterization, and testing of gold catalysts, the reaction mechanisms still remain unclear. This is due partly to the structure sensitivity of the gold-catalyzed reactions and the sharp dependency of gold structure on a number of preparation parameters, such as temperature, pH, type of incorporation, etc. The main issue seems be the limited choice in the gold precursors [12]. The chlorinated $HAuCl_4$ precursor is mostly used; the method (deposition-precipitation, co-precipitation, or ion exchange) is then selected according to the nature of the support on which gold is deposited. This leads, after heat treatment, to gold particles with different sizes on different supports and makes it difficult to investigate any support effects in the catalytic reactions [13]. In addition, these chemical methods suffer not only from low reproducibility but also from unwanted incorporation of chloride residuals and/or other contaminants (Na, etc.) in the catalyst, even after extensive washing and/or postsynthetic heat treatments.

Recently we reported on the preparation of model catalysts using of laser vaporization [14]. With this method, we managed to get highly dispersed small gold particles (2–3 nm) at the surface of the traditional metal oxide powders (Al_2O_3, ZrO_2, and TiO_2) and a narrow size distribution

---

[*] Corresponding author.
E-mail address: rousset@catalyse.cnrs.fr (J.-L. Rousset).

0021-9517/$ – see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2005.01.011

of these particles. Furthermore, it was shown that since the metallic clusters were formed *before* deposition, their size was predetermined and similar size distributions were obtained on all the supports. With this technique, indeed, the metal particle size did not depend on the interaction of a metal precursor with the support (and hence on the nature of the support), since the preformed gold particles were physically deposited on the support. This ligand-free method thus turned out to be a unique way to produce clean model catalysts, avoid heat treatments and make it possible to accurately study the influence of the identity of the support on the catalytic oxidation of CO. A clear support effect on the CO oxidation rates was indeed evidenced: titania was better than zirconia, which was much better than alumina.

In this paper we investigate support effects in the selective oxidation of CO in the presence of hydrogen by using the same gold-based model systems. Results are compared with those obtained from the oxidation of CO. The influence of H_2 on the CO conversion, and its extent depending on the support, will be presented and discussed. The selectivity of the catalysts will also be discussed through a comparison of their behavior in the PROX reaction and in the oxidation of H_2. A possible mechanism for the PROX reaction will be suggested on the basis of these observations. Some conclusions about the type of catalyst that could be suitable for PROX will then be drawn.

2. Experimental

2.1. Catalyst preparation

The three catalysts used in this study (Au/Al_2O_3, Au/ZrO_2, and Au/TiO_2) were prepared by low-energy cluster beam deposition, which has been described in detail elsewhere [14]. In brief, the second harmonic of a Nd:YAG pulsed laser is used to vaporize the metal from the rod, which creates a plasma. Cluster nucleation and growth occur when a continuous flow of inert gas (a mixture of He and Ar) is introduced into the vacuum chamber. Differential pumping extraction of the clusters through a skimmer yields a cluster beam that carries neutral and ionized species. After removal of the ionized clusters by electrostatic deflection, the neutral clusters are deposited on the substrates. To deposit the clusters on the supports, which in the present case are alumina (Condea Puralox Sc-Fa-215, 221 $m^2\,g^{-1}$), titania (Hombikat T100 20-S20 Type, anatase 60 $m^2\,g^{-1}$), and zirconia (MEL chemical, 79 $m^2\,g^{-1}$) powders, a device was developed that stirs the powder in front of the cluster beam. This device favors homogeneous cluster deposition on most of the powder grains. After deposition, the samples are air-transferred, characterized, and used for catalytic reactions. For these experiments, a gold rod of 99.99% purity from Goodfellow was used. The metal content of each catalyst measured by chemical analysis (ICP or ICP-MS) is reported in Table 1. The catalyst characterization (TEM-EDX, XPS) is well described in a previous paper [14]; the results are summarized in Table 1. The gold clusters deposited on the different supports have similar and narrow size distributions centered around 3 nm. They are in the metallic state Au^0.

Table 1
Metal loadings (ICP analysis) and mean diameters of the gold particles in fresh and used catalysts (TEM). In parentheses are the standard deviations

Sample	Gold metal content (wt%)	Mean diameter (nm)	
		Fresh catalysts	Used catalysts
$Au/\gamma\text{-}Al_2O_3$	0.080	2.6 (1.6)	3.1 (1.6)
Au/ZrO_2	0.054	2.9 (1.7)	3.8 (1.9)
Au/TiO_2	0.023	2.9 (1.7)	3.2 (1.3)
Au/TiO_2 (Ref. WGC)	1.47[a]	3.7 (1.5)	N/A

[a] In house measurements give Au 1.38 wt%, Na 0.055 wt%, Cl 47 ppm.

2.2. Catalytic activity measurements

The materials were tested in three reactions—the oxidation of CO, the selective oxidation of CO in the presence of H_2 and the oxidation of H_2—according to the same protocol. Only the incoming gas mixture was changed from one reaction to the other. These tests were carried out at atmospheric pressure in a continuous-flow fixed-bed reactor. 750 mg of the as-obtained gold-based powders was loaded into the quartz reactor, located in a ceramic furnace, which resulted in a length of $\sim$ 10 mm for the catalytic bed. No pretreatment was applied (an important advantage of this catalyst over catalysts prepared from salt precursors is the negligible amount of impurities and residuals). A Au/TiO_2 reference catalyst (Type A, Sample Number 53) was also purchased from the World Gold Council [15] and tested. To allow direct comparison of the catalytic results, 11.6 mg of this catalyst was diluted in 740 mg γ-Al_2O_3 (which is inactive for the three reactions studied under the present conditions). This ensures a gold content (0.17 mg) similar to that in the test with the model Au/TiO_2 catalyst (prepared by laser vaporization).

The reactant flow consisted of a mixture of 2% CO + 2% O_2 + 96% He for the oxidation of CO, 2% CO + 2% O_2 + 48% H_2 + 48% He for the preferential oxidation of CO (PROX) and 48% H_2 + 2% O_2 + 50% He for the oxidation of H_2 (all percentages are vol%). All the high-purity ($>$ 99.995%) gases were purchased from Air Liquide. Mass-flow controllers (Brooks) were calibrated for the above gases with a soap-bubble flow meter. In this way, accurate and reproducible $CO/O_2/He$, $H_2/O_2/He$ or $CO/O_2/H_2/He$ mixtures could be generated at a typical flow rate of 50 Nml min^{-1}. The gas mixture could then be sent either through the reactor or directly to the gas chromatograph for analysis and calibration of the GC. Calibration of the GC was done with a gas mixture containing 3% CO, 3% CO_2 and 6% O_2 in N_2. The reactor was heated to 450 °C and then cooled to 25 °C at a heating (and cooling) rate of 1 °C min^{-1}. Several reaction cycles, each consisting of a heating and a cooling period, were recorded to monitor possible hysteresis, deactivation or activation. Product analysis was carried out on-line with a Varian-Micro GC (CP2003) equipped with a TCD detector. Two columns, operated at 50 °C, were used in parallel: a Molsieve 5A column (Ar as carrier gas) to quantify O_2 and CO, and a poraPLOT Q column (He as carrier gas) to quantify CO_2. To avoid polluting the Micro GC columns, the steam was trapped at the exit of the reactor in a condenser held at 3 °C, using a Peltier gas cooler (M&C cooler ECP 1000). We used the usual procedure to ensure that the activity was measured in the kinetic regime: the flow rates and the mass of catalyst were varied in the same proportions to provide a constant contact time and consequently a constant space velocity. The conversion did not vary as the mass flow was changed, indicating that the measured rate was not limited by external transfers (film diffusion).

3. Results

As mentioned above, several reaction cycles, each consisting of a heating and a cooling period, were performed. The CO conversion (under CO oxidation conditions) was found to be always lower in the first heating stage than in the following runs. Later on, no modification of the catalytic activity was observed in further cycles, indicating a stabilization of the catalysts. To better understand this activation of the catalyst during the first run, an experiment was made with a pre-cycle (heating and cooling) under He (reactant-free) before two cycles under reactive mixture. After this first cycle in helium, the two subsequent cycles under CO oxidation conditions were then found to be similar to those obtained after a first cycle under a $CO + O_2$ mixture. This indicates that activation of the catalyst is not related to the formation of active species during contact with the reactive mixture. Activation of the catalyst through engineering of irreversible metal–support interactions during heating to 450 °C is also ruled out on the basis of an experiment showing the same first-cycle activation on the same used catalyst left for 45 days in air/moisture. Desorption of water from the catalyst surface upon heating at 450 °C seems to be responsible for the catalyst activation. Hence results corresponding to the second cycle (and further cycles), which were already found to be more representative of the intrinsic activity of gold catalysts [14,16], are used for the following discussion.

3.1. CO oxidation in a H_2-free atmosphere (2% CO, 2% O_2 in He)

It is widely accepted that titania is currently the best support for gold nanoparticles in the catalytic oxidation of CO. This result was confirmed in a previous paper [14], where gold nanoparticles were dispersed on alumina, zirconia, and titania supports with the same size distribution and found to convert more CO on TiO_2 than on ZrO_2; Al_2O_3 yielded the poorest conversion of CO. Here we compare our model catalysts with the Au/TiO_2 reference catalyst prepared by deposition-precipitation according to a protocol developed by AIST (Japan). As can be seen in Fig. 1d, this catalyst is superior for CO conversion compared with our catalyst prepared by laser vaporization (Fig. 1c). Given that the average particle size of gold (3.7 nm) is even larger than in our material (2.9 nm), we attribute this higher activity to some side effects due to the presence of other elements (Na 0.034 wt%, Cl 47 ppm) or, more probably, to a specific interaction of the gold particle with the support engineered during the heat treatment that is required in the chemical methods of preparation. In any case, this comparison shows that the activity of our model catalyst is of the same order of magnitude as that of the reference catalyst for the oxidation of CO. Actually, this is also the case for the oxidation of H_2 and the oxidation of CO in the presence of H_2, but since the point of the present study is to compare catalytic properties on model systems, the following discussion will focus only on them.

3.2. H_2 oxidation in a CO-free mixture (48% H_2, 2% O_2 in He)

Before proceeding to the PROX reaction, we performed H_2 oxidation with a large excess of hydrogen. Because of the large error in the quantification of H_2O and the small change in the H_2 concentration due to the large excess of hydrogen (for total O_2 consumption, only 8% of the hydrogen can be oxidized), we evaluated the activity of the catalyst in the oxidation of H_2 by quantifying the O_2 conversion. As can be seen from Figs. 1a and 1b, Au/Al_2O_3 and Au/ZrO_2 are more active for the oxidation of H_2 than for the oxidation of CO, whereas Au/TiO_2 is more active for the oxidation of CO (Fig. 1c). Temperatures of half-maximum conversions are indeed 230 °C lower, 25 °C lower, and 25 °C higher in H_2 oxidation than in CO oxidation for Au/Al_2O_3, Au/ZrO_2, and Au/TiO_2, respectively. Maximum H_2 conversion is readily achieved at 170 °C on Au/Al_2O_3, at 225 °C on Au/ZrO_2, and at 250 °C on Au/TiO_2. We note that Haruta et al. [17] found, for a standard gas containing 1 vol% H_2 or CO in air, rather identical activities for the two reactions over a Au/ZrO_2 catalyst prepared by coprecipitation; the better activity found for H_2 oxidation as compared with CO oxidation over our model Au/ZrO_2 catalyst could come from the large partial pressure of hydrogen we employed. It is also worth noting that, if we take into account the catalyst loadings (Table 1), the rate of H_2 oxidation (Fig. 2) is similar for all our model catalysts. This has already been observed, under Haruta's conditions, with silica-, alumina-, and titania-supported gold catalysts, over which H_2 oxidation is much less influenced by metal–support interactions than is CO oxidation [18].

3.3. PROX reaction (2% CO, 2% O_2, 48% H_2 in He)

Because the ability of the catalyst to oxidize CO more readily than H_2 is generally thought to be a prerequisite for

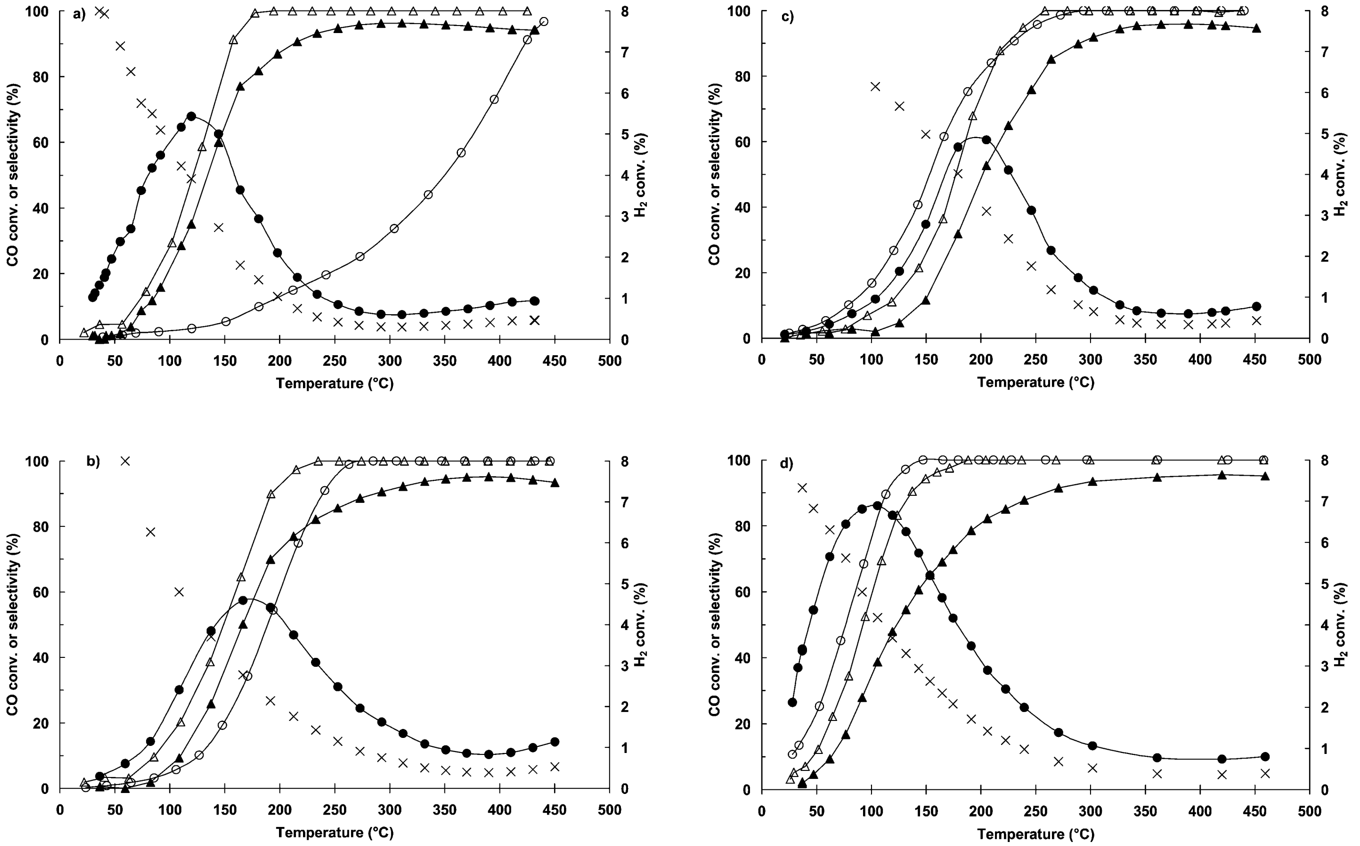


Fig. 1. CO and H_2 conversion and selectivity as a function of temperature over Au/Al_2O_3 (a), Au/ZrO_2 (b), Au/TiO_2 (c) and Au/TiO_2-WGC (d). (○) CO conversion in H_2-free mixture, (△) H_2 conversion in CO-free mixture, (●) CO conversion in PROX, (▲) H_2 conversion in PROX and (×) selectivity.

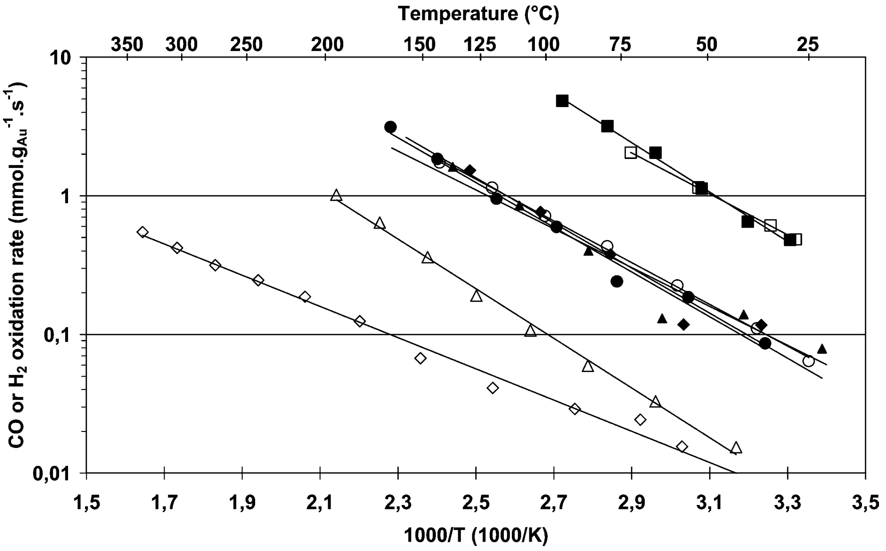


Fig. 2. CO oxidation rate vs temperature in H_2-free mixture (open symbols) and H_2 oxidation rate vs temperature in CO-free mixture (dark symbols) over Au/Al_2O_3 (◇ and ◆), Au/ZrO_2 (△ and ▲), Au/TiO_2 (○ and ●) and Au/TiO_2-WGC (☐ and ■). Only the points corresponding to a conversion below 50% are plotted.

selective CO oxidation in the presence of H_2 [11,18–21], we expected the support effect to be the same in the PROX reaction as in the CO oxidation; that is, titania is better than zirconia and much better than alumina.

However, it is clear for all systems (Fig. 1) that, in the presence of H_2, the conversion of CO reaches a maximum at a relatively low temperature (65% on Au/Al_2O_3 at 119 °C, 60% on Au/TiO_2 at 196 °C, and 55% on Au/ZrO_2

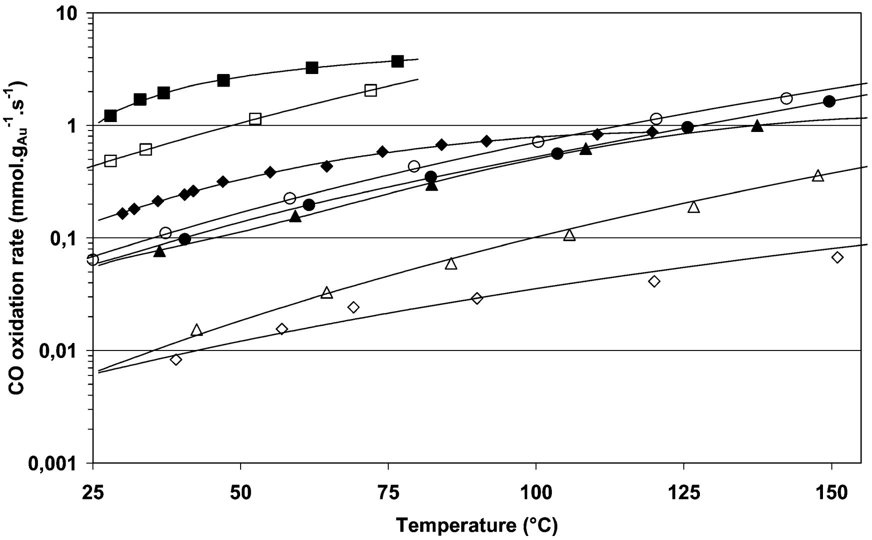


Fig. 3. CO oxidation rate vs temperature in H_2-free mixture (open symbols) and in PROX mixture (dark symbols) over Au/Al_2O_3 (◇ and ◆), Au/ZrO_2 (△ and ▲), Au/TiO_2 (○ and ●) and Au/TiO_2-WGC (□ and ■). Only the points corresponding to a conversion below the maximum conversion reached in the PROX reaction are plotted.

Table 2
Temperature of half-conversion, reaction rates and activation energies for the oxidation of CO, the oxidation of H_2 and the PROX reaction over our catalysts[a]

Catalyst	CO oxidation (H_2 free)			H_2 oxidation (CO free)			CO oxidation in PROX		
	$T_{1/2}$ (°C)	Rate	E_a	$T_{1/2}$ (°C)	Rate	E_a	T_{max} (°C)	Rate	$T_{1/2}(H_2)$[b] (°C)
Au/γ-Al_2O_3	350	0.02	22	121	0.39	31	119	0.62	135
Au/ZrO_2	188	0.05	34	150	0.38	27	172	0.29	166
Au/TiO_2	153	0.42	29	177	0.36	31	196	0.32	201
Au/TiO_2 (Ref. WGC)	77	2.6	28	92	3.2	34	102	3.7	123

[a] $T_{1/2}$ = temperature of half-conversion, i.e. temperature at which 50% of the reactant has been converted; E_a = activation energy (kJ mol^{-1}) derived from Fig. 2; Rate = reaction rates (mmol g_{Au}^{-1} s^{-1}) calculated at 80 °C from Fig. 1; T_{max} = temperature corresponding to the maximum CO conversion reached in the PROX reaction.

[b] Temperature of half-conversion of H_2.

at 172 °C) and then decreases rapidly, which is attributed first to the competition of adsorption between H_2 and CO (favorable to hydrogen when temperature increases) and second to the consumption of the oxidant in the oxidation of hydrogen. Indeed, the temperatures of the maxima correspond approximately to the temperatures of half-conversion of H_2 in the oxidation of H_2 in the presence of CO (Table 2). At this point about 75% O_2 is converted (50% for the oxidation of H_2 and about 25% for the oxidation of CO).

Nevertheless, below those temperatures, the efficiency order of the catalysts in the PROX reaction seems to be reversed as compared with that in the CO oxidation reaction: CO conversion is now higher on the alumina-supported catalyst than on the zirconia- and titania-supported catalysts. Indeed, CO oxidation is largely enhanced on the alumina-supported catalyst, when H_2 is present in the reactive mixture, whereas it is only slightly enhanced on the zirconia-supported catalyst and basically unaffected on the titania-supported catalyst. If we take into account the loadings of the catalysts (Table 1), the rates in the catalytic oxidation of CO in the PROX reaction are rather similar for all three systems, as seen in Fig. 3. In other words, in the presence of hydrogen, gold on alumina will convert as much CO as gold on titania or gold on zirconia. It seems that hydrogen masks the effect of the support in the oxidation of CO or, more precisely, that the effect of hydrogen makes our catalysts equivalent for the PROX reaction.

Hence the actual selectivity is found to be much higher than that expected from the results obtained for CO and H_2 oxidation when O_2 is the only counterpart reactant gas (Fig. 1). A high selectivity for CO_2 is achieved at low temperatures on all the catalysts, and it decreases rapidly with increasing temperature. Actually, the activities of the catalysts for the oxidation of H_2 decrease a little in the presence of CO; the alumina-supported catalyst is the least affected. With maximum H_2 conversions reached at 230 °C over Au/Al_2O_3, 300 °C for Au/ZrO_2, and 325 °C for Au/TiO_2, Au/Al_2O_3 remains superior for H_2 oxidation compared with H_2-free CO oxidation (see Fig. 1, dark triangles and open circles), Au/TiO_2 remains better for CO oxidation, while the activity of Au/ZrO_2 is now similar in both reactions. In any case, as in the CO-free H_2 oxidation reaction (Section 3.2), H_2 oxidation rates are similar for all supports.

4. Discussion

4.1. H_2-induced boost in the CO oxidation rate

Generally, the CO conversion over supported Au catalysts [11,16,22] is reported to decrease when H_2 is introduced into the reaction mixture, even if some exceptions exist [9], like Au/MgO/Al_2O_3 [16]. Only for Pt catalysts supported on alumina was it reported in the literature that CO oxidation was enhanced by the presence of hydrogen [23]. In this case, the physical origin of the H_2-induced increase in the CO oxidation rate has not been fully explained so far, but possible mechanisms include the effect of hydrogen on the heat of adsorption of CO and on the interaction of the hydroxylated Al_2O_3 support with CO adsorbed on Pt [23].

On the other hand, for gold catalysts, beneficial effects of H_2 on the CO oxidation reaction are mostly related to the prevention of deactivation and regeneration. Costello and co-workers [24] have indeed demonstrated that while the activity of Au/Al_2O_3 catalyst declined rapidly with time on stream in CO oxidation, the presence of hydrogen during selective CO oxidation successfully prevented deactivation. They also showed that a deactivated Au/Al_2O_3 catalyst (after reaction in CO oxidation) could be regenerated by exposure to H_2 or even water vapor at room temperature. These results suggest [24,25] that the active sites probably contain hydroxyl groups, which can be removed by CO oxidation. These hydroxyl groups would participate in the reaction, possibly by reaction with CO, forming an active intermediate in the CO_2 production pathway. Deactivation during CO oxidation would then be due to the depletion of the hydroxylated active sites when the reaction intermediate transforms into a stable surface species. These surface species, possibly surface carbonates, can be removed by reaction with hydrogen to regenerate the hydroxyl groups. However, in this work, H_2 only helps to prevent deactivation of the catalyst and to reactivate it; no beneficial effect on the intrinsic activity for CO oxidation has been mentioned. Choudhary and co-workers [26] have also reported that Au/TiO_2 catalysts, which are known to generally undergo rapid deactivation during the CO oxidation reaction, could be completely regenerated after subsequent H_2–O_2 treatments. Moreover, it has been shown very recently [27] that the addition of water to the $CO + O_2$ mixture accelerated the rate of oxidation, in accordance with previous work [28].

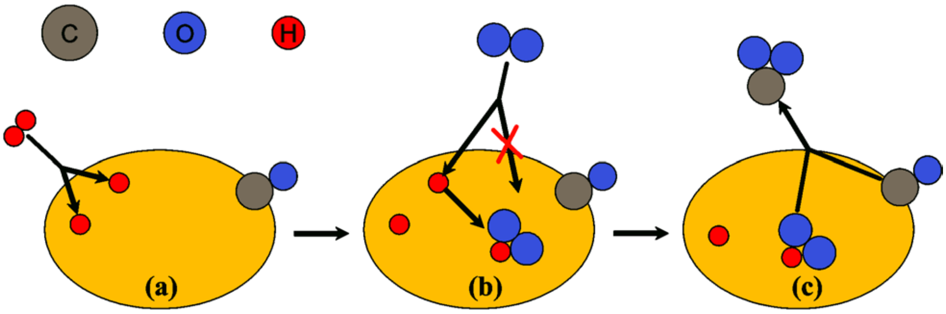
Furthermore, a pronounced effect of the H_2 co-reactant was observed in kinetic measurements. At a temperature of 80 °C and in the pressure range ($0.03\ \text{kPa} < P_{CO} < 2\ \text{kPa}$) investigated by Schumacher et al. [22] during their preferential CO oxidation (PROX) study on Au/TiO_2 catalysts, it was shown that H_2 affects the CO oxidation, most probably by competing with the CO adsorption on the Au nanoparticles and reacting with oxygen, which results in a significantly higher CO reaction order. Indeed, the reaction order for CO increased from about 0.35 to about 0.9 in the presence of H_2. This is consistent with a reduced CO oxidation activity in the whole pressure range investigated. This reduction diminishes as the CO partial pressure increases and vanishes when the CO partial pressure reaches 2 kPa.

In the present work, in the presence of hydrogen, the rate of CO oxidation is boosted and similar on three very different supports, reducible and nonreducible oxides, while they are so different in the pure oxidation of CO. This could be related to the fact that all three catalysts have a similar activity in the oxidation of H_2. It is possible that if hydroxyl groups at the metal–support interface are important for the CO oxidation reaction, the reaction of hydrogen or water with the support produces the same amount of these active species on all the supports, as was recently discussed [29]. It is also possible that, under our conditions, molecular oxygen is transformed, through reaction with hydrogen, into an active species that is capable of oxidizing CO [30]. This phenomenon has already been invoked in the selective oxidation of propylene to propylene oxide (PO). The direct synthesis of PO, with the use of molecular oxygen, is one of the most important chemical reactions to remain unsolved by catalysis [31]. Nevertheless, recent studies have shown that Au catalysts can effectively catalyze the direct vapor-phase conversion of propylene to PO when hydrogen is used in addition to molecular oxygen [31,32]. Many highly reactive intermediates, such as H_2O_2, are known to be involved during the reaction between H_2 and O_2 [33]. It has been proposed that these hydrogen peroxy-like species formed on the Au surface are oxidants for the epoxidation reaction. Neutron experiments from C. Sivadinarayana et al. [34] provide evidence for the formation of hydrogen peroxide H_2O_2 and hydroperoxo radicals ($HOO^{\bullet}$) from the reaction between H_2 and O_2 over supported Au nanoclusters. In addition, a D_2 kinetic isotope effect on the PO formation rate has been observed, indicating that hydrogen is involved in the rate-limiting step of this reaction [35].

Thus it seems obvious that, in the presence of H_2, two phenomena should occur simultaneously. One of these, *which has a negative effect on CO oxidation*, would be a competition of adsorption between H_2 and CO [16,22]. The other one, *which has a beneficial effect on CO oxidation*, would be the appearance of additional reactive intermediates produced in the presence of H_2. The competition between these two phenomena should be closely related to the partial pressure of CO, O_2, and H_2, which would explain why no general trend exists in the literature with respect to an amplification of or a decrease in the CO oxidation rate in the presence of hydrogen.

4.2. Possible mechanism for the PROX reaction

The CO interaction with gold model catalysts on various supports has been shown to be similar [36], and therefore support effects seen in CO oxidation must arise from the interaction of oxygen rather than CO with these catalysts. In the present work, support effects exist neither in the case of



Scheme 1. Possible mechanism involved in the oxidation of CO in the presence of H_2, including (a) adsorption of CO and H_2 and dissociation of H_2 on a gold particle, (b) reaction of gas phase O_2 with adsorbed H atom and (c) reaction of the resulting oxidizing species with adsorbed CO to give CO_2.

H_2 oxidation nor in the case of CO oxidation in the presence of H_2. Hence, in the presence of H_2, the O_2 activation seems to proceed via another pathway as well.

A possible mechanism for the oxidation of CO in the presence of hydrogen must finally be able to account for the following observations:

(1) the absence of a support effect on the H_2 oxidation rate,
(2) the absence of a support effect on the CO oxidation rate in the PROX reaction,
(3) a support-dependent hydrogen effect on the CO oxidation rates.

Hence, although no direct evidence has been obtained, we propose that the presence of H_2 in the $CO + O_2$ mixture will not only prevent deactivation but also contribute, via highly oxidizing intermediate species, to the oxidation of CO, in the same way as in the propylene epoxidation reaction. H_2 oxidation, which controls the rate of formation of these species, would then be an important step in the PROX reaction. The fact that the gold-catalyzed H_2 oxidation rate is basically independent of the support indicates that the catalytic activity for H_2 oxidation is primarily related to the exposed surface area of gold, as noted in Ref. [18]. Since it is generally accepted that dissociation of O_2 does not occur on gold particles, an Eley–Rideal-type mechanism (Scheme 1) could be involved in the oxidation of H_2, that is, dissociation of H_2 on the gold particle followed by reaction with an O_2 molecule from the gas phase. The PROX reaction would then proceed via reaction, on the gold particle, between an adsorbed CO molecule and an adsorbed H–O–O species (or any H_xO_y species). This would explain why the CO oxidation rates are similar on all supports and why no significant support effect but rather a hydrogen effect is observed on the CO oxidation rate for the PROX reaction under our conditions.

However, adsorbed H atoms could also have affected neighbor gold atoms in such a way that they can now chemisorb and possibly dissociate O_2 molecules or directly react at the perimeter of the Au nanoparticle with oxygen bound to the support. This last mechanism has already been invoked for CO interacting with O_2 on Au/MgO and Au/TiO_2 [37,38].

5. Conclusion

In summary, a strong effect of hydrogen on the CO oxidation rate has been demonstrated, implying that the ability of the catalyst to oxidize CO more readily than H_2 is *not* a prerequisite for efficiency in the selective oxidation of CO in the presence of H_2. Under our PROX conditions, Au/Al_2O_3 and Au/ZrO_2 have indeed become as active as Au/TiO_2 for the conversion of CO. No significant effect of the support has been detected for the oxidation of CO in the presence of hydrogen (or for the oxidation of H_2), as opposed to what had been reported for the oxidation of CO in $CO + O_2$ mixtures. Paradoxically, it seems that, to be a good candidate for the PROX reaction, a catalyst must be active for hydrogen oxidation. We conclude that materials other than titania could be interesting supports for gold in the selective oxidation of CO in the presence of H_2.

Acknowledgment

C.R. is grateful to CNRS for a 2003 postdoctoral position.

References

[1] S. Carrettin, P. Concepción, A. Corma, J.M. López Nieto, V.F. Puntes, Angew. Chem. Int. Ed. 43 (2004) 2538.
[2] M.M. Schubert, S. Hackenberg, A.C. Van Veen, M. Muhler, V. Plzak, R.J. Behm, J. Catal. 197 (2001) 113.
[3] G.C. Bond, D.T. Thompson, Gold Bull. 33 (2000) 41.
[4] J.D. Grünwaldt, A. Baiker, J. Phys. Chem. B 103 (1999) 1002.
[5] M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma, M. Haruta, Catal. Lett. 51 (1998) 53.
[6] H. Sakurai, A. Ueda, T. Kobayashi, M. Haruta, Chem. Commun. (1997) 271.
[7] D. Andreeva, V. Idakiev, T. Tabakova, L. Ilieva, P. Falaras, A. Bourlinos, A. Travlos, Catal. Today 72 (2002) 51.
[8] F. Boccuzzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabakova, J. Catal. 188 (1999) 176.
[9] M. Lomello-Tafin, A. Ait Chaou, F. Morfin, V. Caps, J.L. Rousset, Chem. Comm. (2005) 388.
[10] M.M. Schubert, V. Plzak, J. Garche, R.J. Behm, Catal. Lett. 76 (2001) 143.
[11] R.J.H. Grisel, C.J. Weststrate, A. Goossens, M.W.J. Crajé, A.M. van der Kraan, B.E. Nieuwenhuys, Catal. Today 72 (2002) 123.

[12] V. Arunajatesan, CatGoldNews 2 (6) (2004).

[13] G.C. Bond, D.T. Thompson, Catal. Rev. Sci. Eng. 41 (1999) 319.

[14] S. Arrii, F. Morfin, A.J. Renouprez, J.L. Rousset, J. Am. Chem. Soc. 126 (2004) 1199.

[15] Gold reference catalysts, Gold Bull. 36 (2003) 1.

[16] R.J.H. Grisel, B.E. Nieuwenhuys, J. Catal. 199 (2001) 48.

[17] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, J. Catal. 144 (1993) 175.

[18] M. Okumura, S. Tsubota, M. Haruta, J. Mol. Catal. A 199 (2003) 73.

[19] R.H. Torres Sanchez, A. Ueda, K. Tanaka, M. Haruta, J. Catal. 168 (1997) 125.

[20] R. Grisel, K.-J. Weststrate, A. Gluhoi, B.E. Nieuwenhuys, Gold Bull. 35 (2002) 39.

[21] B. Qiao, Y. Deng, Chem. Commun. (2003) 2192.

[22] B. Schumacher, Y. Denkwitz, V. Plzak, M. Kinne, R.J. Behm, J. Catal. 224 (2004) 449.

[23] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. Catal. 171 (1997) 93.

[24] C.K. Costello, M.C. Kung, H.-S. Oh, Y. Wang, H.H. Kung, Appl. Catal. A 232 (2002) 159.

[25] D. Cameron, R. Holliday, D. Thompson, J. Power Sources 118 (2003) 298.

[26] T.V. Choudhary, C. Sivadinarayana, C. Chusuei, A.K. Datye, J.P. Fackler Jr., D.W. Goodman, J. Catal. 207 (2002) 247.

[27] J.T. Calla, R.J. Davis, J. Phys. Chem. B (2005).

[28] M. Daté, M. Haruta, J. Catal. 201 (2001) 221.

[29] M. Daté, M. Okumura, S. Tsubota, M. Haruta, Angew. Chem. Int. Ed. 43 (2004) 2129.

[30] M.A. Sanchez-Castillo, C. Couto, W.B. Kim, J.A. Dumesic, Angew. Chem. Int. Ed. 43 (2004) 1140.

[31] T. Hayashi, K. Tanaka, M. Haruta, J. Catal. 178 (1998) 566, and references cited therein.

[32] T.V. Choudhary, D.W. Goodman, Top. Catal. 21 (2002) 35.

[33] M. Okumura, Y. Kitagawa, K. Yamaguchi, T. Akita, S. Tsubota, M. Haruta, Chem. Lett. 32 (2003) 822.

[34] C. Sivadinarayana, T.V. Choudhary, L.L. Daemen, J. Eckert, D.W. Goodman, J. Am. Chem. Soc. 126 (2004) 38.

[35] E.E. Stangland, K.B. Stavens, R.P. Andres, W.N. Delgass, J. Catal. 191 (2000) 332.

[36] K.Sh. Shaikhutdinov, R. Meyer, M. Naschitzki, M. Bäumer, H.-J. Freund, Catal. Lett. 86 (2003) 211.

[37] L.M. Molina, B. Hammer, Phys. Rev. Lett. 90 (2003) 206102.

[38] L.M. Molina, M.D. Rasmussen, B. Hammer, J. Chem. Phys. 120 (2004) 7673.