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Insights into activation, deactivation and hydrogen-induced promotion of a Au/TiO_2 reference catalyst in CO oxidation

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Abstract

The oxidation of CO was studied over a Au/TiO_2 reference catalyst in a static reactor coupled to a thermodesorption device. The optimal vacuum activation/regeneration temperature is in the range 350–400 °C. The catalyst partly deactivates during the first runs, possibly through poisoning of the active sites by carbonate-like species, whose formation is clearly evidenced. Although a postreaction treatment under pure hydrogen is ineffective toward regeneration, the catalyst gradually recovers its initial activity for CO conversion in the presence of a low amount of hydrogen within the reactant mixture. Increasing the hydrogen pressure only promotes the oxidation of hydrogen, thereby decreasing selectivity in the preferential oxidation of CO. Consequently, we show that hydrogen-induced promotion of Au/TiO_2 is a regeneration effect involving removal of carbonates rather than a boosting effect via new CO oxidation pathways.

Keywords: Gold; Au/TiO_2 reference catalyst; CO oxidation; PrO*x*; Deactivation; Regeneration; Thermodesorption spectroscopy

1. Introduction

Supported gold nanoparticles have proven to be very efficient for catalyzing various reactions [1]. In particular, oxide-supported gold catalysts are highly active at low temperature for CO oxidation [2–11] (for recent reviews see Refs. [12,13]) and preferential CO oxidation in the presence of H_2 (PrO*x*) [14–21]. The latter reaction could be an elegant way to purify hydrogen for fuel cells [22].

Since the pioneer work of Haruta and coworkers, there have been many attempts to elucidate the mechanism of CO oxidation on gold. Three main models can be distinguished that favor (1) the metal–support interaction (interface effect) [12,13,19,23,24], (2) the presence of low-coordinated atoms on the nanoparticles (geometry effect) [25,26], or (3) the low dimensionality of the gold structures (quantum size effect) [5,10]. Actually, these three effects can all be significant in a reaction and can operate simultaneously, thus making it difficult to know which one is more relevant to catalysis. However, the importance of the support is hardly questionable [9], and several mechanisms have been proposed to account for the support contribution. Haruta and coworkers suggest that CO adsorbed on the metallic Au^0 particles reacts with O_2, which is activated at the particle–support interface [13]. Getting into more detail, thanks to theoretical calculations, Molina and Hammer further show that the reaction on Au/TiO_2 and Au/MgO can proceed via the formation of a $CO \cdot O_2$ complex rather than via predissociation of O_2 [23]. In addition, Liu et al. show that TiO_2 enhances electron transfer from Au to the antibonding states of O_2, which facilitates the activation of O_2 [24]. Alternatively, Bond and Thompson [12] and Kung and coworkers [19] claim that CO oxidation involves Au^+–OH^- entities at the periphery of the particles (a model that we refer to as the BTK mechanism hereinafter).

The decline of activity with time on stream [6,11,16,19] is a crucial factor that could hamper the industrial development of gold-based catalysts. In close relation to the mechanism of CO oxidation, the mechanisms of deactivation and regeneration of supported Au catalysts are also debated. It

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has been demonstrated that *carbonate-like species* (namely, carbonate groups, CO_3; bicarbonate groups, HCO_3; and formate/carboxylate/hydroxycarbonyl groups, HCO_2[1]) are formed during CO adsorption and CO reaction with oxygen [6,7,17], some proposed mechanisms involving hydroxyl groups (e.g., via the step $CO + OH \rightarrow HCO_2$). These species are thought to gradually poison the periphery of the particles that contains the O_2 activation sites. Consistent with the BTK mechanism, some authors have alternatively proposed that catalyst deactivation is induced by dehydroxylation and/or reduction of $Au^{\delta+}$ cations [11,19]. It has been shown that adding water and/or hydrogen in the reactant feed regenerates the catalysts or prevents their deactivation during CO oxidation and PrO*x* [4,11,17,19]. In addition, it has been mentioned that the presence of water and/or hydrogen can even enhance the activity of various Au catalysts through additional reaction pathways [4,8,11,18,20,21,27].

In this paper we focus on the mechanism of activation, deactivation, and regeneration of a reference Au/TiO_2 catalyst, which is one of the best catalysts for CO oxidation, even in the presence of water or hydrogen [4,21]. For this purpose, we have performed catalytic measurements in a batch-type reactor and thermodesorption spectroscopy (TDS; also called temperature-programmed desorption [TPD]) under vacuum. These unconventional experiments provide comprehensive insight into CO oxidation and PrO*x* kinetics and also into molecule–catalyst interaction processes.

2. Experimental

The reaction setup comprises an ultrahigh-vacuum (UHV) preparation chamber coupled with a static stainless steel reactor [internal volume, 120 cm^3; temperature, 20–200 °C; pressure, 10^{-9}–10^3 Torr (1 Torr = 133 Pa)]. Powder catalysts are held in small stainless steel "stubs" that allow their manipulation from outside. They can be outgassed in the preparation chamber using a halogen lamp. High-purity reactant gases, provided by Air Liquide, are mixed together before being introduced into the reactor. During the reactions, the reactor content is sampled through a leak valve and analyzed by a UHV-pumped quadrupole mass spectrometer. More details on the experimental setup have been provided elsewhere [28].

Repeated reaction cycles, with each cycle comprising injection of the reactants, a reaction run, and evacuation of the reacted gases by turbomolecular pumping, were performed to investigate catalyst stability. Treatment by exposure to pure gases (H_2, O_2) was carried out inside the reactor, with each treatment followed by evacuation of the reactor. TDS experiments were performed in the preparation chamber, under vacuum, after gas exposure inside the reactor. Reaction/desorption kinetics were followed by analyzing mass spectrometry peaks 2, 18, 28, 32, 40 and 44, corresponding to the masses of H_2, H_2O, CO, O_2, Ar, and CO_2 molecules, respectively. After normalization by the Ar signal, data were corrected for ion fragmentation and spectrometer sensitivity to obtain partial pressures.

The Au/TiO_2 catalyst (type A, lot. no. Au-TiO_2 #02-05, sample no. 53) was manufactured by Süd-Chemie Catalysts (Japan) under the supervision of M. Haruta, characterized by S. Tsubota and coworkers and provided by the World Gold Council (WGC) [29]. Its preparation followed a deposition–precipitation protocol developed by M. Haruta and coworkers [2]. The powder catalyst contained 1.4 ± 0.1 wt% of gold, as checked by inductively coupled plasma (ICP) chemical analysis.[2] The average particle diameter of the fresh catalyst was 3.7 ± 1.5 nm, as analyzed by transmission electron microscopy. The P25 titania support (50 ± 15 m^2/g), provided by Degussa (the same support as that used for the WGC reference catalyst), comprised 75 ± 5 wt% anatase (mean particle diameter,[3] 25 nm) and 25 ± 5 wt% rutile (mean particle diameter,[3] 39 nm). Catalyst samples of 11.6 and 3.5 mg were used in the reactions performed at 22 °C and 80–110 °C, respectively.

3. Results and discussion

3.1. CO oxidation: activation, deactivation, and kinetics

Catalyst pretreatment is a prerequisite for obtaining optimal performance. In many conventional catalytic studies, the preparation procedure ends with calcination in air up to 400 °C [2]. In the present study, the "as-received" Au/TiO_2 reference catalyst was heated under UHV at 280–400 °C for 1 h before the reactions. In particular, the first thermal treatment allowed desorption of water (below ∼350 °C) and especially carbon-containing species (between ∼200 and ∼350 °C) from the support, as verified by TDS on pure P25 titania.

Fig. 1 shows the effect of this treatment on the *mean* rate of CO oxidation (inversely proportional to the time necessary to fully [>99%] oxidize CO). The highest rate was obtained after

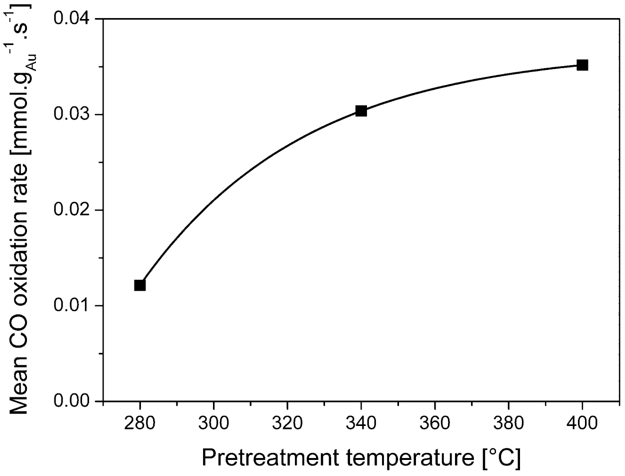

Fig. 1. Mean rate of CO oxidation into CO_2 over Au/TiO_2 as a function of the vacuum-outgassing temperature. Initial reaction conditions: $p_{CO} = p_{O_2} = 1$ Torr; $T = 22$ °C; 11.6 mg of catalyst. The straight line is a guide to eye.

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[1] Formula of formate, carboxylate and hydroxycarbonyl groups are: H–COO–, R–COO– and –COOH, respectively.

[2] ICP analysis by Tsubota and coworkers: 1.47 wt% Au; 0.037 wt% Na. In-house ICP analysis: 1.38 wt% Au; 0.055 wt% Na; 47 ppm Cl.

[3] In-house measurements by X-ray diffraction.

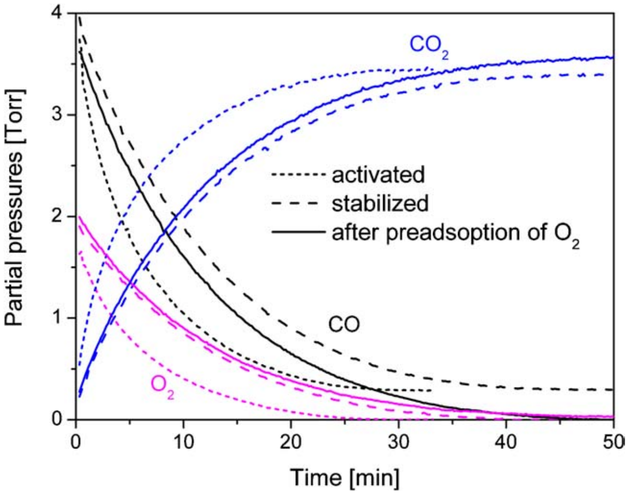

Fig. 2. Partial pressures of CO, O_2, and CO_2 during CO oxidation over Au/TiO_2 (initially p_{CO}:p_{O_2} = 4:2 Torr; $T = 110\,^{\circ}C$; 3.5 mg of catalyst) for the catalyst heated at 400 °C under vacuum (dotted lines: first reaction run), for the stabilized catalyst (dashed lines: third run), and after exposing the catalyst to 2 Torr of O_2 for 20 min and pumping the residual gas (straight lines: fourth run).

heating the catalyst at 400 °C; this rate was about three times higher than that obtained after heating at 280 °C (Fig. 1) and about 10 times higher than that obtained over the used catalyst (not shown). The activity became optimal for treatment above ∼350 °C.

The relevance of using a batch-type reactor to investigate the catalytic properties of a Au/TiO_2 powder-catalyst was evaluated. The CO oxidation reaction was performed under conditions similar to those used previously in a fixed-bed flow reactor [21]: 11.6 mg of catalyst, preheating at 280 °C, and reaction at 22 °C with 2 vol% CO and 2 vol% O_2. Similar reaction rates were obtained on activated catalysts (i.e., 0.5 $\mathrm{mmol_{CO}\,g_{Au}^{-1}\,s^{-1}}$), validating the present experiments. The subsequent reaction experiments were performed with a lower catalyst loading (3.5 mg) at higher temperatures (80–110 °C) and lower total pressures (<10 Torr), for an *activation/regeneration temperature of* 400 °C. The higher reaction temperatures were chosen to minimize CO_2 adsorption on the catalyst (see below). It is important to note that the treatment at 400 °C under UHV allows restoration of the high initial activity from a deactivated (used) catalyst (thermal regeneration), yielding the same CO oxidation activity as that of the thermally activated fresh catalyst.[4]

Fig. 2 presents a typical CO oxidation experiment. The catalyst partly deactivates after the first run (dotted line), and then stabilizes. (Because the second and third runs are similar, only the third run is plotted, indicated by the dashed line.) Strikingly, starting from stoichiometric conditions ($p_{CO} = 2p_{O_2} =$ 4 Torr) with the thermally activated catalyst, some CO molecules (7.5% of the initial amount) are not converted (Fig. 2, run 1). Moreover, this phenomenon is reproduced from cycle to cycle (Fig. 2, run 3). In contrast, preadsorption of pure oxygen on the stabilized catalyst results in full conversion of CO, with similar kinetics, during the reaction performed under the same conditions (Fig. 2, run 4).[5] In this latter case, O_2 probably reacts with oxygen vacancies existing on the partially thermally reduced TiO_2 support; this reoxidized TiO_2 is stable upon pumping (i.e., under vacuum). In the former case (i.e., in the presence of CO), because part of the oxygen does not form CO_2, it can be concluded that some O_2 molecules have reacted with the support, as they did in the absence of CO. But if this were true, then the runs after the first run would evolve toward the behavior of run 4, because the partially reduced TiO_2 would be gradually reoxidized under the reaction conditions. This is not the case, however. Indeed, all subsequent runs are stationary, with CO conversion reaching only 92.5%. The only way to explain these experiments is to assume that O_2 reacts with CO and partially reduced TiO_2 to form other species, such as carbonates. Because the stoichiometry of the carbonate formation reaction (e.g., $CO + O_2 \rightarrow CO_3$) is different than that of the CO_2 formation reaction ($CO + \frac{1}{2}O_2 \rightarrow CO_2$), one can understand why some CO is still present at the end of the reaction runs over the thermally preactivated catalyst.

As proposed by several authors [2,6,7,17], carbonate-like species may be responsible for deactivation of the Au/TiO_2 catalyst. However, as the stabilized catalyst seems to still produce carbonates after the first reaction run (cf. the unreacted CO in run 3; Fig. 2), these species could form at the particle–support interface and migrate toward the support, where they are stored, as suggested by Konova et al. [6].

To get insight into the interaction of CO, O_2, and CO_2 with the activated catalyst, we performed TDS experiments with pure gases. The gases were adsorbed at room temperature in the reaction cell, then thermodesorbed under UHV. As shown in Fig. 3, thermodesorption of O_2 and CO_2 yields mainly O_2 and CO_2, respectively. The amount of desorbed CO_2 is much higher than that of O_2. Surprisingly, heating the catalyst after CO adsorption yields mainly CO_2 and almost no CO. This result implies that most of the CO molecules reacted with oxygen provided by the titania support. In addition, Fig. 3 shows that desorption of CO_2 after CO adsorption partly occurs at higher temperature than desorption of CO_2 after CO_2 adsorption.

These results validate the above hypothesis of CO reaction with Au/TiO_2. This could proceed either by direct reaction of CO with lattice oxygen [3] or by reaction of CO with surface hydroxyls to form carbonate-like species, which would be thermally decomposed to gaseous CO_2 [6]. Our results are consistent with those of Iizuka et al., who also observed a reaction of part (8%) of the injected CO molecules with oxygen belonging to their Au/TiO_2 catalyst during CO adsorption experiments [30]; this reaction was previously ascribed to carbonate and carboxylate formation on TiO_2 [2,3]. Similarly, Konova et al. observed the chemisorption of part (10–15%) of the CO in-

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[4] Later on, the word "activated" is employed for both the thermally-activated fresh catalyst and the thermally-regenerated deactivated catalyst (400 °C during 1 h under UHV in both cases). "Regenerated" is rather used for deactivated catalysts regenerated by the presence of H_2 in the reactor.

[5] Note that full conversion of CO is also observed in oxygen excess with respect to the stoichiometry, e.g., for $p_{CO} = p_{O_2} = 1$ Torr (see Fig. 4, runs 1 and 2).

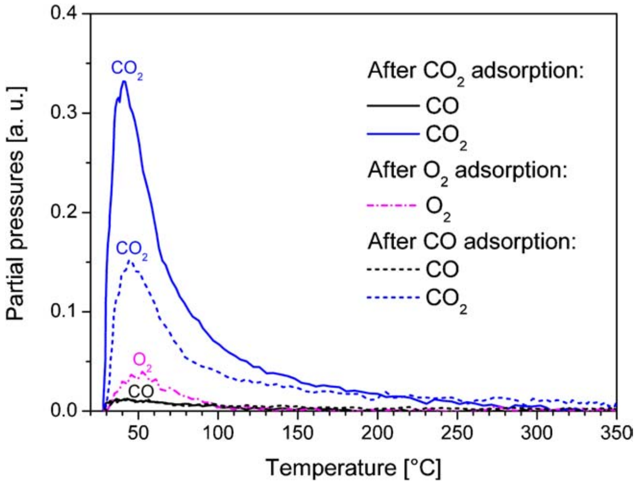

Fig. 3. Partial pressures of the thermodesorbed gases after independent adsorption (1 Torr for 30 min) of pure CO, O_2, and CO_2 over thermally activated Au/TiO_2 at room temperature (heating rate, 0.5 $K\,s^{-1}$). Only non-negligible signals are plotted.

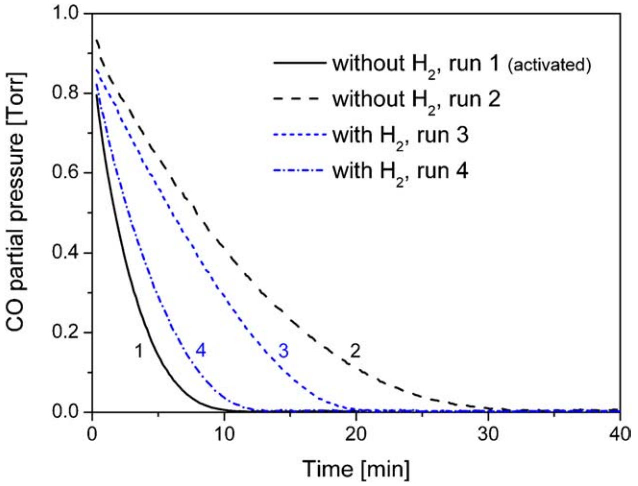

Fig. 4. CO partial pressure as a function of time during CO oxidation on Au/TiO_2 in the absence, and then in the presence of H_2 (two consecutive runs in each case). Initial experimental conditions: $p_{CO}{:}p_{O_2}{:}p_{H_2} = 1{:}1{:}1$ Torr; $T = 110\,^{\circ}C$; 3.5 mg of catalyst.

troduced during activity measurements and partial reduction of the Au/TiO_2 catalyst surface by CO in the absence of gaseous oxygen [6]. Besides, it was noted that the presence of gaseous oxygen enhanced the formation rate of carbonate-like species from adsorbed CO [17,31].

TDS experiments were also carried out after CO oxidation runs at 110 °C on Au/TiO_2 and pure TiO_2. Before each series of reaction runs, the samples were heated at 400 °C under UHV. Carbon dioxide and water desorb mainly below 100 and 150 °C, respectively, from Au/TiO_2 and, in much smaller amounts, from TiO_2. We ascribe these results to the thermal decomposition and desorption of carbonate-like species, such as carbonates and formates, which formed during CO oxidation on Au/TiO_2, as discussed previously from the results of Fig. 2. As mentioned above, these species could poison the oxygen activation sites at the periphery of the gold particles and thereby cause catalyst deactivation. Alternatively, they may behave only as spectators, with deactivation resulting from dehydroxylation of the support during the reaction (assuming that OH groups are involved in the oxidation pathway), as has been suggested by experiments on several types of gold catalysts [11,19]. Our results do not support this hypothesis, because our thermal treatment at 400 °C should decrease the amount of hydroxyl groups, leading to lower rather than higher activity (see, e.g., Fig. 2, run 1 [regenerated catalyst] vs. run 3 [deactivated catalyst]). Moreover, preadsorption of H_2 or O_2 should affect catalytic activity by modifying the amount of hydroxyl groups, which is not the case.

3.2. *Hydrogen-induced regeneration and PrOx reaction*

The effect of hydrogen on the CO oxidation activity of Au/TiO_2 was investigated at 110 °C for equal low pressures (1 Torr) of CO, O_2, and H_2. Fig. 4 shows that without H_2, the catalyst partially deactivates (by a factor of ∼3) from the first run to the second run, similar to the results shown in Fig. 2 for different reaction conditions. The third and the fourth runs, performed in the presence of H_2, partially and almost completely restored the initial activity, respectively. Conversely, treatment of the deactivated catalyst in pure hydrogen (2 Torr for 20 min), followed by evacuation of the reactor, had no effect on its subsequent activity for CO oxidation.

Fig. 5 shows the effect of increasing the hydrogen pressure (by a factor 5) on activity and selectivity of Au/TiO_2 in PrO*x*. As shown in Fig. 5b, the selectivity for CO oxidation is high (>75%) until quasi-complete conversion of CO ($t < 10$ min) for a partial pressure of H_2 equal to that of CO and O_2. In hydrogen excess, the selectivity remains high (>75%) at low CO conversion ($t < 3$ min) but decreases higher conversion. It is interesting to observe (Fig. 5a) that the lower selectivity is due only to a higher rate of H_2 oxidation (to form H_2O). As a matter of fact, the CO oxidation rate remains unaffected by the increased H_2 pressure, which gives rise to a lower O_2 pressure and higher H_2O pressure. This implies that the CO conversion rate is not limited by oxygen supply (i.e., CO oxidation and H_2 oxidation are not competitive), as observed by Kahlich et al. on Au/Fe_2O_3 [15]. The simplest model that would be consistent with the foregoing observation includes CO adsorption on the particles and O_2 activation at the particle–support interface. Water could be produced either from preactivation of H_2 on the support or by direct impact of gaseous H_2 molecules on activated oxygen atoms (Eley–Rideal mechanism).

Thermal desorption performed after the PrO*x* reaction with equal reactant pressures (1 Torr) produced mainly H_2O below 150 °C and CO at 75–200 °C. Compared to the reaction without hydrogen, the amount of desorbed CO_2 was much lower, confirming that the presence of hydrogen is likely to decompose the carbonate-like species, thereby regenerating the catalyst (Fig. 4), or even inhibit their formation. After the PrO*x* reaction in excess of H_2, the amounts of thermodesorbed H_2O and CO_2 increased slightly (but with the latter remaining well under its level after pure CO oxidation), and the amount of CO decreased. The origin of thermodesorbed CO molecules after the PrO*x* reaction remains unclear. More systematic TDS ex-

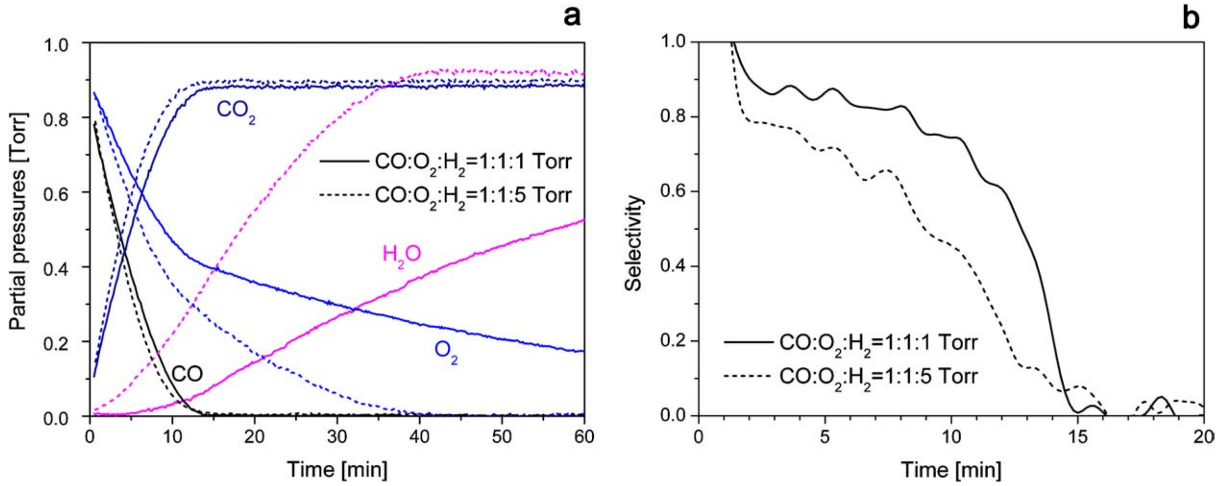

Fig. 5. (a) Evolution of the partial pressures during PrOx reaction on Au/TiO_2 for two different initial hydrogen pressures (run 1: $p_{H_2} = 1$ Torr, activated catalyst [straight lines]; run 2: $p_{H_2} = 5$ Torr [dashed lines]). Other initial reaction conditions were p_{CO}:p_{O_2} = 1:1 Torr, $T = 110\,^\circ C$, and 3.5 mg of catalyst. (b) Selectivity toward CO (CO conversion rate divided by two times the oxygen conversion rate) during the same experiment as in (a).

periments, including isotope-labeling experiments, are needed to clarify this point.

The beneficial effects of H_2 [7,17–21] and H_2O [4,8,11,18–20] have been reported for various gold catalysts. Hydrogen appears to act indirectly by producing water through hydrogen oxidation [17–20]. Our TDS results support the hypothesis formulated by Daté et al. [4] and Schumacher et al. [17] that water reacts with the poisoning carbonate-like species (possibly via $CO_3 + H_2O \rightarrow CO_2 + 2OH$) produced during CO oxidation over Au/TiO_2, preventing catalyst deactivation (or, similarly, regenerating the deactivated catalyst). Indeed, Schumacher et al. observed by infrared spectroscopy that, in the presence of H_2, H_2O-induced conversion and decomposition of formate/carbonate species appear to be fast enough to keep their concentration low, unlike in pure CO oxidation [17].

The fact that increasing hydrogen pressure does not further increase the activity of Au/TiO_2 for CO oxidation suggests that the catalyst activated by heating at 400 °C under vacuum has reached its maximum performance level and that only a small amount of H_2 is needed to restore the activity and prevent further deactivation. Hence it is important to note that for Au/TiO_2, hydrogen exhibits a regenerating effect more than a boosting effect. Similarly, we have previously shown that the presence of H_2 in the feed of a fixed-bed flow reactor did not increase the CO conversion activity of a model Au/TiO_2 catalyst, unlike for Au/Al_2O_3 and Au/ZrO_2 [21]. Moreover, Daté et al. have shown that water had only a moderate effect in the case of Au/TiO_2, unlike for Au/Al_2O_3 and Au/SiO_2, where the positive effect of moisture was high [4] (see their mechanistic model). The idea of a promotional effect of hydroxyl, hydroperoxy, and related species issuing from the presence of both O_2 and H_2 [32], which would provide additional pathways for CO oxidation, may be more relevant for other types of gold catalysts, such as gold-nanotube membranes [8] and certain oxide-supported catalysts [4,11,18–21], which exhibit much greater hydrogen or water-induced activity enhancement than that demonstrated by Au/TiO_2. On those catalysts, unlike on Au/TiO_2, oxygen supply appears to be the rate-limiting step.

In addition, one has to be aware that the extent of gold catalysts' deactivation and regeneration ability depends crucially on the pretreatment method used [19]. Accordingly, the BTK mechanism, involving carbonate-like species as intermediates for CO_2 production [12,19], may be particularly applicable to some air-calcined or unpretreated catalysts in which Au^+–OH^- species remain present on the catalyst surface, as has been reported by Costello et al. on Au/Al_2O_3 [19] and Daniels et al. on Au/Fe_2O_3 [11]. In these studies, thermal treatments deactivated the catalysts, possibly through dehydroxylation/reduction of the catalyst surface. In contrast, the Au/TiO_2 reference catalyst was fully regenerated by our thermal treatment under vacuum.

4. Conclusion

We studied the effect of the pretreatment temperature, gas preadsorption, and the presence of hydrogen on the CO oxidation activity of a Au/TiO_2 reference catalyst. The study was carried out within a static reactor in a temperature range of 20–110 °C and a $CO + O_2$ pressure range of 1–30 Torr (∼0.1–4 kPa). In addition, thermodesorption experiments were performed under UHV after adsorptions and reactions in the elevated-pressure reactor.

The optimal temperature for an activation/regeneration treatment under vacuum was in the range ∼350–400 °C. This temperature allows desorption of water and carbon-containing species poisoning the catalyst after air exposure and pure CO oxidation reactions. CO reacts with the catalyst to form adsorbed carbonate-like species in both the absence and the presence of O_2 in the reactor. These species further evolve to CO_2 upon thermodesorption. The catalyst partially deactivates during the first CO oxidation run after thermal activation at 400 °C, and then stabilizes. Thermal treatment at 400 °C before reaction or addition of a small amount of hydrogen in the reactive $CO + O_2$ mixture restores the CO oxidation activity; treatment under pure hydrogen is inefficient. Increasing the H_2 pressure does not further modify the catalyst activity for CO oxidation, but lowers its selectivity toward CO.

Deactivation of the catalyst can be ascribed to the poisoning of metal–support interface sites by carbonate-like species formed during pure CO oxidation. Water produced by H_2 oxidation during PrOx reacts with these species, which are likely to desorb in the form of CO_2, thus regenerating the catalyst. Finally, because oxygen activation is not found to be rate-limiting, the participation of highly oxidative H_xO_y species is not necessary to explain the promoting effect of H_2 over Au/TiO_2.

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