

CuO–CeO₂ mixed oxide catalysts for the selective oxidation of carbon monoxide in excess hydrogen

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Received 23 November 2000; accepted 6 February 2001

A series of mixed oxide CuO–CeO₂ catalysts were prepared by coprecipitation and tested for the selective oxidation of carbon monoxide in the presence of excess hydrogen. These catalysts were found to be very active and exceptionally selective for this reaction and exhibited a good resistance towards CO₂ and H₂O. The catalytic performance of these non-noble metal containing catalysts is compared with that of other selective CO oxidation catalysts reported in literature.

KEY WORDS: carbon monoxide oxidation; selective oxidation; excess hydrogen; copper; ceria

1. Introduction

The development of efficient catalysts for the selective oxidation of carbon monoxide in the presence of excess hydrogen has attracted renewed interest during the last years due to the potential application of such catalysts in the environmentally important fuel cell technology. Fuel cells are considered to be the propulsion system of the near future, as they possess the specific power, the power density and the durability needed to replace internal combustion engines from their current applications [1]. Among the various types of fuel cells, the low temperature, hydrogen fuelled, polymer electrolyte membrane fuel cells (H₂-PEMFC) seem to be the actually most technically advanced energy conversion system for zero emission vehicles (ZEV), and appear also very attractive for stationary small facilities and portable generators [2–7].

In order to avoid the problems associated with the distribution and storage of hydrogen for the H₂-PEM fuel cells used in vehicle applications, the H₂ feed gas can be produced on-board, in a fuel processing unit, by converting a conventional fuel such as natural gas, gasoline or methanol to a H₂-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 with additional steam in a water–gas shift reactor. In this way the gas stream becomes richer in hydrogen and the concentration of CO drops to ca. 1 vol%; a typical composition is: 45–75 vol% H₂, 15–25 vol% CO₂, 0.5–2 vol% CO, a few vol% H₂O and N₂ [12–15]. However, even this low CO concentration cannot be tolerated by

the H₂-PEM fuel cells. In fact, conventional pure Pt electrocatalysts require less than 5 ppm CO, while the more CO tolerant bimetallic alloy catalysts (such as PtRu) less than 100 ppm CO [5,16–19]. It is thus imperative to purify further the hydrogen feed gas reducing the CO concentration below 100 ppm.

Of the currently available methods for removing CO from H₂-rich atmospheres, the selective catalytic oxidation of CO with molecular oxygen is undoubtedly the most straightforward, simpler, and the most cost effective one [5,14,20]. The most important requirements from a catalyst for the selective CO oxidation are:

- (i) high CO oxidation activity;
- (ii) high selectivity with respect to the undesired H₂ oxidation. Ideally, the catalyst should be inactive for the oxidation of H₂, in order to avoid losses of fuel hydrogen;
- (iii) operation at a temperature in the region defined by the temperature level of the fuel processing unit (250–300 °C) and that of the H₂-PEMFC (80–100 °C);
- (iv) resistance towards deactivation by CO₂ and H₂O present in the feed.

Catalysts so far proposed for this process are alumina-supported platinum group metals Pt/Al₂O₃, Rh/Al₂O₃ and Ru/Al₂O₃ [20–26], zeolite-supported platinum catalysts (Pt/A-zeolite [27] and Pt/mordenite [28]), and gold-based catalysts (Au/MnO_x [29] and Au/ α -Fe₂O₃ [30]). Recently, a non-noble metal containing catalyst, namely CoO, has been proposed [31] for the selective oxidation of carbon monoxide.

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Liu and Flytzani–Stefanopoulos have reported that CuO–CeO₂ catalysts are very active for the complete CO oxidation exhibiting a specific activity several orders of magnitude higher than that of conventional Cu-based catalysts and comparable or superior to Pt-based catalysts [32,33].

In the present work we examine the catalytic properties of coprecipitated CuO–CeO₂ mixed oxide catalysts for the selective CO oxidation [34]. For comparison, the performance of these catalysts for the CO oxidation, in the absence of hydrogen in the feed, is also reported. The influence of both the composition of the CuO–CeO₂ samples and the presence of CO₂ in the reaction feed is investigated for both reactions. The best sample is also studied for the selective CO oxidation in the presence of both CO₂ and H₂O in the feed. Finally, the observed catalytic properties of the CuO–CeO₂ mixed oxide catalysts for the selective CO oxidation are compared with those of the other catalysts reported in literature.

2. Experimental

2.1. Preparation of catalysts

The CuO–CeO₂ catalysts were synthesized by coprecipitation from the mixtures of equimolar, with respect to common anion, water solutions of copper and cerium nitrates. The 0.15 mol/l Cu(NO₃)₂ and 0.10 mol/l Ce(NO₃)₃ solutions were mixed with a turbine stirrer (Ultra Turrax T50, Janke & Kunkel) with the rate of 4000 rpm in suitable volume proportions (25, 50 and 75 ml of 0.15 mol/l Cu(NO₃)₂ solution was added to 475, 450 and 425 ml of 0.10 mol/l Ce(NO₃)₃ solution, respectively) to give 500 ml of solution. The equivalent quantity of 7% water solution of Na₂CO₃ was added dropwise with a rate of 1.5 ml/min and the pH of the mixed solution was kept below 6.0. The coprecipitation was ended quantitatively after mixing the suspension for another 30 min when the equivalent quantity of Na₂CO₃ solution has been added. The resulting suspension was then filtered through filter paper of “Blue ribbon” quality. The obtained coprecipitate was rinsed with a three-fold volume of boiling demineralised water. The coprecipitate was then dried at 110 °C for 12 h. The powdered coprecipitate was subsequently heat-treated in a shallow bed and in the flow of dry air (6 l/h⁻¹) at 650 °C for 4 h. The obtained catalysts had Cu/(Cu + Ce) molar ratio equal to 0.073, 0.143 and 0.209 calculated on the basis of mixed oxide formula Cu_xCe_{1-x}O_{2-δ}. The composition of the prepared samples and their BET specific surface areas are presented in table 1. The chemicals used for synthesis were: Cu(NO₃)₂·3H₂O (99.5 wt% purity, Kemika, Zagreb, Croatia), Ce(NO₃)₃·6H₂O (99 wt% purity, Fluka Germany) and Na₂CO₃·10H₂O (99 wt% purity, Kemika, Zagreb, Croatia).

2.2. Apparatus and method used for activity measurements

The catalytic tests for the selective oxidation of CO in the presence of excess hydrogen were carried out in a conventional flow, fixed-bed reactor at atmospheric pressure. The

Table 1

Composition and BET specific surface areas of the CuO–CeO₂ catalysts and reaction rates, r_{CO} , determined at 75 °C for the CO oxidation in the absence of H₂ and the selective CO oxidation in the presence of excess H₂. The reaction rate values in parentheses were determined at 100 °C when the above two reactions were carried out in the presence of 15 vol% CO₂ in the corresponding reactant feeds.

| Composition (wt% Cu) | BET specific surface area (m ² g ⁻¹) | r_{CO} (10 ⁻⁶ mol _{CO} s ⁻¹ g _{cat} ⁻¹) | |
|-------------------------|--|--|--------------------------------------|
| | | In the absence of H ₂ | In the presence of H ₂ |
| 2.8 | 8.4 ± 0.08 | 0.66 (0.56) | 0.89 (0.97) |
| 5.7 | 16.6 ± 0.09 | 2.26 (2.45) | 2.28 (2.16) |
| 8.7 | 11.2 ± 0.03 | 1.37 (1.45) | 1.62 (1.40) |

reactor was a 4 mm i.d. (6 mm o.d., length 31 cm) quartz tube housed in a furnace. An enlargement of 9 mm i.d. at the central part of the quartz tube contained the catalyst bed. A PID control thermocouple was placed at the outside surface of the reactor tube in order to control the temperature of the furnace. The catalyst temperature values were measured with another thermocouple enclosed in a 3 mm o.d. quartz thermowell placed coaxially into the reactor tube and arriving at the middle of the catalyst bed. Unless specifically noted, a quantity of 50 mg of catalyst (in the form of powder with particle size in the region 90 < d_p < 160 μm) was used for each run. This particle size was chosen such that, on the one hand, a significant pressure drop over the catalyst bed was avoided and, on the other hand, significant internal concentration and temperature gradients could be neglected.

The feed gas was passed downward through the reactor containing the catalyst bed, while electronic mass flow controllers (AERA FC-7700C) adjusted its composition and flow rate. Unless specifically noted, the total flow rate of the reaction mixture was equal to 100 cm³ min⁻¹ (yielding a W/F ratio equal to 0.03 g s cm⁻³). In the case of CO oxidation experiments the reaction mixture consisted of 1 vol% CO and 0.5 vol% O₂ in He, while in the case of experiments for the selective CO oxidation it consisted of 1 vol% CO, 1.25 vol% O₂ and 50 vol% H₂ in He. The effect of CO₂ on both reactions was examined, at separate runs, with the addition of 15 vol% CO₂ in the respective feed gases. The effect of H₂O was investigated by the addition of 10 vol% H₂O in the feed with a syringe pump, while heating the gas lines leading to the reactor at 100 °C in order to avoid condensation. The excess oxygen with respect to the minimum amount of oxygen required for CO oxidation to CO₂ (in the absence of side reactions) is characterized by the process parameter λ , with $\lambda = 2[\text{O}_2]/[\text{CO}]$. Therefore, for the CO oxidation experiments the stoichiometric concentration of oxygen was used ($\lambda = 1$), while, unless specifically noted, an excess of oxygen was used for the selective CO oxidation experiments ($\lambda = 2.5$).

Prior to all catalytic experiments the sample was heated *in situ* the reactor at 400 °C under a flowing 20% O₂/He mixture (20 cm³ min) for 30 min to yield clean surfaces, followed by cooling down to the reaction temperature under pure He.

Product and reactant analysis was carried out by a gas chromatograph (Shimadzu GC-14B) equipped with a thermal conductivity detector and using helium as carrier gas. A Carbosieve column was used to separate CO and O₂ at 70 °C. A Porapak column was used to separate CO₂ and H₂O at 70 °C. Methane formation was not detected under our experimental conditions.

The CO conversion was calculated based on the CO₂ formation as follows:

$$\% \text{ conversion of CO} = \frac{C_{\text{CO}_2}^{\text{out}}}{C_{\text{CO}}^{\text{in}}} \times 100\%.$$

When 15 vol% CO₂ 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 CO₂ concentration.

The O₂ conversion was based on the oxygen consumption as follows:

$$\% \text{ conversion of O}_2 = \frac{C_{\text{O}_2}^{\text{in}} - C_{\text{O}_2}^{\text{out}}}{C_{\text{O}_2}^{\text{in}}} \times 100\%.$$

Finally, the selectivity of the CO oxidation in the presence of excess hydrogen was calculated from the oxygen mass balance as follows:

$$\% \text{ selectivity} = \frac{0.5(C_{\text{CO}}^{\text{in}} - C_{\text{CO}}^{\text{out}})}{C_{\text{O}_2}^{\text{in}} - C_{\text{O}_2}^{\text{out}}} \times 100\%.$$

3. Results and discussion

3.1. Effect of composition on the CO oxidation activity

The effect of Cu loading of the CuO–CeO₂ catalysts on their CO oxidation activity (expressed as the % conversion of CO), in the absence of CO₂ in the feed, is shown in figure 1. It can be seen that an increase of the Cu loading from 2.8 to 5.7 wt% provokes a marked increase of the activity. Indeed, the temperature at which 50% conversion of CO is obtained, T_{50} , is lowered from 131 to 96 °C for the catalysts containing 2.8 and 5.7 wt% Cu, respectively. In addition, with the 2.8 wt% Cu sample CO is not completely oxidized to CO₂ even at 340 °C, while an almost complete CO conversion is observed at ca. 200 °C over the 5.7 wt% Cu catalyst. Increasing further the Cu content from 5.7 to 8.7 wt% results in diminished activity as evidenced by the increase of the corresponding T_{50} temperatures from 96 to 112 °C. However, the 8.7 wt% Cu catalyst remains significantly more active than the 2.8 wt% Cu one, and both the 5.7 and 8.7 wt% Cu catalysts give almost complete CO conversion at ca. 200 °C.

The same trend of the activity variation with the composition is evidenced by the values of the reaction rate, which were determined at 75 °C and are reported in table 1. The highest rate was achieved with the 5.7 wt% Cu catalyst ($2.26 \times 10^{-6} \text{ mol s}^{-1} \text{ g}^{-1}$) followed by the 8.7 and the 2.8 wt% Cu samples.

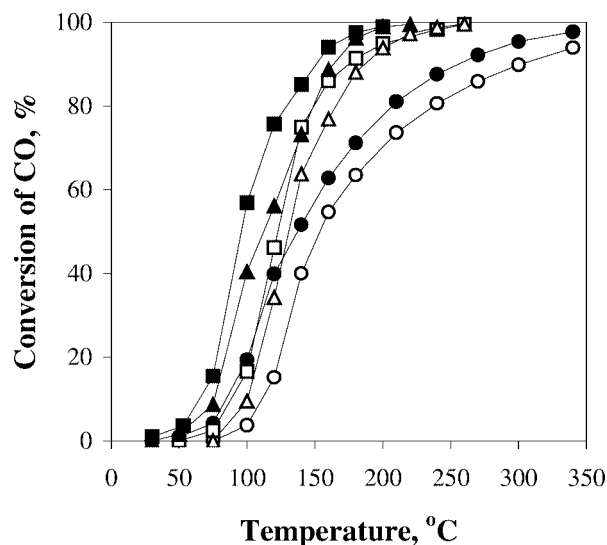


Figure 1. Variation of the CO conversion with the reaction temperature for the oxidation of CO (in the absence of H₂) over the CuO–CeO₂ catalysts with 2.8 (●, ○), 5.7 (■, □) and 8.7 (▲, △) wt % Cu. Solid and open symbols denote, respectively, the absence and the presence of CO₂ in the reactant feed.

3.2. Effect of CO₂ on the CO oxidation activity

The activity of the CuO–CeO₂ catalysts for CO oxidation in the presence of 15 vol% CO₂ in the feed is also shown in figure 1. There are two main observations:

- The presence of CO₂ in the reactant feed diminishes the activity of all samples. In fact, a given CO conversion, achieved in the absence of CO₂, can now be obtained at a temperature higher by about 20–40 °C.
- Regardless of the presence of CO₂, the same trend of the activity with the Cu loading of the catalysts is observed. Namely, the 5.7 wt% Cu catalyst gives the best results ($T_{50} = 123$ °C), followed by the 8.7 ($T_{50} = 131$ °C) and the 2.8 wt% Cu samples ($T_{50} = 154$ °C). The same trend of the activity variation with the composition is evidenced by the values of the reaction rate reported in table 1. As it was also the case when CO₂ was absent from the feed, the activities of the 5.7 and 8.7 wt% Cu samples tend to become the same for CO conversions higher than 90% and both these samples give almost complete CO conversion at ca. 250 °C. In the presence of CO₂, a complete CO conversion was not observed over the 2.8 wt% Cu sample even at the highest temperature employed in our experiments (375 °C).

3.3. Effect of composition on the CO selective oxidation activity

The % conversions of CO and O₂, as well as the selectivity achieved with the CuO–CeO₂ catalysts in the selective CO oxidation in the presence of excess hydrogen are presented in figure 2 for the reaction temperature range of 50–260 °C. It can be seen that the CuO–CeO₂ catalysts are

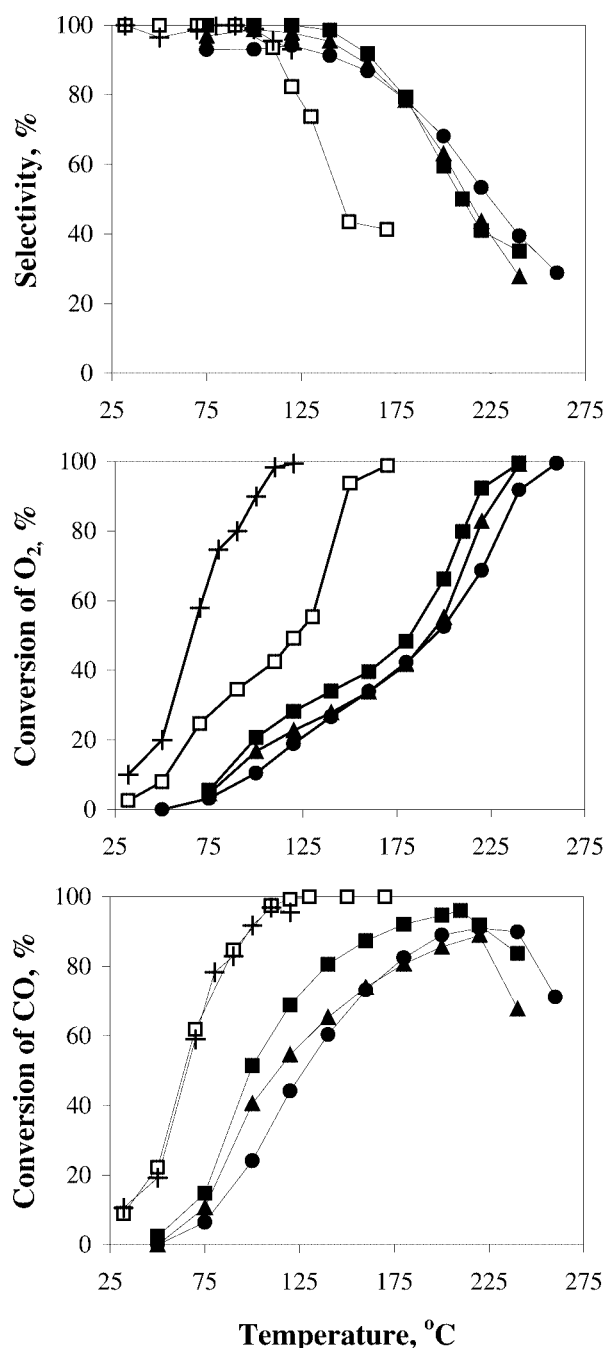


Figure 2. Variation of the CO and O₂ conversions and of the selectivity with the reaction temperature for the selective oxidation of CO, in the absence of CO₂, (with $\lambda = 2.5$ and $W/F = 0.030 \text{ g s cm}^{-3}$) over the CuO–CeO₂ catalysts with 2.8 (●), 5.7 (■) and 8.7 (▲) wt% Cu, and over the 5.7 wt% Cu sample with $W/F = 0.36 \text{ g s cm}^{-3}$ and $\lambda = 2.5$ (□) or $\lambda = 1$ (+).

very active and remarkably selective for this reaction. For example, at 140 °C the % conversion of CO achieved over the 5.7 wt% Cu sample was 80%, while the selectivity was higher than 98%. The selectivity diminishes for all catalysts for reaction temperatures higher than 150 °C. However, it still remains significant at high CO conversions. For example, at 210 °C the % conversion of CO achieved over the 5.7 wt% Cu sample was higher than 95%, while the selectivity was 50%.

The effect of Cu loading on the catalytic performance for the CO oxidation is more complex when the reaction is done in excess of hydrogen; namely, the influence of composition on the selectivity and the CO and O₂ conversions depends on the reaction temperature. For low reaction temperatures (<150 °C), where selectivity is higher than 90% for all samples, the 5.7 wt% Cu catalyst gives the best results (both in selectivity and CO conversion) followed by the 8.7 and then by the 2.8 wt% Cu samples. This trend is also evident from the corresponding reaction rates (table 1). As the reaction temperature increases beyond 150 °C, the 2.8 wt% Cu sample progressively outperforms the 8.7 and, at higher reaction temperature, also the 5.7 wt% Cu sample.

Under our standard experimental conditions ($W/F = 0.03 \text{ g s cm}^{-3}$, $\lambda = 2.5$, 1 vol% CO), the highest CO conversion (96%) was achieved at 210 °C over the 5.7 wt% Cu sample with selectivity equal to 50%. The highest selectivity (>95%) was obtained in the reaction temperature range of 75–140 °C over the same sample giving CO conversions in the range of 15–80%, respectively. An additional set of experiments was carried out with the 5.7 wt% Cu sample at higher W/F ratio (0.36 g s cm^{-3}) and with two λ values (2.5 and 1.0). These results, also presented in figure 2, show the remarkable catalytic performance of the 5.7 wt% Cu sample for the selective CO oxidation in excess hydrogen. Indeed, with stoichiometric concentration of oxygen ($\lambda = 1$) this sample gave a CO conversion higher than 96% with a selectivity of 95% at 110 °C.

3.4. Effect of CO₂ and H₂O on the activity for selective CO oxidation

The % conversions of CO and O₂, as well as the selectivity achieved with the CuO–CeO₂ catalysts in the selective CO oxidation in the presence of both excess hydrogen and 15 vol% CO₂ are presented in figure 3 for the reaction temperature range of 50–260 °C. A comparison of the data presented in this figure with those of figure 2, and of the selective CO oxidation reaction rates reported in table 1, shows that the presence of CO₂ in the reactant feed provokes a decrease in the activity of all samples. As it was the case in the oxidation of CO, a given CO conversion, achieved in the range 75–175 °C during selective CO oxidation in the absence of CO₂, can be obtained at a temperature higher by about 15–35 °C when CO₂ is present in the reactant feed.

Besides this moderate decrease of their activity, the CuO–CeO₂ catalysts retain their remarkable selectivity even when CO₂ is present in the feed. Indeed, as seen from figure 3, the 5.7 wt% Cu sample exhibits selectivity higher than 99% when the CO conversion is equal to 60% at 140 °C. For reaction temperatures higher than 150 °C the selectivity of all samples decreases progressively, however it still remains significant at very high CO conversions. For example, the 5.7 wt% Cu catalyst gives, at 200 °C, a CO conversion of 90% with selectivity equal to 67%.

The effect of Cu loading on the catalytic performance for the selective CO oxidation in the presence of CO₂ in the

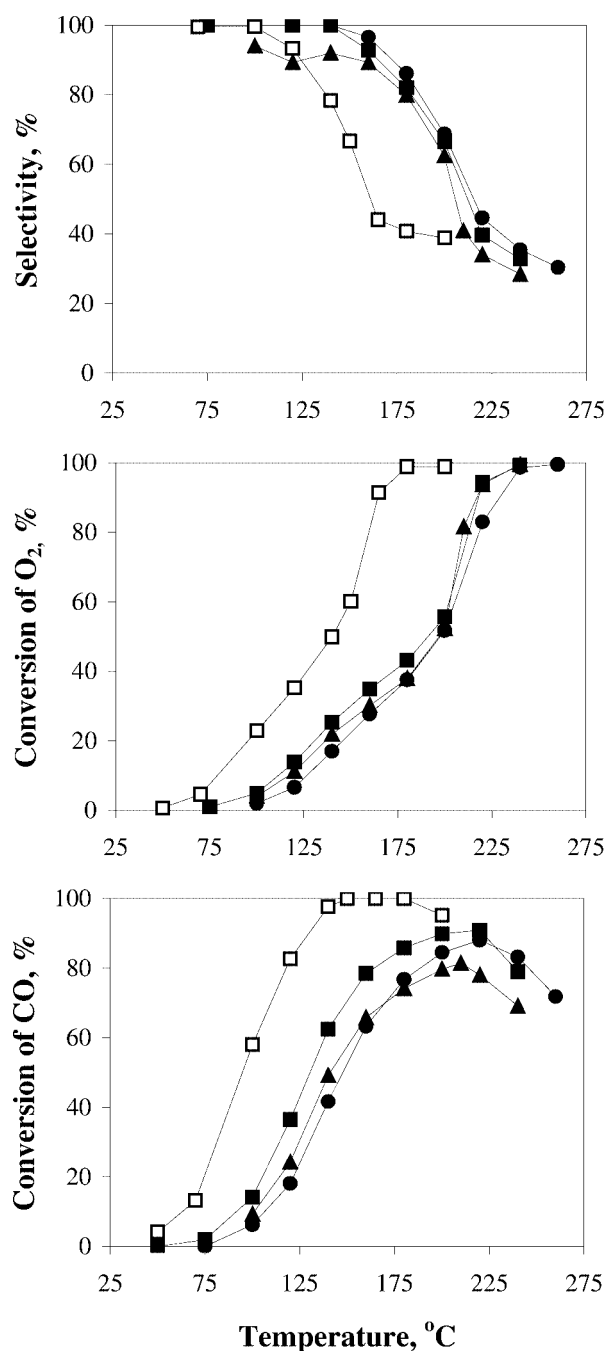


Figure 3. Variation of the CO and O₂ conversions and of the selectivity with the reaction temperature for the selective oxidation of CO, in the presence of CO₂ (with $\lambda = 2.5$ and $W/F = 0.030 \text{ g s cm}^{-3}$) over the CuO–CeO₂ catalysts with 2.8 (●), 5.7 (■) and 8.7 (▲) wt% Cu, and over the 5.7 wt% Cu sample with $W/F = 0.36 \text{ g s cm}^{-3}$ and $\lambda = 2.5$ (□).

feed is reaction temperature dependent as it was also the case during selective CO oxidation in the absence of CO₂. For low reaction temperatures ($<150^\circ\text{C}$), where selectivity is higher than 90% for all samples, the 5.7 wt% Cu catalyst gives the best results both in selectivity and CO conversion ($T_{50} = 130^\circ\text{C}$). In this temperature range the 8.7 wt% Cu sample is more active ($T_{50} = 141^\circ\text{C}$) but less selective than the 2.8 wt% Cu one ($T_{50} = 148^\circ\text{C}$). This activity trend is also evident from the corresponding selective CO oxidation

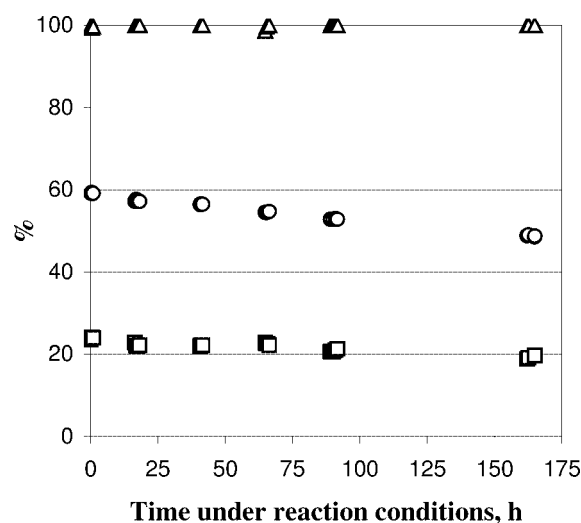


Figure 4. Variation of the CO (○) and O₂ (□) conversions and of the selectivity (Δ) with the reaction time during the selective oxidation of CO, in the presence of CO₂ (with $\lambda = 2.5$ and $W/F = 0.030 \text{ g s cm}^{-3}$ at 140°C) over the 5.7 wt% Cu sample.

in the presence of CO₂ reaction rates (table 1). As the reaction temperature increases beyond 150°C , the 2.8 wt% Cu sample becomes the most selective and progressively outperforms also in activity the 8.7 and, at higher reaction temperature, the 5.7 wt% Cu sample.

A long time catalytic run was performed with the 5.7 wt% Cu sample in order to explore the stability of the CuO–CeO₂ catalysts under reaction conditions. The variation of the CO and O₂ conversions and of the selectivity with the time this sample remained under reaction conditions at 140°C (in the presence of CO₂) are depicted in figure 4. After this seven-day period the sample had gradually lost ca. 18% of its initial activity, as evidenced by the decrease of the CO conversion from 60 to 49%. However, it retained its remarkable selectivity ($>99\%$) throughout this period.

Finally, the influence of the presence of 10 vol% H₂O in the CO₂-containing reaction feed was investigated for the best CuO–CeO₂ catalyst. As seen from the results presented in figure 5, the presence of water vapor decreases the activity of this sample; a given CO conversion is now obtained at a reaction temperature higher for ca. $20\text{--}40^\circ\text{C}$. However, besides this moderate decrease in activity, the catalytic performance of this sample remains exceptionally good. Indeed, in the absence of H₂O, it exhibited a CO conversion higher than 99% with a selectivity of 67% at 150°C . Under the same conditions, but with 10 vol% H₂O added in the feed, the same CO conversion is obtained at a reaction temperature higher by only 20°C with almost the same selectivity, namely at 170°C with selectivity equal to 63%.

3.5. Comparison with other CO selective oxidation catalysts

At this stage a first comparison between the catalytic performance of the CuO–CeO₂ catalysts with that of the best

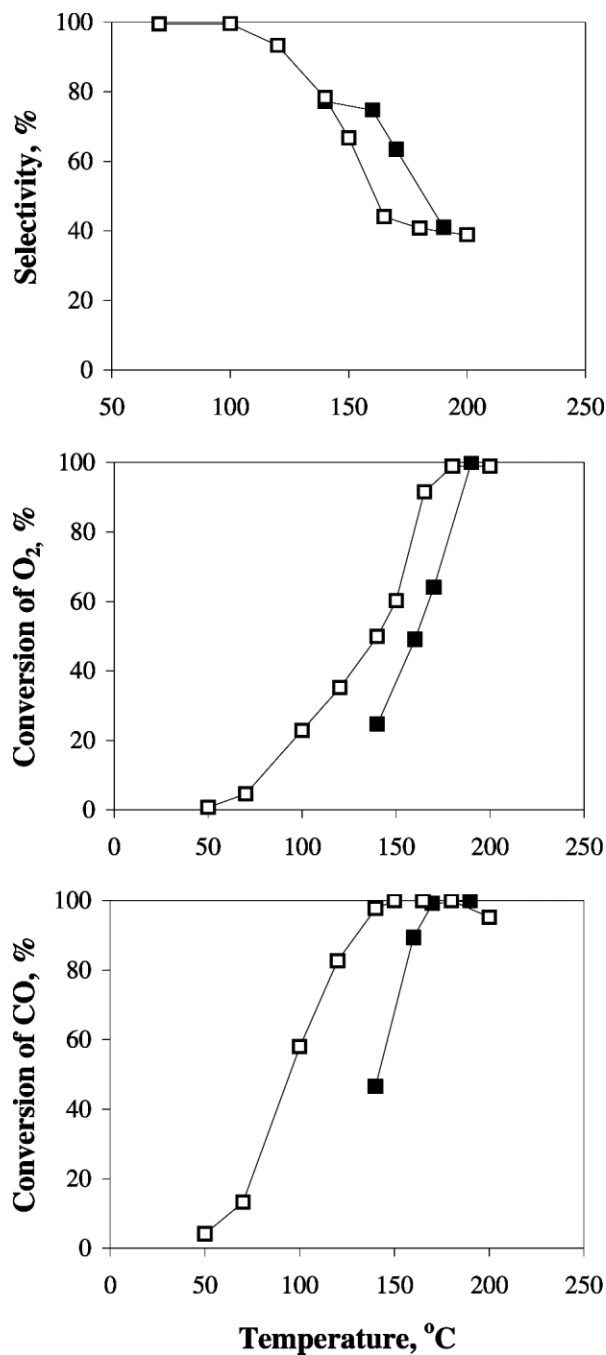


Figure 5. Variation of the CO and O₂ conversions and of the selectivity with the reaction temperature for the selective oxidation of CO (with 15 vol% CO₂, $\lambda = 2.5$, and $W/F = 0.36 \text{ g s cm}^{-3}$) over the 5.7 wt% Cu catalyst in the absence (□) and in the presence (■) of 10 vol% H₂O in the reaction feed.

CO selective oxidation catalysts reported so far in literature may be attempted.

Igarashi et al. [28] concluded that, for the oxidation of CO in the presence of excess hydrogen, Pt supported on mordenite was the more active and selective catalyst among the other Pt-based catalysts they investigated; namely, the state of the art Pt/Al₂O₃ catalyst, as well as the Pt supported on A- and X-type zeolite catalysts. According to these authors, the reaction temperature of 200 °C is the most suitable for

selective oxidation of CO over Pt/mordenite. At this temperature (with 1 vol% CO and 1 vol% O₂ in H₂, thus $\lambda = 2$, and $W/F = 0.06 \text{ g s cm}^{-3}$) both the maximum CO conversion and the maximum selectivity, respectively, equal to 63 and 57%, were achieved over this catalyst. As seen from figure 2, under similar experimental conditions (1 vol% CO, 1.25 vol% O₂ and 50 vol% H₂ in He, thus $\lambda = 2.5$, and $W/F = 0.03 \text{ g s cm}^{-3}$), the CuO–CeO₂ catalyst loaded with 5.7 wt% Cu gave a CO conversion of 80% with 99% selectivity at 140 °C, while at 200 °C the CO conversion and the selectivity achieved over the same CuO–CeO₂ sample were equal, respectively, to 95 and 60%. Moreover, Igarashi et al. also studied the activity of Pt/mordenite at 200 °C and $W/F = 0.12 \text{ g s cm}^{-3}$ with various values of λ . For $\lambda = 1$ the CO conversion and the selectivity were, respectively, 78 and 83% [28]. We tested under similar conditions ($\lambda = 1$ and $W/F = 0.09 \text{ g s cm}^{-3}$) the 5.7 wt% Cu catalyst and obtained a CO conversion and selectivity equal, respectively, to 84 and 94%, at a much lower reaction temperature, namely at 130 °C. Based on these facts we may conclude that, with respect to the Pt-based catalysts, the non-noble metal containing CuO–CeO₂ catalysts seem to exhibit superior activity and selectivity for the CO oxidation in the presence of excess hydrogen while operating at significantly lower reaction temperatures.

Besides platinum-based catalysts which operate close to the temperature level of the fuel processing unit, metal-oxide-supported gold catalysts, able to operate near the temperature level of the H₂-PEMFC (80–100 °C), have been reported to be promising candidates for the selective CO oxidation [29,30].

Torres Sanchez et al. [29] studied coprecipitated Au/MnO_x catalysts for this reaction in the temperature range 16–120 °C using a reactant stream composed of 1 vol% CO and 1 vol% O₂ in H₂ (thus with $\lambda = 2$) and $W/F = 0.364 \text{ g s cm}^{-3}$. The Au/MnO_x sample with Au/Mn atomic ratio equal to 1/50 exhibited maximum CO conversion (>95%) in the temperature range 50–80 °C. Under practically the same W/F (figure 2), but with stoichiometric concentration of oxygen ($\lambda = 1$), the 5.7 wt% Cu catalyst gave its maximum CO conversion (>95% with a selectivity of 95%) at a higher temperature, namely at 110 °C. The comparison between these two catalysts cannot be complete, however, since selectivity data, determined for the Au/MnO_x catalysts during CO oxidation in the presence of excess hydrogen, are not reported.

Kahlich et al. [30] reported kinetic measurements of the selective CO oxidation over a Au/ α -Fe₂O₃ with 3.15 wt% Au. The reaction rate determined for this sample at 80 °C, with $\lambda = 2$ (1 vol% CO, 1 vol% O₂ and 75 vol% H₂ in N₂) was ca. $9.1 \times 10^{-4} \text{ mol s}^{-1} \text{ g}_{\text{Au}}^{-1}$ with a selectivity equal to ca. 64%. Under similar conditions ($\lambda = 2.5$, 1 vol% CO, 1.25 vol% O₂ and 50 vol% H₂ in He) the 5.7 wt% Cu catalyst was less active (reaction rate, on a copper weight basis, determined at 75 °C equal to $4.0 \times 10^{-5} \text{ mol s}^{-1} \text{ g}_{\text{Cu}}^{-1}$), but highly more selective (with a selectivity of 100%). Thus, as compared to the low temperature operating gold catalysts,

the CuO–CeO₂ catalysts seem to be less active, but more selective.

Recently, Teng et al. [31] investigated 3d transition metal oxides as catalysts for the selective CO oxidation, and reported that, among the various oxides tested, those containing tetrahedrally coordinated Co(II) (such as CoO and CoFe₂O₄) gave very good results. The CoO oxide was found to be the best catalyst for this process; for a reaction feed gas composed of 1 vol% CO, 1.86 vol% O₂ ($\lambda = 3.72$) and 90.2 vol% H₂ in N₂ and space velocity equal to $1.2 \times 10^4 \text{ cm}^3 \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$ it gave a CO conversion of 99% at 100 °C with a selectivity of ca. 95%. The catalytic performance of the 5.7 wt% Cu catalyst is comparable to that of the CoO catalyst. Indeed, under similar space velocity (equal to $1.0 \times 10^4 \text{ cm}^3 \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$ when $W/F = 0.36 \text{ g s cm}^{-3}$) but with stoichiometric concentration of oxygen ($\lambda = 1$) the 5.7 wt% Cu sample gave, at 100 °C, a CO conversion of 93% with a selectivity >99%, while at 110 °C it gives practically the same activity and selectivity as the CoO sample does at 100 °C (figure 2).

A comparison of the performance of the CuO–CeO₂ catalysts with the other catalysts reported in literature for the selective CO oxidation cannot be made when CO₂ and H₂O are present in the reaction feed gas, since, to our knowledge, no relevant data have yet been published. Only Torres Sanchez et al. [29] stated that coprecipitated Au/MnO_x catalysts are resistive to various concentrations of CO₂, but neither experimental evidence nor data are provided to enable a quantitative comparison.

4. Conclusions

A series of mixed CuO–CeO₂ catalysts, with Cu loading in the range 2.8–8.7 wt%, were prepared by coprecipitation and studied in both the CO oxidation and the selective CO oxidation in excess hydrogen. Both reactions were carried out with and without CO₂ in the reactant feed. In addition, a long time catalytic run in the presence of CO₂, and a test in the presence of both CO₂ and H₂O in the feed were performed for the selective CO oxidation in excess hydrogen over the best CuO–CeO₂ catalyst. The following main conclusions may be drawn from this work:

- The coprecipitated CuO–CeO₂ catalysts are very active and remarkably selective for the CO oxidation in the presence of excess hydrogen.
- These catalysts exhibit good tolerance towards CO₂, retaining a significant portion of their activity and selectivity when CO₂ is present in the reactant feed. They also appeared to be quite stable under reaction conditions, especially in what concerns their selectivity.
- For the catalysts' composition range studied, best results were obtained with the CuO–CeO₂ specimen having an atomic ratio Cu/(Cu + Ce) = 0.143 (5.7 wt% Cu). Moreover, this sample exhibited good tolerance towards H₂O during the selective CO oxidation.

- The performance of the CuO–CeO₂ catalysts for the selective CO oxidation is superior to that of state of the art Pt-based catalysts; the CuO–CeO₂ catalysts are more active and selective while operating at significantly lower reaction temperature. As compared to Au-based catalysts, these non-precious metal containing catalysts are less active but significantly more selective. Thus, the mixed oxide CuO–CeO₂ system seems to be a promising candidate catalyst for the selective removal of CO from H₂-rich gas streams used as fuel for the H₂-PEM fuel cells.

Acknowledgement

The financial support of the General Secretariat for Research and Technology, Ministry for Development of Greece and of the Ministry of Science and Technology of the Republic of Slovenia in the frame of a joint research and technological program is gratefully acknowledged. JB and SH are also grateful to the Ministry of Science and Technology of the Republic of Slovenia for financial support through Grant J2-7500.

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