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A comparative study of $Pt/\gamma\text{-}Al_2O_3$, $Au/\alpha\text{-}Fe_2O_3$ and $CuO–CeO_2$ catalysts for the selective oxidation of carbon monoxide in excess hydrogen

G. Avgouropoulos [a,d], T. Ioannides [a], Ch. Papadopoulou [b],
J. Batista [c], S. Hocevar [c], H.K. Matralis [a,b,*]

[a] *Foundation for Research and Technology-Hellas (FORTH), Institute of Chemical Engineering and High Temperature Chemical Processes (ICE/HT), P.O. Box 1414, GR-26500 Patras, Greece*
[b] *Department of Chemistry, University of Patras, GR-26500 Patras, Greece*
[c] *National Institute of Chemistry, Laboratory of Catalysis and Chemical Reaction Engineering, Hajdrihova 19, P.O. Box 3430, SI-1001 Ljubljiana, Slovenia*
[d] *Department of Chemical Engineering, University of Patras, Greece*

Abstract

Three different catalysts, namely $Pt/\gamma\text{-}Al_2O_3$, $Au/\alpha\text{-}Fe_2O_3$ and $CuO–CeO_2$ were prepared (by wet impregnation, coprecipitation and a sol–gel method, respectively) and their catalytic performance for the selective oxidation of carbon monoxide in the presence of excess hydrogen was evaluated and compared. The effects of the presence of CO_2 and H_2O in the reactant feed on the activity and selectivity of these catalysts, as well as their stability under realistic reaction conditions were also investigated.

Regardless of whether CO_2 or both CO_2 and H_2O are present in the reactant feed, the $Au/\alpha\text{-}Fe_2O_3$ catalyst is superior to the other two for the selective CO oxidation at relatively low reaction temperatures ($<80–120\,^{\circ}C$, depending on contact time and feed composition employed), while at higher reaction temperatures, best results are obtained with the $CuO–CeO_2$ catalyst, which proved to be more active and remarkably more selective than the $Pt/\gamma\text{-}Al_2O_3$ catalyst. The $Au/\alpha\text{-}Fe_2O_3$ catalyst was the most sensitive, while the $Pt/\gamma\text{-}Al_2O_3$ the most resistant towards deactivation caused by the presence of CO_2 and H_2O in the feed. Finally, while the $Au/\alpha\text{-}Fe_2O_3$ catalyst lost a considerable portion of its activity during the first 80 h under reaction conditions, the $CuO–CeO_2$ and $Pt/\gamma\text{-}Al_2O_3$ catalysts exhibited a stable catalytic performance, at least during the time period tested in this work (7–8 days).

Keywords: Carbon monoxide selective oxidation; Excess hydrogen; Influence of carbon dioxide; Influence of water; Stability; Alumina-supported platinum; Gold; Iron oxide; Copper; Ceria

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1. Introduction

Fuel cells are considered to be the propulsion system of the near future, since they can produce electricity without polluting the environment, and possess the necessary specific power, power density and durability to replace conventional internal combustion engines from their current applications [1]. Among the various types of fuel cells, the low temperature, H_2-fuelled, polymer electrolyte membrane fuel cells (H_2-PEMFCs) seem to be the actually most technically advanced energy conversion system for such purpose [2–7].

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[*] Corresponding author. Present address: Department of Chemistry, University of Patras, GR-26500 Patras, Greece.
Fax: +30-61-994796.
E-mail address: matralis@chemistry.upatras.gr (H.K. Matralis).

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However, the use of H_2-PEMFCs in vehicle applications is opposed with serious problems associated with the distribution and storage of hydrogen. A promising way to overcome these problems is to produce the H_2 feed gas on-board, in a fuel-processing unit, by converting a conventional fuel such as natural gas, gasoline or methanol to a H_2-rich gas mixture [8–11]. This can be done either by steam reforming or by autothermal reforming. In either case, the resulting gas mixture contains significant amounts of CO and it is further processed in a water gas shift reactor. In this way the gas stream becomes richer in H_2 and the concentration of CO drops to ca. 1 vol.%; a typical composition being: 45–75 vol.% H_2, 15–25 vol.% CO_2, 0.5–2 vol.% CO, a few vol.% H_2O and N_2 [12–15]. Unfortunately, even this low CO concentration cannot be tolerated by the H_2-PEMFCs, which are highly sensitive towards trace CO contamination in the H_2 feed gas. It is thus imperative to purify further the hydrogen feed gas reducing the CO concentration below 100 ppm [5,16–19].

This need has triggered, in the last few years, an intense research effort to develop catalysts able to selectively oxidize CO in the presence of excess H_2. Indeed, among the various available methods for removing CO from H_2-rich atmospheres, the selective catalytic oxidation of CO with molecular oxygen is undoubtedly the most straightforward, simpler, and cost effective one [5,14,20]. Such a catalyst should fulfill several important requirements; namely: (i) to possess high CO oxidation activity, (ii) to exhibit high selectivity with respect to the undesired H_2 oxidation (ideally, the catalyst should be inactive for the oxidation of H_2, in order to avoid losses of fuel hydrogen), (iii) to function at the temperature region defined by the temperature level of the fuel-processing unit (250–300 °C) and that of the H_2-PEMFC (80–100 °C), and (iv) to be resistant towards deactivation by CO_2 and H_2O present in the feed.

A number of platinum group metal-based catalysts supported on alumina, namely Pt/Al_2O_3, Rh/Al_2O_3 and Ru/Al_2O_3 [20–26], and zeolite-supported platinum catalysts (Pt/A-zeolite [27] and Pt/mordenite [28]), have been studied for this process, and among these, platinum-based catalysts gave the best results. Besides platinum, gold-based catalysts such as Au/Al_2O_3 [29,30], $Au/MnO_x/MgO/Al_2O_3$ [30], Au/MnO_x [31] and especially $Au/\alpha\text{-}Fe_2O_3$ [32] were found to be very active for this process. We have recently reported that mixed $CuO–CeO_2$ oxides constitute a promising candidate catalytic system for the selective oxidation of CO in the presence of excess hydrogen [33,34].

In the present work we compare, under identical reaction conditions, the catalytic properties for the selective CO oxidation in the presence of excess hydrogen of three important candidate catalysts, namely: the $Pt/\gamma\text{-}Al_2O_3$, $Au/\alpha\text{-}Fe_2O_3$ and $CuO–CeO_2$ catalysts. In addition, we investigate and report the effects of the presence of CO_2 and of both CO_2 and H_2O in the reactant feed on the catalytic performance (activity and selectivity) of these catalysts, as well as their stability with time under reaction conditions.

2. Experimental

2.1. Preparation of catalysts

The $Au/\alpha\text{-}Fe_2O_3$ catalyst was prepared by coprecipitation. Aqueous solutions of $HAuCl_4\cdot 3H_2O$ (Alfa), $Fe(NO_3)_3\cdot 9H_2O$ (Alfa) and Na_2CO_3 (Merck) were gradually and simultaneously added into a continuously stirred flask with distilled water. The reaction mixture was kept at 60 °C while the pH was maintained at 8.3 ± 0.2 during the addition of the solutions. After a period of 1 h, the resulting precipitate was filtered, washed with hot water several times in order to remove residual Cl^-, and then dried under static air at 80 °C for 12 h. Finally, the sample was calcined in flowing air at 400 °C for 2 h. The Au content of this sample, as determined by atomic absorption spectroscopy (AAS), was 2.9 wt.%.

The $CuO–CeO_2$ catalyst was synthesized by sol–gel peroxo route method by reacting 0.085 g $CuCl_2\cdot 2H_2O$ (Fluka) with 48 ml of 30 vol.% H_2O_2 and in separate vessel by reacting 12 ml of 30 vol.% H_2O_2 with 3.54 g of $CeCl_3\cdot 7H_2O$ (Fluka). After the reactions in both vessels were completed, the two solutions were mixed and the excess peroxide was evaporated at 80 °C. At the end of evaporation 20 ml of ethanol was added. The sample was then dried at room temperature to obtain the xerogel, which was subsequently gradually heated at 650 °C under static air and remained at that temperature for 4 h.

Table 1
Composition and BET specific surface areas of the Au/α-Fe_2O_3, CuO–CeO_2 and Pt/γ-Al_2O_3 catalysts

Catalyst	Composition	BET specific surface area ($m^2\,g^{-1}$)
Au/α-Fe_2O_3	2.9 wt.% Au	49.8
CuO–CeO_2	1.9 wt.% Cu	19.5
Pt/γ-Al_2O_3	5.0 wt.% Pt	224.0

The Pt/γ-Al_2O_3 catalyst was prepared by wet impregnation of γ-Al_2O_3 (AKZO, 290 $m^2\,g^{-1}$) with an aqueous solution of tetraammineplatinum(II) nitrate (Alfa). The resulting mixture was dried at 40 °C under vacuum and then at 110 °C under static air for 12 h. The temperature was then gradually increased to 300 °C under a stream of Ar (40 $cm^3\,min^{-1}$) and the sample remained at that temperature under flowing H_2 (40 $cm^3\,min^{-1}$) for 2 h and then it was cooled down to room temperature under Ar.

The composition of the prepared samples and their BET specific surface areas are presented in Table 1.

2.2. Apparatus and method used for activity measurements

The catalytic tests were carried out in a conventional flow, fixed-bed reactor at atmospheric pressure. Unless specifically noted, a quantity of 50 mg of catalyst (particle size in the region $90 < d_p < 160\,\mu m$), and a total flow rate of the reaction mixture equal to 100 $cm^3\,min^{-1}$ ($W/F = 0.03\,g\,s\,cm^{-3}$) was used for each run. The reaction mixture consisted of 1 vol.% CO, 1.25 vol.% O_2 and 50 vol.% H_2 in He.

The effect of CO_2 was examined, at separate runs, with the addition of 15 vol.% CO_2 in the respective feed gases. The effect of H_2O was investigated by the addition of 10 vol.% H_2O in the feed. Unless specifically noted, an excess of oxygen was used for the selective CO oxidation experiments ($\lambda = 2[O_2]/[CO] = 2.5$).

Prior to all catalytic experiments the Au/α-Fe_2O_3 and CuO–CeO_2 samples were heated in situ at 400 °C under a flowing 20% O_2/He mixture (20 $cm^3\,min^{-1}$) for 30 min to yield clean surfaces, followed by cooling down to the reaction temperature under pure He, while the Pt/γ-Al_2O_3 samples were heated at 300 °C under flowing H_2 (20 $cm^3\,min^{-1}$) for 30 min and cooled down to the reaction temperature also under pure He.

Gas chromatography was used for the analysis. Methane formation was not detected under our experimental conditions.

The CO conversion was calculated based on the CO_2 formation as follows:

$$\%\text{ of conversion of CO} = \frac{[CO_2]_{out}}{[CO]_{in}} \times 100$$

When 15 vol.% CO_2 was added in the reaction mixture, the CO conversion calculation was based on the CO consumption, because of the large error in the quantification of small changes in the CO_2 concentration.

The O_2 conversion was based on the oxygen consumption as follows:

$$\%\text{ of conversion of } O_2 = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100$$

Finally, the selectivity was calculated from the oxygen mass balance as follows:

$$\%\text{ of selectivity} = \frac{0.5([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} \times 100$$

3. Results and discussion

3.1. Comparison of the title catalysts for the CO selective oxidation

The percentage conversions of CO and O_2, as well as the selectivity achieved with the Au/α-Fe_2O_3, CuO–CeO_2 and Pt/γ-Al_2O_3 catalysts in the selective CO oxidation in the presence of excess H_2 are presented in Fig. 1. Among the three catalysts tested, the Au/α-Fe_2O_3 sample is the most active while the CuO–CeO_2 is the most selective. Indeed, under these conditions ($W/F = 0.03\,g\,s\,cm^{-3}$), the temperature at which 50% conversion of CO is obtained, T_{50}, was found equal to 37 °C (95%), 94 °C (100%), and 161 °C (51%), respectively, for the Au/α-Fe_2O_3, CuO–CeO_2, and Pt/γ-Al_2O_3 catalysts, where the values in parenthesis denote the corresponding selectivity. The maximum CO conversion achieved over the Au/α-Fe_2O_3 sample was 99% (with 40% selectivity) at 110 °C. The temperature at which a similar CO conversion ($\geq$99%) was obtained with the CuO–CeO_2 and

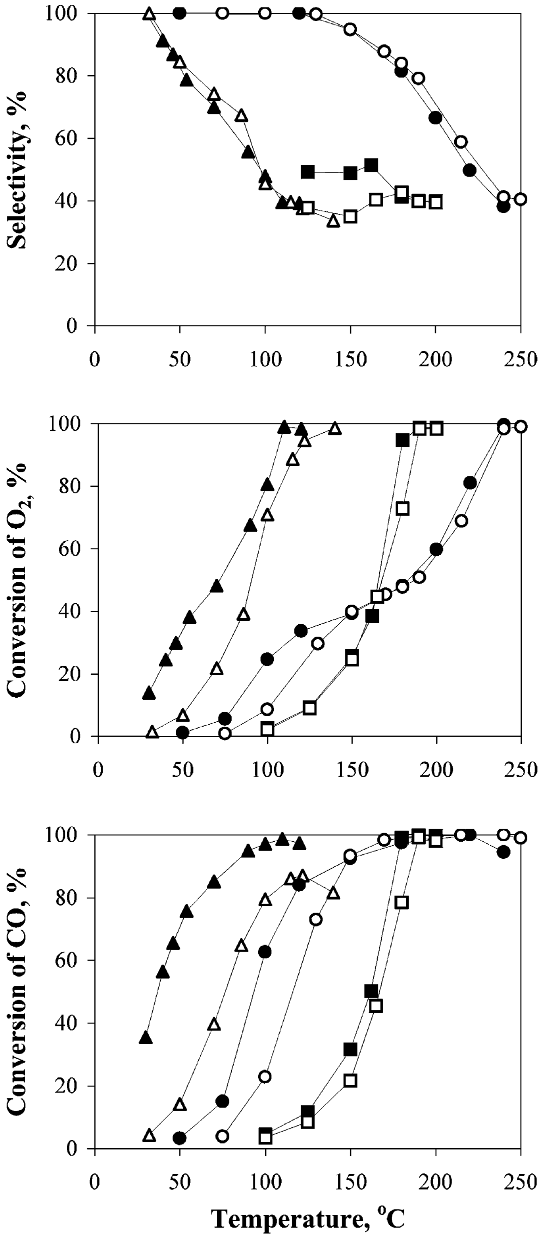

Fig. 1. Variation of the CO and O_2 conversion and of the selectivity with the reaction temperature for the selective oxidation of CO, at $W/F = 0.030\,\mathrm{g\,s\,cm^{-3}}$, over the Au/α-$Fe_2O_3$ (△), CuO–CeO_2 (○), and Pt/γ-Al_2O_3 (☐) catalysts in the absence of CO_2 (filled symbols) and in the presence of 15 vol.% CO_2 in the reactant feed (open symbols).

Pt/γ-Al_2O_3 catalysts was, respectively, 200 °C (with 66% selectivity) and 180 °C (with 41% selectivity).

As seen from the same figure, the influence of the reaction temperature on the selectivity depends strongly on the nature of the catalyst. For the Au/α-Fe_2O_3 sample, the increase of the reaction temperature is accompanied by a continuous decrease of the selectivity, indicating higher apparent activation energy for the H_2 oxidation than for the CO oxidation. Over the CuO–CeO_2 catalyst the selectivity remains constant at 100% as the temperature increases from 50 to 120 °C, although the conversion of CO greatly increases in this temperature range (namely, from 3 to 84%). As the reaction temperature increases further, from 120 to 240 °C, the selectivity decreases progressively from 100 to 38%. Contrary to these two samples, the decrease of the selectivity with the reaction temperature was not so pronounced with the Pt/γ-Al_2O_3 catalyst in the temperature range 125–200 °C, in agreement with results reported by Kahlich et al. [26]. Indeed, in the temperature region 125–160 °C the selectivity remained constant at ca. 50% (while the CO conversion increased from 4 to 50%) and decreased to ca. 40% at higher temperatures when the CO conversion reaches 99.6%.

These catalytic samples were also tested under a higher contact time, namely at $W/F = 0.144\,\mathrm{g\,s\,cm^{-3}}$, with all other conditions being the same as previously. The results are presented in Fig. 2. Under these conditions the Au/α-Fe_2O_3 catalyst exhibited a 100% CO conversion with 82% selectivity already from 45 °C. The maximum CO conversion achieved with the CuO–CeO_2, and Pt/γ-Al_2O_3 catalysts was, respectively, 100% (with 94% selectivity) at 120 °C, and 99% (with 40% selectivity) at 165 °C. It should be noted that in the temperature range 120–200 °C the CuO–CeO_2 sample exhibits superior results as compared to the Pt/γ-Al_2O_3 catalyst. Indeed, in this temperature range the CO conversion obtained with the CuO–CeO_2 sample was 100% (falling to 99.4% only at 200 °C) and the selectivity decreased gradually from 94 to 40%, while the CO conversion achieved over the Pt/γ-Al_2O_3 sample varied from 47 to 99% with an almost constant selectivity at ca. 40%.

We may, thus, conclude that for the selective CO oxidation in the absence of CO_2 and H_2O vapor in the reactant feed, the Au/α-Fe_2O_3 catalyst is superior to the other two in the low reaction temperature region

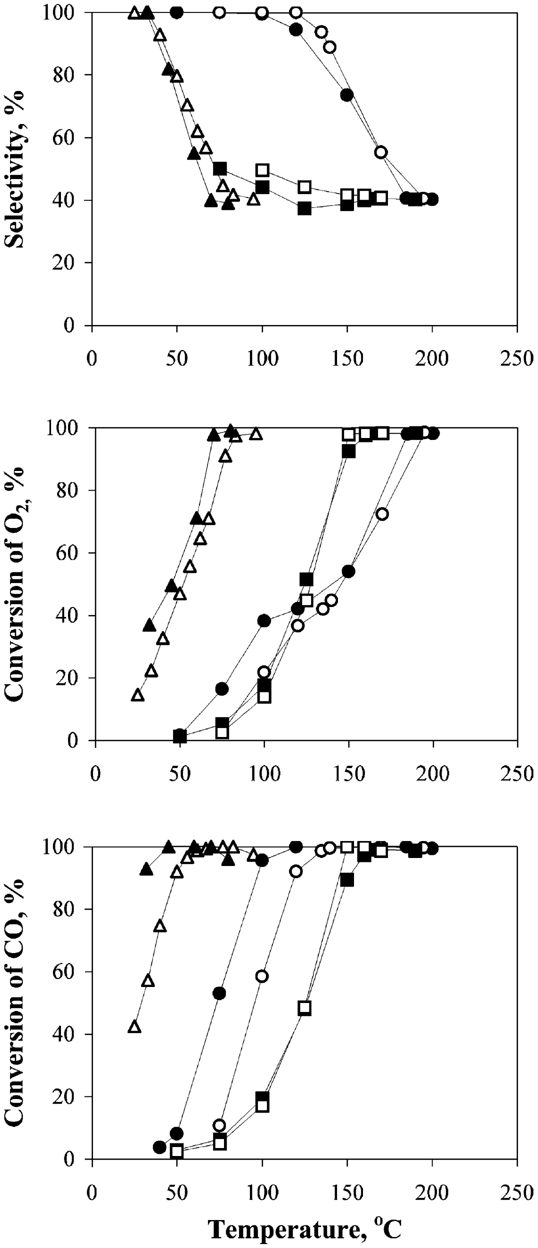

Fig. 2. Variation of the CO and O_2 conversion and of the selectivity with the reaction temperature for the selective oxidation of CO, at $W/F = 0.144\,g\,s\,cm^{-3}$, over the Au/α-$Fe_2O_3$ (△), CuO–CeO_2 (○), and Pt/γ-Al_2O_3 (□) catalysts in the absence of CO_2 (filled symbols) and in the presence of 15 vol.% CO_2 in the reactant feed (open symbols).

(namely at temperature lower than 120 or 50 °C, depending on the *W*/*F* employed). At the higher reaction temperature range (namely at temperature higher than 150 or 100 °C, depending on the *W*/*F*) the CuO–CeO_2 sample outperforms the Pt/γ-Al_2O_3 catalyst, being more active and remarkably more selective.

3.2. Effect of CO_2 on the CO selective oxidation

The results obtained in the presence of 15 vol.% CO_2 in the reactant feed are also presented in Figs. 1 and 2 for the *W*/*F* values of 0.03 and $0.144\,g\,s\,cm^{-3}$, respectively.

A comparison of the CO conversion versus reaction temperature curves obtained for the three catalysts in the absence and in the presence of CO_2 shows that CO_2 generally decreases their catalytic activity for the selective CO oxidation. Indeed, the presence of CO_2 provokes an increase at the temperature T_{50} of 40, 22 and 6 °C for the Au/α-Fe_2O_3, CuO–CeO_2, and Pt/γ-Al_2O_3 catalysts, respectively, when these are tested with $W/F = 0.03\,g\,s\,cm^{-3}$. The corresponding increases of the T_{50} when the CuO–CeO_2, and Pt/γ-Al_2O_3 catalysts are tested with $W/F = 0.144\,g\,s\,cm^{-3}$ are equal to, respectively, 22 and ca. 0 °C.

With $W/F = 0.144\,g\,s\,cm^{-3}$ a complete (100%) CO conversion is now obtained with the Au/α-Fe_2O_3 catalyst at 77 °C with 45% selectivity as compared to 45 °C with 82% selectivity in the absence of CO_2. Over the CuO–CeO_2 sample, CO is now completely converted at 140 °C with 88% selectivity as compared to 120 °C with 94% selectivity in the absence of CO_2. Finally, the catalytic performance of the Pt/γ-Al_2O_3 catalyst seems to be rather unaffected by the presence of CO_2. In the absence of CO_2 this sample exhibited its maximum CO conversion (>99%) in the temperature region 165–170 °C with a selectivity of ca. 40%, while in the presence of CO_2 the CO conversion is complete in the region 150–160 °C with a selectivity of ca. 41%. This resistance of the Pt/γ-Al_2O_3 catalyst towards deactivation by CO_2 during the selective CO oxidation is in full agreement with previous studies of the CO oxidation over Pt/γ-Al_2O_3 catalysts reporting that the CO_2 partial pressure does not significantly affect the CO_2 production rate [35–38].

A comparison of the selectivity versus reaction temperature curves obtained for the three catalysts in the absence and in the presence of CO_2 shows that at a given reaction temperature the selectivity achieved over any of the three catalysts is rather slightly affected by the presence of CO_2 in the feed. However, since a given CO conversion is generally obtained at a higher temperature when CO_2 is present in the feed, it turns out that now a given CO conversion over any of the three samples is generally achieved less selectively.

It is, thus, evident that the magnitude of the negative effect provoked by the presence of CO_2 on both the activity for the selective CO oxidation, and the selectivity, is strongly dependent on the nature of the catalyst. Among the three samples tested, the Au/α-Fe_2O_3 catalyst is the most sensitive, while the Pt/γ-Al_2O_3 catalyst is the most resistant towards deactivation by CO_2.

Based on the results presented in Figs. 1 and 2, we may conclude that for low reaction temperatures (namely, lower than 125 or 100 °C, depending on whether *W/F* was equal to 0.03 or 0.144 g s cm^{-3}, respectively), the Au/α-Fe_2O_3 catalyst is superior to the other two for the selective oxidation of CO in the presence of CO_2. At higher reaction temperatures the CuO–CeO_2 and Pt/γ-Al_2O_3 catalysts give better results, and the CuO–CeO_2 sample outperforms the Pt/γ-Al_2O_3 one, as it was also the case in the absence of CO_2 in the reactant feed. Indeed, when $W/F = 0.144\,\mathrm{g\,s\,cm^{-3}}$, a CO conversion higher than 98% was obtained over the Pt/γ-Al_2O_3 catalyst in the range 150–170 °C with a selectivity of ca. 41%, while over the CuO–CeO_2 catalyst in the temperature range 135–170 °C with a considerably higher selectivity (namely in the range 94–55%).

3.3. Effect of the presence of both CO_2 and H_2O on the CO selective oxidation

The results obtained with the three catalysts in the presence of both 15 vol.% CO_2 and 10 vol.% H_2O in the reactant feed (with $W/F = 0.144\,\mathrm{g\,s\,cm^{-3}}$) are presented in Fig. 3. For comparison, the corresponding curves obtained under the same conditions but without water vapor in the feed are also presented in the same figure.

The presence of H_2O provokes a significant decrease on the activity of both Au/α-Fe_2O_3 and CuO–CeO_2 catalysts. In fact, for both of these samples, a given CO conversion (obtained in the absence of H_2O) is achieved at about 40–45 °C higher reaction temperature in the presence of H_2O in the feed.

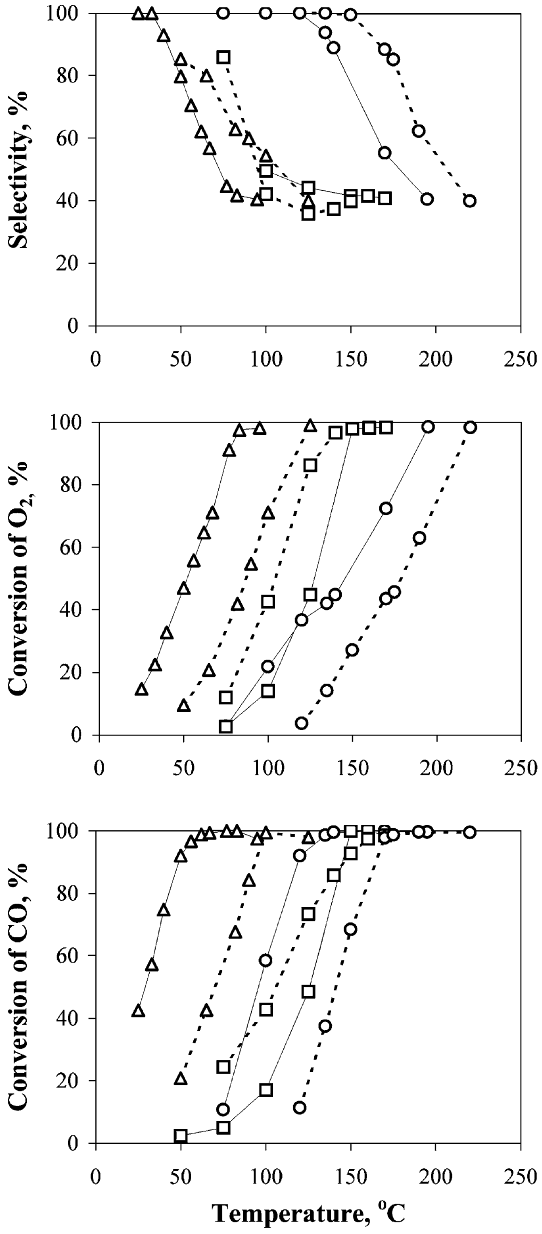

Fig. 3. Variation of the CO and O_2 conversion and of the selectivity with the reaction temperature for the selective oxidation of CO, at $W/F = 0.144\,\mathrm{g\,s\,cm^{-3}}$, over the Au/$\alpha$-$Fe_2O_3$ (△), CuO–CeO_2 (○), and Pt/γ-Al_2O_3 (□) catalysts in the presence of 15 vol.% CO_2 (solid lines) and in the presence of both 15 vol.% CO_2 and 10 vol.% H_2O in the reactant feed (dotted lines).

A slightly lower inhibition of the activity is observed regarding the O_2 conversion for both samples. In addition to this negative effect on the activity, the presence of H_2O also diminishes the selectivity exhibited by these two catalysts. Indeed, a given CO conversion achieved in the absence of H_2O is less selectively obtained in its presence. However, this effect is much more pronounced in the case of the Au/α-Fe_2O_3 sample. For example, in the CO conversion range of 60–95%, the selectivity achieved with the Au/α-Fe_2O_3 sample was decreasing from ca. 100 to 74% in the absence of H_2O and from 76 to 56% in the presence of H_2O. For the same CO conversion range (60–95%), the selectivity achieved with the CuO–CeO_2 sample was practically constant at 100% (dropping to 98% only when the CO conversion was 95%) in the absence of H_2O, while in its presence it was gradually decreasing from 100 to 89%.

As compared to the Au/α-Fe_2O_3 and CuO–CeO_2 catalysts, the effect of H_2O on the Pt/γ-Al_2O_3 catalyst was markedly different. For reaction temperatures lower than 145 °C (at that temperature range the CO conversion is lower than 90%), the Pt/γ-Al_2O_3 sample is more active (giving both higher CO and higher O_2 conversions) when H_2O is present in the reactant feed. Taking into account that, in this reaction temperature range, the activity of this sample was practically unaffected by the presence of CO_2 (see Fig. 2), it turns out that when both CO_2 and H_2O are present in the feed then this catalyst is more active than when both of these compounds are absent from the feed. However, this beneficial effect does not manifest itself for higher reaction temperatures (when the CO conversion becomes higher than 90%). Indeed, for temperatures higher than 145 °C, the CO conversion achieved at a given temperature is significantly lower in the presence of H_2O than in its absence. For example, at 150 °C, the CO conversion obtained over the Pt/γ-Al_2O_3 sample was 100% (with 41.5% selectivity) in the absence of H_2O but only 92.8% (with 39.8% selectivity) in its presence. The observed beneficial effect of H_2O (namely, the increase of CO conversion at low reaction temperatures) cannot possibly be attributed to a part of CO being consumed by the water gas shift reaction, since at this low reaction temperature range ($<$145 °C) the extend of this reaction should be negligible, if any at all [39,40]. Thus, we may conclude that the observed increase of the CO conversion during selective CO oxidation in the presence of H_2O is due to an enhancement provoked by the presence of H_2O on the CO oxidation rate. This conclusion is corroborated by previous investigations on the CO oxidation over alumina-supported platinum catalysts reporting that the presence of H_2O in the CO/O_2 reactant feed enhances the rate of CO oxidation [26,38,41]. Moreover, this enhancement of the CO oxidation rate was reported to decrease as the reaction temperature increases [38].

The influence of H_2O on the selectivity of the Pt/γ-Al_2O_3 sample is similar to that for the Au/α-Fe_2O_3 and CuO–CeO_2 catalysts; namely, a given CO conversion achieved over the Pt/γ-Al_2O_3 catalyst in the absence of H_2O is less selectively obtained in its presence, and this was observed for the whole reaction temperature region studied. However, due to the fact that the selectivity of Pt/γ-Al_2O_3 was already low without water in the feed, the decrease of the selectivity provoked by its presence is not as pronounced as it was for the other two catalysts. For example, in the CO conversion range of 60–95%, the selectivity achieved with the Pt/γ-Al_2O_3 sample was gradually decreasing from 44 to 42% in the absence of H_2O, while in its presence it is varied in the region 36–39%.

Under these reaction conditions, the Au/α-Fe_2O_3 sample was again superior to the other two at the low reaction temperature range, exhibiting its best catalytic performance (99.5% CO conversion with 54.5% selectivity) at 100 °C. The Pt/γ-Al_2O_3 sample gave its best results at 160 °C with 97.5% CO conversion and 41.5% selectivity. At practically the same reaction temperature (170 °C), the CuO–CeO_2 catalyst gave the same CO conversion but with the remarkably higher selectivity of 88%. The CuO–CeO_2 sample exhibited its best catalytic performance (99.6% CO conversion with 62.3% selectivity) at 190 °C. Thus, the CuO–CeO_2 sample, being remarkably more selective, outperforms the Pt/γ-Al_2O_3 at the high reaction temperature range, also in the presence of H_2O in the reactant feed.

3.4. Stability of the catalysts under reaction conditions

A long time (7–8 days) catalytic run was performed with each of the Au/α-Fe_2O_3, CuO–CeO_2 and

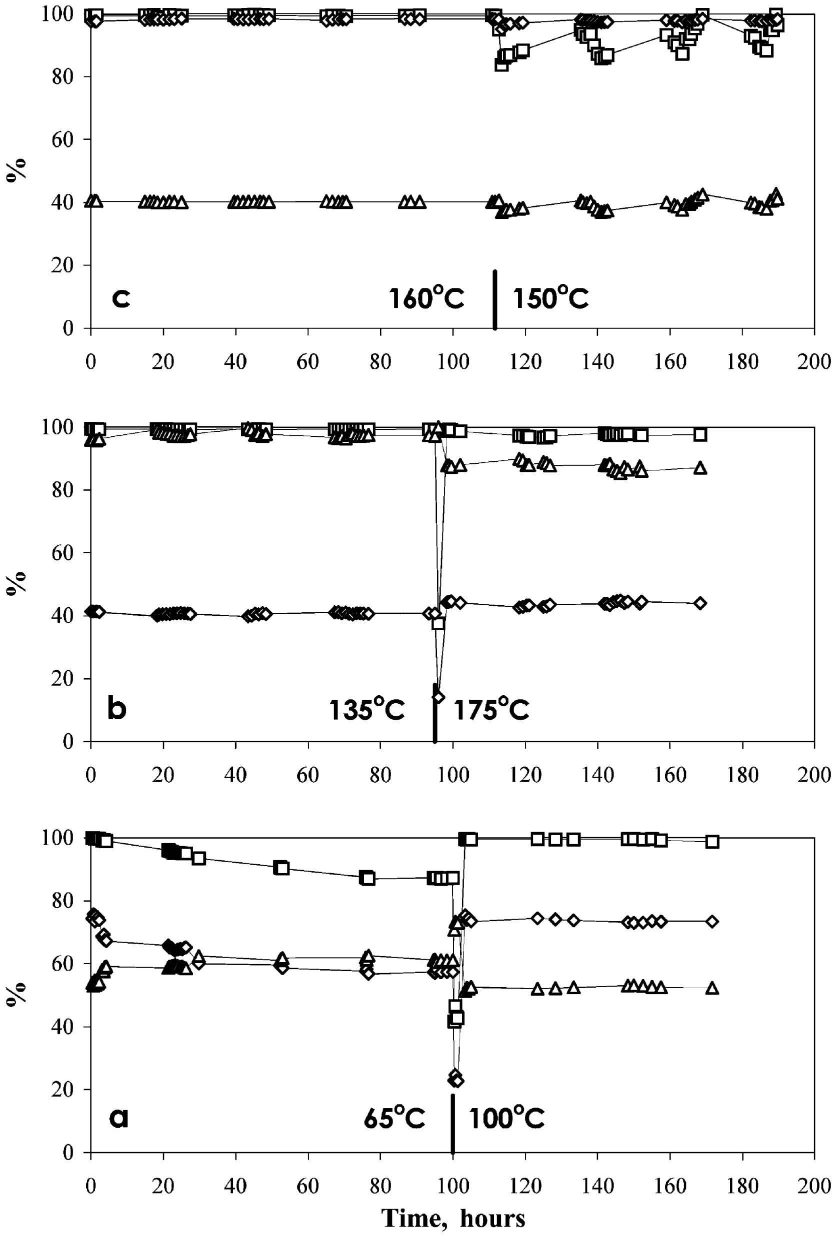

Fig. 4. Variation of the CO (□) and O_2 (◇) conversion and of the selectivity (△) with the reaction time during the selective oxidation of CO, at $W/F = 0.144\,\mathrm{g\,s\,cm^{-3}}$, in the presence of 15 vol.% CO_2 (from the beginning up to the time marked by the small vertical line), and in the presence of both 15 vol.% CO_2 and 10 vol.% H_2O in the reactant feed (for the remaining time period) over the Au/α-Fe_2O_3 (a), CuO–CeO_2 (b), and Pt/γ-Al_2O_3 (c) catalysts. The reaction temperatures at each portion of the long time catalytic test are indicated alongside the small vertical line.

Pt/γ-Al_2O_3 catalysts in order to explore their stability under reaction conditions for the CO selective oxidation in the presence of CO_2 and in the presence of both CO_2 and H_2O.

Each sample remained for a period of ca. 100 h under reaction conditions for selective CO oxidation in the presence of 15 vol.% CO_2 (with $W/F = 0.144\,\mathrm{g\,s\,cm^{-3}}$) at a, particular for each sample, reaction temperature. At that reaction temperature each sample exhibited an initial CO conversion of ca. 99%. The variations of the CO and O_2 conversions and of the selectivity with the time each sample remained under these reaction conditions are depicted in Fig. 4a–c for the Au/α-Fe_2O_3, CuO–CeO_2 and Pt/γ-Al_2O_3 catalysts, respectively. As it can be seen from these figures, both the CuO–CeO_2 and Pt/γ-Al_2O_3 catalysts exhibited a perfectly constant catalytic behavior during this first period. In contrast, the Au/α-Fe_2O_3 sample lost a significant part of its activity during the first 75 h and remained stable for the rest 25 h.

Following this first 100 h period, the stability of the catalysts was tested under reaction conditions for the CO selective oxidation in the presence of both CO_2 and H_2O in the reactant feed. The time at which H_2O was first added in the feed for each sample is indicated in the corresponding figure by a small vertical line. Due to the deactivation caused by the presence of H_2O, the reaction temperature was increased to a new value in order for the CO conversion to continue being close to ca. 99%. Specifically, for the Pt/γ-Al_2O_3 catalyst, the temperature had to be slightly decreased in order to avoid the O_2 conversion being too close to the 100% value. The samples remained under these conditions for an additional period of 70–80 h. As seen from Fig. 4c, in the presence of both CO_2 and H_2O the CO conversions achieved over the Pt/γ-Al_2O_3 catalyst varied in the region $93 \pm 7\%$ without any sign, however, of a continuous deactivation with the time on stream. Similar (but of lower amplitude) variations around a steady mean value are also observed for the selectivity and the O_2 conversion. The reasons for these variations are not yet clear. However, we have performed an additional long time run with the Pt/γ-Al_2O_3 sample at a lower reaction temperature (125 °C) and this behavior was not repeated; no variation of the CO conversion, unless within experimental error, was observed in the presence of both CO_2 and H_2O. Finally, both the Au/α-Fe_2O_3, and CuO–CeO_2 catalysts exhibited a stable catalytic performance when both CO_2 and H_2O were present in the feed (Fig. 4a and b).

4. Conclusions

Three different catalysts (Au/α-Fe_2O_3, CuO–CeO_2 and Pt/γ-Al_2O_3) were prepared and compared for their catalytic behavior for the selective oxidation of CO in the presence of excess hydrogen. The effects of the presence of CO_2 and H_2O in the reactant feed on the activity and selectivity of these catalysts, as well as their stability under realistic reaction conditions were also investigated. The following main conclusions may be drawn from this work:

- At relatively low reaction temperatures (<80–120 °C, depending on *W*/*F* and feed composition) the Au/α-Fe_2O_3 catalyst is superior to the other two for the selective CO oxidation, regardless of whether CO_2 or both CO_2 and H_2O are present in the reactant feed.
- At higher reaction temperatures, best results for the selective CO oxidation (regardless of whether CO_2 or both CO_2 and H_2O are present in the reactant feed) are obtained with the CuO–CeO_2 catalyst, which proved to be more (or equally, depending on conditions) active but in all cases remarkably more selective than the Pt/γ-Al_2O_3 catalyst.
- Adding 15 vol.% CO_2 in the reactant feed, generally, provokes a decrease in both the activity and selectivity of all three catalysts for the selective CO oxidation. The magnitude of this negative effect depends on the nature of the catalyst. Au/α-Fe_2O_3 was found to be the most sensitive, while the Pt/γ-Al_2O_3 catalyst was the most resistant towards deactivation by CO_2.
- The presence of 10 vol.% H_2O (in addition to the presence of CO_2) in the reactant feed causes a significant decrease on the activity of the Au/α-Fe_2O_3 and CuO–CeO_2 catalysts. The activity of the Pt/γ-Al_2O_3 catalyst was decreased only for reaction temperatures higher than 145 °C (at $W/F = 0.144\,\mathrm{g\,s\,cm^{-3}}$), while the presence of both CO_2 and H_2O had a beneficial effect on the activity of this sample at lower reaction temperatures. The selectivity of all samples was diminished in the

presence of both CO_2 and H_2O, the effect being more pronounced in the case of the Au/α-Fe_2O_3 catalyst.

- With the exception of the Au/α-Fe_2O_3, the CuO–CeO_2 and Pt/γ-Al_2O_3 catalysts exhibited a stable catalytic performance, at least during the time period tested in this work (7–8 days). The Au/α-Fe_2O_3 catalyst lost a considerable portion of its activity during the first 80 h under reaction conditions.

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