Selective oxidation of CO in H₂-rich stream over gold/iron oxide: An insight on the effect of catalyst pretreatment

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Abstract

Selective oxidation of CO in H₂-rich stream was studied on iron oxide supported Au catalysts prepared by deposition-precipitation (AuDP) or coprecipitation (AuCP) and for comparison on commercial gold reference catalyst (AuRef), investigating in detail the effect of catalyst pretreatment towards the catalytic performance. On AuDP and AuCP samples CO conversion strongly decreased on increasing calcination temperature. On the AuRef sample the influence of calcination was, instead, less evident. On all tested catalysts a higher reduction temperature resulted in a lower CO conversion, the effect of reduction on catalysts activity exceeding that of calcination. On all samples selectivity towards CO oxidation decreased appreciably on increasing reaction temperature. The dependence of selectivity from pretreatment was negligible.

On the basis of characterization data (H₂-TPR, XRD, TEM) it was pointed out that, provided gold particles are small enough to be able to activate CO and H₂, the catalytic behaviour of the Au/iron oxide system in the PROX reaction is strongly related to the support phase, being sensitive to the microcrystalline structure and the oxidation state of the iron oxide. CO oxidation activity of different iron oxide species was found in the order: ferrihydrite > hematite > magnetite. It was concluded that on Au/iron oxide the PROX reaction occurs through a Mars-van Krevelen type mechanism which involves lattice oxygen of the iron oxide and CO and H₂ adsorbed on gold particles.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are currently considered among the most advanced systems for energy production starting from hydrogen [1]. However, for this application H₂ stream must be almost free of CO, in order to avoid poisoning of the Pt anode catalyst [2]. When hydrogen is produced by steam reforming of hydrocarbons or alcohols followed by water gas shift reaction, it is still contaminated with around 1% of CO and therefore requires further purification in order to abate the CO concentration to below 50 ppm, which can be tolerated by PEM fuel cells. Selective oxidation of CO in H₂-rich stream (known as PROX reaction, PReferential OXidation of carbon monoxide) is regarded as one of the most promising technology to reduce CO concentration to acceptable levels [3,4]. Several

catalysts have been investigated for the PROX reaction, such as supported Pt [5–10], Ru [5,9], Rh [5,11], Ir [10], Pd [5,9] and more recently Au [12–23] and CuO [24–28].

Supported gold catalysts are considered particularly attractive for PROX in so far as the rate of CO oxidation over Au-based systems has been found to exceed that of H₂ oxidation, thus resulting in high selectivity towards the removal of CO in the presence of excess of H₂. The influence of the nature of the metal oxide support on the PROX activity of supported Au catalysts have been extensively studied. A wide range of metal oxide supports, such as Al₂O₃ [12–17], Fe₂O₃ [15,16,18,19], TiO₂ [15–17], CeO₂ [15,16,21,22], CoOₓ [15,16], MnOₓ [15,16,23], NiOₓ [15,16], SnO₂ [15,16], ThO₂ [20], ZrO₂ [17], have been, in fact, up to now considered for PROX reaction over gold catalysts.

There is general agreement that CO oxidation over supported Au catalysts follows a scheme where both reactants are bound to the surface of the catalyst and CO is activated by adsorption on the gold particles [29–34]. However, different models on the possible mechanism for oxygen activation have been

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proposed. Some researchers suggest that oxygen adsorption proceeds directly on the gold particles [35–39], the role of the support being limited to the stabilization of very small reactive gold particles, for other ones the oxygen adsorption is believed to occur on the support (or at the metal–support interface), especially in the nearby of the Au particles [15,16,30,32–34,40–42].

In the last years our group has been involved in investigating gold catalysts for the oxidation of CO [43] and the combustion of volatile organic compounds [44–46]. We demonstrated that performances of Au catalysts are strongly affected not only from the support used, but also from the preparation method as well as pretreatment conditions of catalysts.

On these bases we here report a study on the PROX reaction on gold/iron oxide catalysts, investigating in detail the effect that pretreatment conditions play on the performance of these catalysts towards selective removal of CO in excess of H_2 with the aim to elucidate the changes induced by the thermal pretreatment both on the support and the metal and the influence of these changes on the PROX activity. In particular two Au/iron oxide samples prepared by us, respectively, by deposition precipitation (DP) and coprecipitation, and one commercial gold reference catalyst (Type C, sample no. 10), were used in this study.

2. Experimental

Au/iron oxide catalysts were prepared by coprecipitation (sample coded AuCP) or deposition-precipitation (coded AuDP), using $HAuCl_4$ (Fluka) and $Fe(NO_3)_3 \cdot 9H_2O$ (Fluka) as precursors. In the case of the coprecipitation (CP) method, an aqueous mixture of the precursors was poured at 7.5 ml/min rate into an aqueous solution of Na_2CO_3 (1 M and pH 11.9) maintained at 70 °C under vigorous stirring (500 rpm).

In the deposition-precipitation method, after the pH of the aqueous solution of $HAuCl_4$ was adjusted to the value of 8 using 0.1 M NaOH, iron oxide, was added under vigorous stirring (500 rpm) to the gold solution, keeping the slurry at 70 °C for 2 h. Both in CP and DP methods the obtained slurries were kept digesting for 24 h, washed several times (until disappearance of nitrates and chlorides), then dried under vacuum at 70 °C and finally ground before use. Iron oxide was prepared by precipitation from $Fe(NO_3)_3 \cdot 9H_2O$ following the same procedure employed in the coprecipitation method. One gold reference catalyst (Type C, sample no. 10), coded AuRef, was also tested in the reaction. The gold content of Au/iron oxide catalysts used in this work was measured by atomic absorption and is reported in Table 1.

Table 1
Code and physicochemical properties of Au/iron oxide catalysts (samples calcined at 200 °C and successively reduced at 150 °C

	Au content (%)	Au mean size[a] (nm)	BET Surface Area (m^2/g)
AuDP	3.5	3	195
AuCP	4.0	8	190
AuRef	4.5	4	40

[a] Evaluated by TEM.

Catalytic activity tests were carried out in the gas phase at atmospheric pressure in a continuous-flow microreactor filled with catalyst (0.015–0.05 g, 80–140 mesh) diluted with an inert glass powder. The gas composition (total flow rate: 80 ml/min) was 1% of CO, 1% of O_2, the rest being H_2. Before activity tests, catalysts were calcined (in air) and/or reduced (in H_2) at different temperatures. The effluent gases were analyzed by a online gas chromatograph with a packed column (Carboxen 1000) and TCD.

X-ray powder diffraction (XRD) analysis of the samples was performed with a Bruker AXS D5005 X-ray diffractometer using a Cu Kα radiation. Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS Data File.

Temperature programmed reduction (H_2-TPR) tests were carried out in a conventional flow apparatus with a TCD detector, at heating rate of 5 °C/min using 5 vol.% H_2 in Ar.

Surface area measurements were carried out using the BET nitrogen adsorption method with a Sorptomatic series 1990 (Thermo Quest). Before the tests all samples were outgassed (10^{-3} Torr) at 120 °C.

Metallic gold particles were characterized by transmission electron microscopy using a TEM JEOL 2010 F instrument, equipped with the Gatan imagining filter, operating at 200 KeV. The powdered samples were ultrasonically dispersed in isopropyl alcohol and a few droplets of the suspension were deposited on a Cu grid coated by a holey carbon film. After the solvent evaporated, the specimens were introduced into the microscope column. The average Au size diameter estimated by TEM (d_{TEM}) was calculated using the following formula: $d_{TEM} = \Sigma(n_i d_i)/n_i$, where n_i is the number of Au particles of diameter d_i.

3. Results

3.1. Catalytic activity

Fig. 1 reports catalytic activity results, in terms of conversion of CO (full lines) and selectivity towards CO oxidation (dotted lines), defined as the ratio of O_2 consumption for the CO oxidation to the total O_2 consumption, over investigated Au/iron oxides samples (AuDP, AuCP and AuRef) calcined at 200 °C and successively reduced at 150 °C. No methane was formed in all experiments. It must be also reminded that no significant CO conversion was observed up to 200 °C on the pure iron oxide.

From the figure it can be seen that on all three investigated samples CO conversion increased with increasing temperature reaching a maximum, which was respectively, 95% for AuDP at 70 °C, 80% for AuRef at 90 °C and 45% for AuCP at 140 °C, and then decreasing at higher temperature. These results point out that the CO oxidation activity of Au/iron oxides systems is strongly affected by the preparation method of catalysts being in the order: AuDP > AuRef > AuCP.

Selectivity data reported in Fig. 1 show that for each sample selectivity is strongly influenced from the reaction temperature, the higher the reaction temperature the lower the selectivity. The observed drop of CO selectivity with temperature agrees
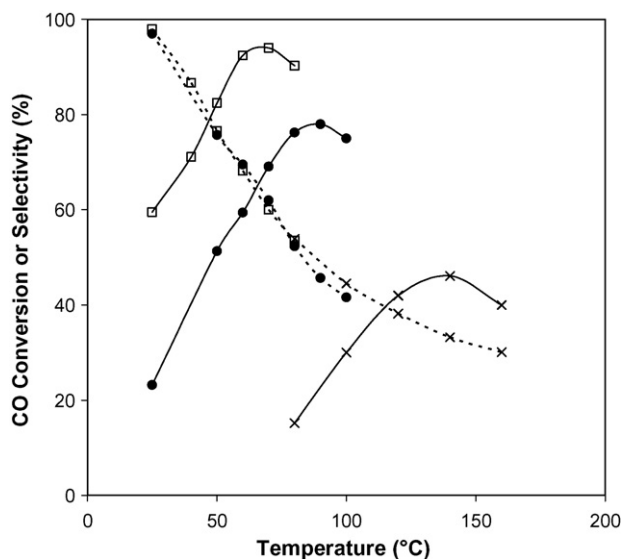
Fig. 1. CO conversion (full lines) and CO selectivity (dotted lines) vs. reaction temperature over Au catalysts calcined at 200 °C and reduced at 150 °C. (□) AuDP; (●) AuRef; (×) AuCP.

with results reported in the literature and it is due to the fact that activation energy of H$_2$ oxidation was found to be sensibly higher than that of CO oxidation [18]. Moreover, this is also in accordance to the finding that the ratio of surface coverage between CO and H (θ_{CO}/θ_{H}) on gold particles strongly decreases as temperature increases [47]. It is also important to stress that, at the same reaction temperature, selectivity resulted to be roughly independent from the level of conversion (see the behaviour of the AuRef sample reported in Fig. 2). Therefore, it can be suggested that the higher selectivities observed on AuDP and AuRef samples compared to AuCP are substantially related to the higher reaction temperatures employed on this latter sample compared to the more active AuDP and AuRef samples.
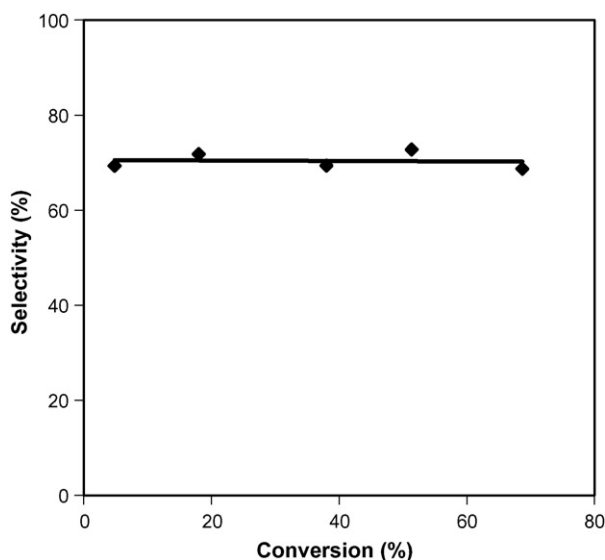

Fig. 2. Selectivity towards CO oxidation vs. CO conversion ($T_{reaction} = 60$ °C) over AuRef calcined at 200 °C and reduced at 150 °C.

Fig. 3 reports the effect of catalyst pretreatment towards CO conversion for AuDP, AuCP and AuRef samples. In the figures samples were labelled Cxxx-Ryyy where xxx and yyy are the calcination and the reduction temperatures (°C), respectively, employed during the pretreatment phase (reduction always followed calcination). From the figure it can be seen that CO conversion was strongly dependent on pretreatment conditions of catalysts. In particular on AuDP and AuCP samples CO conversion decreased continuously on increasing calcination temperature. On AuRef the influence of calcination was, instead, negligible for calcination temperature up to 300 °C, becoming evident only at 400 °C.

Fig. 3 shows also that a reductive pretreatment of gold catalysts also affects the activity of tested systems. In particular a higher reduction temperature resulted in a much lower CO conversion, as it can be easily seen by comparing conversion curves of samples calcined at the same temperature (300 °C) and reduced at 150 °C and 300 °C, respectively. It is noteworthy that the effect of reduction on catalytic activity far exceeded that of calcination.

With regard to the dependence of CO selectivity from catalysts pretreatment data reported in Fig. 4 point out that the selectivity was almost unaffected by calcination or reduction pretreatments, being only related to the reaction temperature employed.

3.2. Catalysts characterization

The effect of catalyst pretreatment on the nature of Au/iron oxide samples has been studied by XRD. Fig. 5 compares the spectra of AuDP catalyst after calcination at three different temperatures (200 °C, 300 °C and 400 °C). All samples have been successively exposed to H$_2$ at 150 °C.

In all spectra typical reflection of Fe$_2$O$_3$ hematite phase can be observed. In particular, XRD patterns of the 400 °C calcined sample show all the typical hematite reflection with intensity ratios consistent with polycrystalline hematite powders. Patterns obtained for samples calcined at 200 °C and 300 °C show hematite reflection peaks of lower intensity compared to the 400 °C calcined sample pointing to a lower cristallinity of low temperature calcined samples. It is also interesting to note that on the 200 °C calcined samples trace of magnetite phase can be noted. In fact the presence of a reflection at 43.2° can be assigned to the ($h\,k\,l$) reflection of the magnetite. In addition, peak at 35.6° showed (compared to 33.2° peak) an increased intensity with respect to the values expected from JPDF files. This observation can be explained by the presence of the ($h\,k\,l$) reflection of magnetite overlapping the reflection of hematite at 35.6°. Note that an intermediate situation, in which the intensity of peaks 35.6° (relatively to that at 33.2°) is only slightly higher compared to pure hematite reference powders, is obtained for a calcination temperature of 300 °C. It is noteworthy that on the 400 °C calcined sample a broad peak at about 38°, attributed to metallic gold, can be also observed [48,49]. The average size of gold particles, estimated from the line-width of this peak by using the Sherrer equation, was 6 nm.
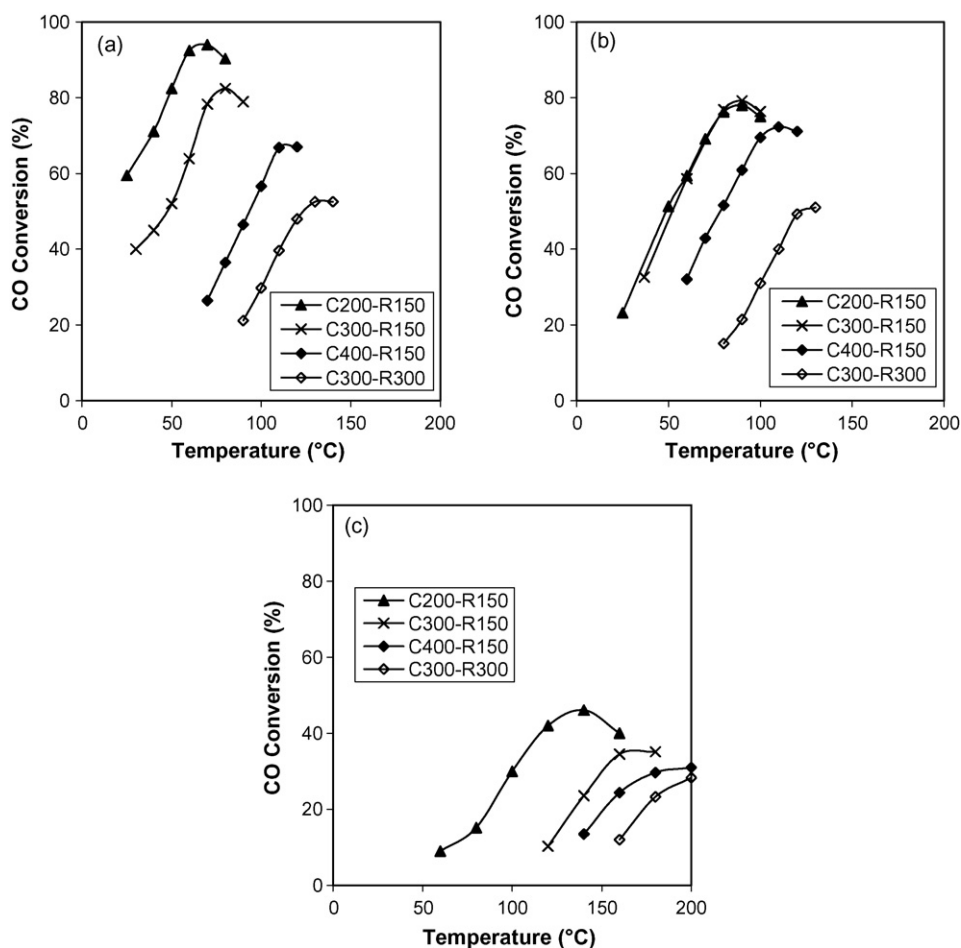
Fig. 3. Effect of catalyst pretreatment towards CO conversion over (a) AuDP, (b) AuRef, and (c) AuCP. Samples were labelled Cxxx-Ryyy where xxx and yyy are the calcination and the reduction temperatures, respectively, employed during the pretreatment phase.

Fig. 6 shows the effect of H_2 reduction at 150 °C and 300 °C on samples obtained after calcination at 300 °C. The corresponding patterns obtained for the reference gold catalyst after the same reduction treatment have been added for comparison. From the XRD patterns it is evident that high temperature reduction causes a relevant phase transformation from hematite to magnetite. Note, in addition, that a significant reduction to magnetite can be observed for the reference sample also at low reduction temperature (150 °C), as shown by the presence of the reflection at 43.2° and by the increased intensity of peak at 35.6°. By contrast, low temperature reduction of the AuDP sample determines only a negligible reduction to magnetite.

The effect of catalyst pretreatment on the nature of Au/iron oxide samples has been also studied by H_2-TPR. Fig. 7 reports TPR profiles of AuDP (a) and AuRef (b) samples calcined at different temperatures. On the AuDP sample calcined at 200 °C it is possible to observe three main reduction peaks with a maximum at about 150 °C (P_1), 230 °C (P_2) and 630 °C (P_3). According to the literature [44,48,50], the two low temperature peaks (P_1 and P_2) can be attributed to the reduction of Fe_2O_3 species, respectively, hydroxylated (P_1) and not hydroxylated (P_2) to Fe_3O_4 (magnetite). The hydrogen consumption related to both peaks, calculated from the area under these peaks, is in good agreement with this attribution. It must be underlined that the Fe_2O_3 to

Fe_3O_4 reduction occurs to a much lower temperature compared to that of the pure iron oxide sample on which this transformation has been observed at 390 °C (P_1) and 450 °C (P_2) [44], thus indicating that the presence of gold strongly facilitates the reduction of Fe_2O_3 species. In what concerns the P_3 peak, in accordance to the literature, it can be assigned to the further transformation of magnetite to FeO [44,48,50]. It is noteworthy that on the pure iron oxide sample the P_3 peak was found at ca 630 °C [44], indicating that the presence of Au does not affect the $Fe_3O_4 \rightarrow$ FeO transformation.

Fig. 7(a) shows that an increase in the calcination temperature of the AuDP sample leads to a strong decrease in the intensity of the P_1 peak, which appears as a very small shoulder in the 300 °C calcined sample and is practically absent in the 400 °C calcined sample. This behaviour is a consequence of the fact that calcining at higher temperature results in the transformation of the hydroxylated iron oxide species (ferrihydrite) into less reducible iron oxide species (hematite) [44,49]. Fig. 7(a) shows also that calcination causes a shift to higher temperature of the P_2 peak (maximum at 250 and 360 °C for the AuDP sample calcined at 300 °C and 400 °C, respectively), which can be attributed to an increase in the cristallinity degree of the iron oxide with calcination temperature as confirmed by XRD (Fig. 5) and surface area data (Table 2). The easier reducibility of low temperature
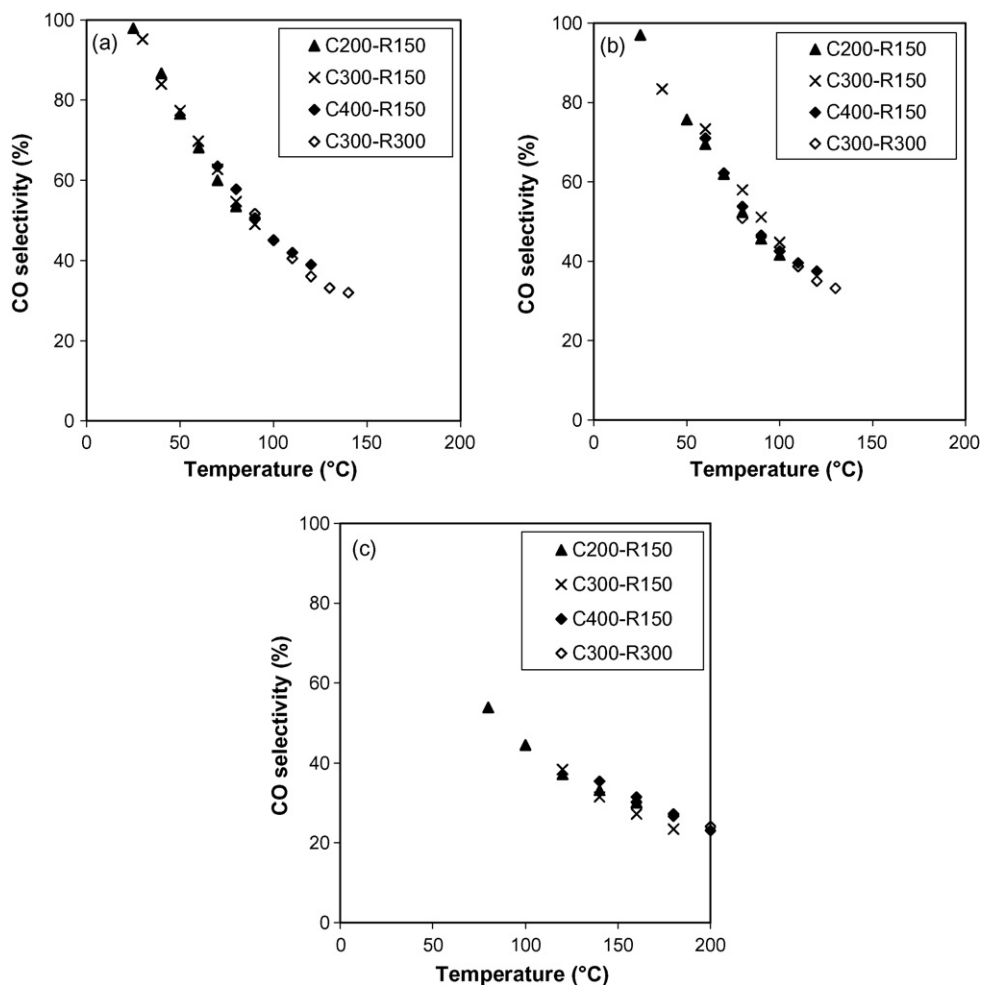
Fig. 4. Effect of catalyst pretreatment towards CO selectivity over (a) AuDP, (b) AuRef, and (c) AuCP. Samples were labelled Cxxx-Ryyy where xxx and yyy are the calcination and the reduction temperatures, respectively, employed during the pretreatment phase.

calcinated samples is in line with XRD data of Fig. 5, which showed the presence of higher amount of magnetite on sample calcined at lower temperatures.

The H_2-TPR profiles of the AuRef catalyst calcined at different temperatures (Fig. 7b), show the presence of the P_2 and
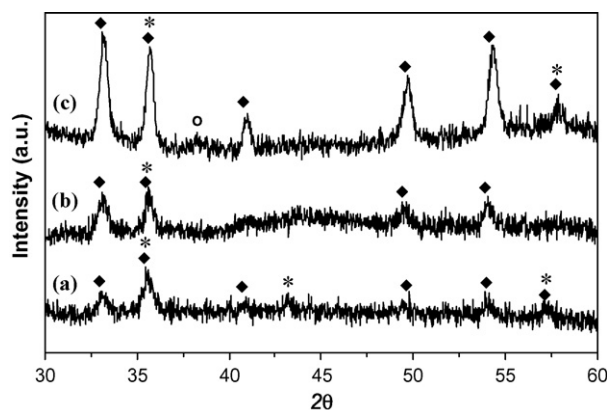

Fig. 5. XRD spectra of AuDP samples after calcination at 200 °C (spectrum a), 300 °C (spectrum b) and 400 °C (spectrum c). All samples have been successively reduced in H_2 at 150 °C. (♦ Hematite, * Magnetite, ○ Gold).

P_3 peaks only, whereas the P_1 peak is absent. This indicates that AuRef, differently from AuDP, does not contain amorphous hydroxylated species neither if calcined at low temperature. This fits well XRD data which show that AuRef is more crystalline than AuDP. Moreover, it can be observed that the shift to higher temperature of the P_2 peak with calcination is much less evident compared to AuDP. It must be also stressed that also in this case P_3 peak is substantially insensible to catalyst pretreatment.

4. Discussion

The catalytic data reported in the present paper show that the PROX activity of the Au/iron oxide system strongly depends from both the preparation method and the thermal pretreatment of the catalyst. In what concerns the influence of the preparation method the activity order observed, for samples calcined at 200 °C and successively reduced at 150 °C, was AuDP > AuRef ≫ AuCP. The influence of the preparation method on the catalytic performance of Au/iron oxide catalysts towards several reactions has been reported in literature [51]. In our case the much lower activity of the AuCP sample can be justified considering the higher mean size of gold particles
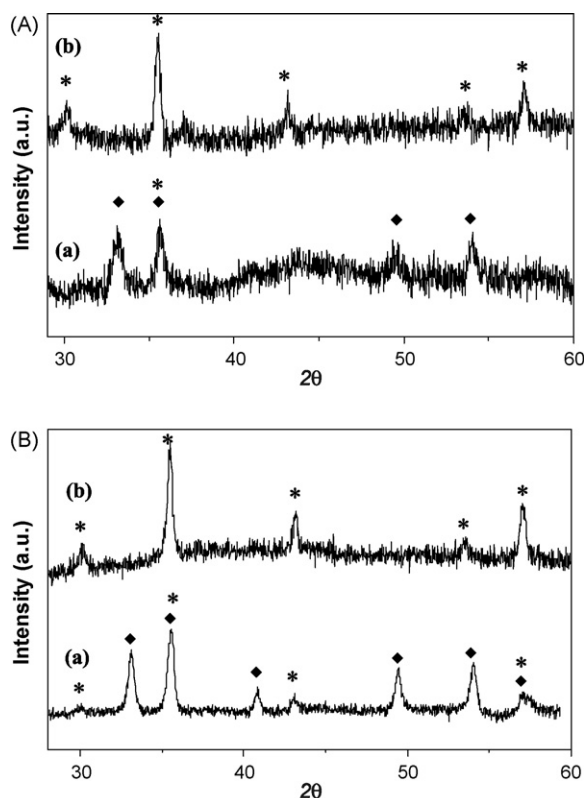
Fig. 6. XRD spectra of (A) AuDP and (B) AuRef samples calcined at 300 °C and reduced in H$_2$ at 150 °C (spectrum a) and 300 °C (spectrum b). (♦ Hematite, * Magnetite).

detected on this sample (8 nm) compared to that of AuDP (3 nm) and AuRef (4 nm). In fact, according to Haruta [38] gold shows a good activity only if Au particles are <5 nm.

Taking into consideration the influence of thermal pretreatment of catalysts, data here reported show that the activity towards CO conversion is influenced by the pretreatment temperature both in oxidating (air) and in reducing (hydrogen) atmosphere. In particular on AuDP and AuCP samples the higher the calcination temperature, the lower the CO conversion, the detrimental effect being more evident when the calcination temperature exceeded 300 °C. On the AuRef sample the influence of calcination was, instead, noticeable only when calcination was carried out at 400 °C being anyway much lower than on AuDP. This behaviour can be rationalized considering that AuRef was prepared according to the Haruta procedure, i.e. by coprecipitation followed by high temperature calcination [38]. With regard to the effect of the pretreatment in reducing atmosphere, catalytic results showed that on all tested catalysts a higher reduction temperature resulted in a lower CO conversion, the effect of reduction on catalysts activity exceeding that of calcination.

Characterization experiments carried out on Au/iron oxide catalysts at different calcination and reduction temperatures aimed to elucidate the changes induced by the thermal pretreatment on the support and the metal and influence of these changes on the catalytic activity towards PROX reaction. XRD profiles of the AuDP catalyst calcined at 200 °C or 300 °C have shown that the sample has a structure with a low cristallinity with the presence of some Fe$_2$O$_3$ hematite phase. In accordance to the preparation method it can be supposed that most part of
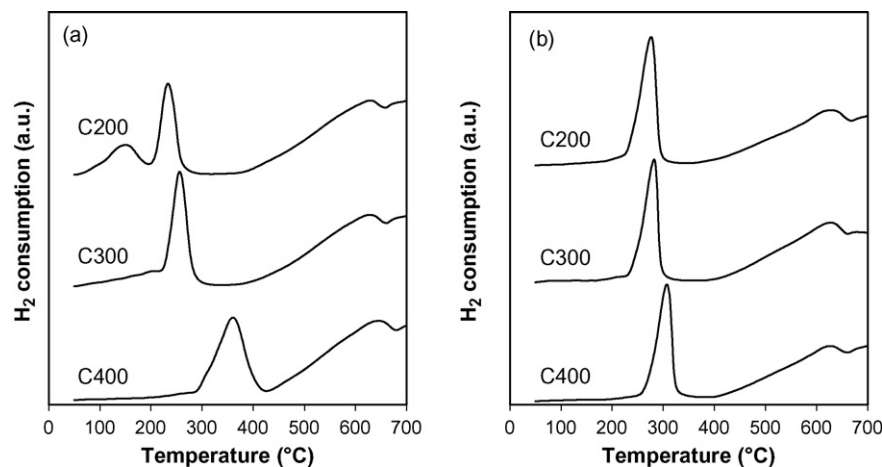

Fig. 7. TPR profiles of (a) AuDP and (b) AuRef samples calcined at different temperatures. Samples were labelled Cxxx where xxx are the calcination temperatures employed during the pretreatment phase.

Table 2
Effect of calcination temperature on the BET surface area of investigated samples

	Surface area of samples calcined at 200 °C (m^2/g)	Surface area of samples calcined at 300 °C (m^2/g)	Surface area of samples calcined at 400 °C (m^2/g)
AuDP	195	170	80
AuCP	190	150	75
AuRef	40	40	35

iron oxide is present as amorphous ferrihydrite [45,48,49]. The absence in the 200 °C and 300 °C calcined AuDP samples of peaks due to gold can be probably justified considering that the preparation method used leads to gold particles with a mean particle size of 3 nm ca. (see Table 1), which is smaller than particle sizes detectable by XRD [35,52]. At higher calcination temperature (400 °C) hematite is the prevailing crystallographic phase of the AuDP sample indicating that a phase transition of the iron oxide mainly occurs between 300 °C and 400 °C. This is in agreement with the results reported in the literature by several authors [31,45,48,49,53] and fits also well the BET surface area values reported in Table 2. In fact, the surface area of AuDP was found to decrease on increasing calcination temperature (being 195, 170 and 80, respectively, on the 200 °C, 300 °C and 400 °C calcined sample). It must be also noted that on the 400 °C AuDP calcined sample a diffraction peak related to the presence of metallic gold (with an estimated mean size of 6 nm ca.) was found. On the basis of these observations it can be stated that high calcination temperatures lead both to a change in the iron oxide phase and to an enlargement of gold particles [45,54,55]. According to reaction mechanisms reported for PROX reaction [15,16] both these effects can be claimed to explain the remarkable drop of the CO oxidation activity observed when Au/iron oxide samples were calcined at high temperatures (400 °C). Effectively our research group has previously reported that the catalytic behaviour of the Au/iron oxide system in several reactions, such as CO and VOC oxidation, is related both to the gold state and/or the iron oxide phase [43–46]. However, it is noteworthy that a pretreatment in reducing atmosphere negatively affected the CO conversion of all samples. The effect of reduction on catalysts activity was much stronger for AuDP and AuRef samples than for AuCP, in any case exceeding for all samples that of calcination. In this case characterization data (XRD and TPR) showed that high temperature reduction (300 °C) caused on all samples a chemical transformation of the iron oxide from ferryhydrite/hematite into magnetite. On the contrary the reduction pretreatment did not seem to affect the dimension of gold clusters, which remained substantially of very small size, as confirmed by the lack of the Au peak in the XRD spectra of both 150 °C and 300 °C reduced samples. Therefore, it can be inferred that the strong decrease in the CO oxidation activity observed when Au/iron oxide samples were reduce at 300 °C is strictly related to the change in the status of the support, magnetite (Fe_3O_4) being much less active than hematite (Fe_2O_3). A higher activity of hematite compared to magnetite in the CO oxidation has been already reported in the literature [56,57].

TPR experiments here reported showed that on Au/iron oxide a strong interaction between gold and iron oxide occurs. Gold strongly enhances the reducibility of iron species favouring essentially the reduction of Fe_2O_3 to Fe_3O_4. It is highly probable that the presence of gold causes a decrease in the strength of the Fe–O bonds located nearby the gold atoms thus leading to a higher lattice oxygen mobility [44,45,48]. From the comparison of TPR and XRD data here reported one can also infer that hydroxylated iron oxide species (ferrihydrite) are more reducible than hematite, thus indicating that lattice oxygen of hematite has

a lower reactivity/mobility compared to that of ferrihydrite. This is in good agreement with catalytic activity results reported in this paper, the higher calcination temperature the lower CO conversion activity. A further confirm derives from the observation that the activity of the AuRef sample, on which the amount of ferrihydrite was very low already on low temperature calcined samples, was much less affected by the calcination pretreatment compared to AuDP and AuCP samples.

These data support the hypothesis that on the Au/iron oxide system the PROX reaction occurs through a Mars-van Krevelen type reaction mechanism [58,59], which involves active lattice oxygen species of the support reacting with CO adsorbed on gold particles and/or at the metal–support interface. This also agrees with the fact that in the absence of oxygen in the feed we observed that the reaction proceeds for a very short time and then the activity drops to zero. A Mars-van Krevelen mechanism has been already proposed by Schubert et al. for gold catalysts supported on semiconductor materials [15,16].

Therefore, it appears clear that the support has a key role in directing the PROX reaction over Au/iron oxide. This makes the catalytic performance highly sensitive toward both the microcrystalline structure and the oxidation state of the iron oxide. Our data showed in particular that the activity of CO oxidation of different iron oxide species is in the order: ferrihydrite > hematite > magnetite. A positive correlation between the amount of ferrihydrite and the catalytic activity of Au/iron oxide catalysts in the CO oxidation has been reported [45,60], ferrihydrite being proposed as responsible for the activation of oxygen [60].

It is important to stress the fact that the role of the iron oxide support is crucial, provided that gold particles are small enough to be able to easily activate CO. In fact, when the dimension of gold particle increases the activation of CO on gold becomes so far more difficult and at a certain point presumably the rate determining step in the CO oxidation. Only in this case, therefore, the status of gold should be determinant in directing PROX activity.

In what concern PROX selectivity of investigated Au/iron oxides samples data reported in Fig. 1 point out that on all catalysts selectivity decreases with the reaction temperature exhibiting a trend which is similar on all samples. Moreover, at the same reaction temperature selectivity was roughly independent from the level of conversion (Fig. 2). It is also important to stress the fact that selectivity of different samples resulted to be almost unaffected by calcination or reduction pretreatments (Fig. 4), being only related to the reaction temperature employed. Considering that pretreatment conditions were found to strongly affect mainly the status of the support, the observed independence of selectivity from pretreatment conditions suggests that the activation of CO and H_2 on investigated Au/iron oxide catalysts is not substantially affected by the iron oxide phase. This is quite reasonable considering that both CO and H_2 are adsorbed/activated on gold particles [47]. According to the above proposed reaction mechanism for PROX, when gold particles are small enough, the rate determining step is the activation of oxygen. Therefore, an increase in the oxygen reactivity results in a higher activity in the oxidation of both CO and H_2, thus being

indifferent for the CO_2 selectivity, which only depends from the reaction temperature. On the basis of these considerations, AuDP and AuRef can be considered more suitable than AuCP for a practical use in the PROX reaction in so as the lower temperature at which the reaction can be carried out on these more active samples leads a higher selectivity than that achievable on the less active AuCP sample.

5. Conclusions

On the basis of the results reported in this paper the following conclusions can be drawn:

(a) The performance of Au/iron oxide catalysts towards PROX reaction was found to be strongly affected by catalyst pretreatment. In particular on AuDP and AuCP samples CO conversion strongly decreased on increasing calcination temperature. On the AuRef sample the influence of calcination was, instead, less evident. On all tested catalysts a higher reduction temperature resulted in a lower CO conversion, the effect of reduction on catalysts activity exceeding that of calcination. On all samples selectivity towards CO oxidation decreased appreciably on increasing reaction temperature. The dependence of selectivity from pretreatment was negligible.

(b) The effect of catalyst pretreatment towards PROX was related to the change in the iron oxide phase caused by the pretreatment. Providing that gold particles are small enough to be able to activate CO and H_2, the catalytic performance towards PROX reaction was highly sensitive to the microcrystalline structure and the oxidation state of the iron oxide. CO oxidation activity of different iron oxide species was in the order: ferrihydrite > hematite > magnetite.

(c) On the Au/iron oxide system the PROX reaction occurs through a Mars-van Krevelen type reaction mechanism which involves lattice oxygen of the iron oxide and CO and H_2 adsorbed on gold particles.

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