Supported CuO/Ce_{1-x}Zr_xO₂ Catalysts for the Preferential Oxidation of CO in H₂-Rich Gases¹

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Abstract—The catalytic properties of CuO supported on ceria or ceria-zirconia mixed oxides have been investigated in the preferential oxidation of CO in H₂-rich gases. CuO/CeO₂ shows very high activity towards the oxidation of CO with a light-off temperature of about 70°C. This catalyst is very selective for the oxidation of CO rather than of H₂ in the low temperature region (70–120°C), while at higher temperatures, the oxidation of hydrogen begins, causing of a maximum of CO conversion to arise with increasing temperature.

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Increasing the contact time in the catalytic tests does not have any effect on the selectivity of the process, yet it increases the conversion of CO. This result, together with catalytic tests of CO and H₂ oxidation fed one reactant at a time, allows us to assume that the very high selectivity of these catalysts is a unique function of temperature and probably stems from the different activation energy of the two competitive reactions. The presence of ZrO₂ in the support has been revealed as not beneficial for catalyst performances, while an optimal content of CuO supported on pure ceria at about 5 wt % has been found. Finally, good resistance to the presence of reformate species (carbon dioxide and water) in concentrations close to those of practical interest has been verified.

INTRODUCTION

The great energy demand required by industrial development brings about serious economical and environmental problems. On the one hand, these are strong driving forces to find novel processes of energy production able to exploit alternative raw materials. On the other hand, use of traditionally employed fossil fuels in energy-production processes should be rationalized in order to achieve a higher efficiency for such processes. For this purpose, hydrogen-fuelled fuel cells are becoming a reliable option to replace internal combustion engines in vehicle applications because of their higher potential efficiency in energy production and lack of environmental impact. Unfortunately, H₂ is not quite a raw material and must be produced from other H-sources. One attractive route could be the production of H₂ from water by means of renewable energy forms (such as solar or wind sources), but up to now these technologies appear quite far from large-scale application for both technical and economic reasons. The only way to sustain the great demand for energy needed by our industrialized society remains the conversion of fossil fuels into H_2 and the direct conversion of it into electricity via processes that would be globally more exothermic and efficient than traditional ones.

Processes of hydrogen production have been developed over a long time and have been consolidated in the chemical industry to produce valuable chemicals in stationary applications (primarily ammonia and methanol production) and we should turn to these for automotive applications. The autothermal reforming of light hydrocarbons, followed by processes of high-temperature and low-temperature water gas shift can be easily reconverted in car engines, but it produces a gaseous stream typically containing 40-70 vol % H₂, 15-20 vol % CO₂, 5-10 vol % H₂O, and 0.5-1 vol % CO (nitrogen as balance). Even this relatively low CO concentration represents a poison for polymer electrolyte membrane fuel cells (PEMFCs), which are the most promising fuel cells for vehicle applications due to their low operation temperature (80°C) and high resistance towards reformate species. The standard CO tolerance limit for PEMFCs is about 10 ppm, although new Pt-Ru anode catalysts have increased this limit up to 100 ppm [1]. For nonstationary applications, the simplest method to decrease CO concentration appears the preferential oxidation of carbon monoxide (CO-PROX). The process would be effective provided a proper catalyst is designed. Ideal features of the catalytic system needed for the CO-PROX process can be summarized as follows: high activity towards CO oxidation in the range fixed by the fuel processor (80–200°C), high selectivity towards the oxidation of CO rather than H₂ to limit fuel consumption, high resistance towards CO₂ and H₂O in the gas mixture, and inactivity towards the reverse

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water gas-shift reaction that could limit the maximum CO conversion.

The most investigated catalysts are those of the platinum group, with particular attention paid to Pt- and Au-based catalysts [2-7]. Platinum-based catalysts work in a high temperature range (150-200°C) and exhibit an optimal resistance to the presence of reformate species in the gas mixture and good selectivity towards CO oxidation (~40%) even at a low O₂/CO ratio [3], due to the properties of strongly adsorbing carbon monoxide at low temperatures. Gold-based catalysts applied in CO-PROX process are much more active and selective than the Pt ones showing very low operation temperatures (80°C) and an intrinsic selectivity towards CO oxidation rather than H_2 oxidation [8]. However, the activity of gold-based catalyst is significantly depressed by the presence of high concentration of CO_2 and H_2O in the gas mixture.

More recently, Avgouropoulos [9] tested the CuO/CeO_2 catalyst for the CO-PROX reaction, obtaining values of activity and selectivity higher than on Ptbased catalysts and comparable to gold catalysts. The catalytic activity of such materials appears potentially less sensitive to the presence of CO_2 and H_2O than a gold-based catalyst but more than a Pt-based catalyst [10]. However, the significantly lower cost of copper makes this system very interesting and promising for possible application.

Unfortunately, CuO/CeO₂, analogously to noble metal-based catalysts, is very selective towards the oxidation of CO only up to a certain temperature, above which H_2 oxidation become more relevant and the conversion of CO paradoxically decreases. A maximum in CO conversion with temperature hence arises, whose value can be only increased by a more active catalyst if the contact time is taken around values significant for practical application. The reasons for the presence of such a maximum is still debated [9].

To improve the activity of this promising catalyst in the presence of reformate species, an attempt has been made to change the preparation method using coprecipitation [9, 11], urea-nitrate combustion [12], and sol-gel [10]. Even if the literature results often refer to different operating conditions, it seem possible to conclude that the best results are obtained with those preparation methods that allow increasing dispersion of copper oxide on the support [11].

The increased activity of copper-based catalysts when deposited on CeO_2 certainly correlates to the interaction between the active phase and support. Such a catalytic system has been quite largely studied, primarily due to the interest in its potential use in the threeway catalyst [13]. However, there is a quite evident lack of knowledge about the properties that make it seem like a very promising catalyst for the preferential oxidation of CO.

For the CO-PROX reaction, a Mars–Van Krevelen redox mechanism [14] has been proposed. Thus, the

activity of this catalyst certainly correlates to the high oxygen storage capacity of cerium oxide, that is, proportional to the concentration of defects in the oxide structure. Defect concentrations can be increased by doping ceria with other metals or compounds. In particular using zirconium oxide as promoter, it is possible to increase not only the thermal stability, but also redox and oxygen supplier properties of ceria [15]. Moreover, the state of copper when supported on ceria has been quite well investigated [16–17], but the kind of species active and selective for CO PROX remains doubtful; as well, the reasons for its high selectivity are still not completely understood.

Ratnasamy et al. [18] studied the catalytic activity of CuO samples supported over high-surface area CeO₂, CeO₂–ZrO₂, and ZrO₂ samples synthesized by coprecipitation and evidenced a significant effect of the support. However, the CO oxidation activity/selectivity increases in the order CuO–ZrO₂ < CuO–CeO₂-ZrO₂ < CuO–CeO₂; i.e. doping the support with zirconia has no beneficial effects on PROX performance. Moreover, they exhibit an optimal CuO content existing at around 5 wt %.

In this work we propose screening different catalytic systems constituted by copper oxide supported on commercial mixed Ce-Zr oxides with different contents of copper and zirconium. One aim of the study is to establish the optimal catalyst composition with a comparison of the activity in the CO PROX reaction under experimental conditions as closest as possible to those of the practical application and an attempt to correlate such experimental results to the effect of the different active species that are generated with different catalyst compositions. Another important goal of this study is to elucidate the basic reasons for the high selectivity of such catalysts by means of catalytic and TPR tests. The effect of the presence of water vapor and CO₂ under large amounts of hydrogen has been characterized, while comparison of CO PROX tests with conventional CO and H₂ oxidation tests carried out separately, along with a study of the reducibility of active sites with either CO or H_2 , has allowed to explain the different reaction kinetics between the desired CO oxidation and the undesired oxidation of H_2 .

EXPERIMENTAL

Supported Cu-based catalysts were prepared by wet impregnation using copper acetate as a precursor. Commercial CeO₂ and CeO₂/ZrO₂ (with two different ceria/zirconia ratios (CZ): 85/15 and 60/40 w/w) powders from GRACE were used as supports. The support was suspended in an aqueous solution of copper salt and mixed in vacuum in a rotating evaporator at 100 rpm, 80 mbar, and 50°C. Subsequently, the samples were dried overnight at 110°C and calcined for 2 h at 450°C. The amount of CuO loaded on CeO₂ was varied (2 to 8 wt %), while the effect of the support was studied on samples at identical CuO contents (5 wt %).

Table 1. Code, content of CuO and ZrO₂, crystalline mean size, and BET surface area for all catalysts and supports investigated

Catalyst code	wt %		Mean	$\mathbf{PET} \ \mathbf{m}^2/\mathbf{q}$
	CuO	ZrO ₂	size, nm	DE1, III /g
CeO ₂	0	0	11.2	56
CZ (85/15)	0	15	6.43	_
CZ (60/40)	0	40	5.4	85
2 CuO/CeO ₂	2	0	12.09	55
5 CuO/CeO ₂	5.4	0	11.6	50
8 CuO/CeO ₂	7.8	0	12.5	48
5 CuO/CZ (85/15)	4.8	15	6.8	-
5 CuO/CZ (60/40)	4.7	40	5.6	79

The catalysts were characterized by means of a Carlo Erba Sorptomatic 5 (BET analysis) and a Philips PW 1710 diffractometer (XRD analysis).

The activity tests were performed in a lab-scale apparatus where a mixture containing 0.5-1 vol % of CO, at $\lambda = 2P_{O_2}/P_{CO} = 2$, together with 50 vol % H₂, 0–15 vol % CO $_2$ and 0–1.4 vol % H $_2O$ (N $_2$ as balance), was fed to the catalytic reactor. The apparatus was equipped with five Brooks 5850 mass flow controllers for all components except water, which was instead fed by saturating the reactive mixture in a thermostatic bath at room temperature. A hydrogen CLAIND generator was used to feed H_2 by distilled water electrolysis. Heated lines were used from the saturator to the reactor, which was placed in an electrical oven. The reactor for catalytic activity measurements consisted of a fixed bed of 250 mg of catalyst, to which a flow rate of 30 l/h was fed. The gas mixture was continuously analyzed by two different ND-IR detectors for the measurements of CO and CO₂ concentrations, by a TCD for H₂, and a paramagnetic detector for O2 (EMERSON NGA2000 online analyzer), after water removal by a chemical trap $(CaCl_2)$.

The following conditions were used in TPR analysis. Heating rate: 10 K/min; Catalyst load: 300 mg; Flow rate: 14 l/h; Feed gas: 1 vol % CO or 2 vol % H₂ and balance N₂.

RESULTS AND DISCUSSION

The physical properties of all the samples prepared were investigated by BET and XRD analyses. From BET data, it resulted that the samples supported on ceria-zirconia exhibit higher values of surface area, while XRD spectra showed that copper oxide homogeneously deposed on all the investigated supports and was well dispersed in the porous structure, not evidencing the characteristic signals of CuO_x phases up to the highest copper concentration (8 wt % CuO).

Table 1 lists the results of the analyses of copper content, XRD, and surface area on all the samples prepared (labeled with specific codes that will be used in what follows). The copper content was evaluated by spectrophotometric analysis.

In agreement with the results of Fernandez-Garzia et al. [16] and Trovarelli et al. [15], the average crystalline size estimated by XRD spectra tends to diminish when ceria is mixed with zirconia, since they form a solid solution with higher defect concentrations. The CeO₂ and 5 CuO/CeO₂ samples exhibit a mean size of crystallines of about 11 nm; CZ (60/40) and 5 CuO/CZ (60/40), of about 5 nm. The distortion of the fluorite-type structure of ceria induced by the introduction of Zr⁴⁺ results in a cell contraction since the ionic radius of Zr⁴⁺ (84 pm) is lower than that of Ce⁴⁺ (97 pm). Moreover, the presence of CuO dispersed in the support does not significantly alter the crystalline average size; the small difference listed in Table 1 is attributable to experimental noise.

In the X-rays of 8 CuO/CeO₂, the signal of bulk CuO was clear, suggesting that the segregation of a fraction of copper occurs, which can be explained taking into account that the theoretical monolayer coverage corresponds to about 5 wt %.

Hocevar et al. [19], coupling XRD and XPS analyses, showed a reduction of the unit cell parameter with increasing Cu content in Cu/ceria catalysts prepared by coprecipitation and a corresponding increase in the concentration of both Ce³⁺ and Cu⁺ species. This result was interpreted with the formation of a CuO–CeO₂ solid solution, which should be possible only between Cu⁺ and Ce⁴⁺ ions, which exhibit similar values of ionic radius and consequent reduction of Ce⁴⁺ ions to Ce³⁺ to compensate the charge defect.

Nevertheless, phase identification for Cu/ceria catalysts prepared by coprecipitation is still debated. Actually, the hypothesis by Hocevar et al. [19] of a solid solution is contrasted with an alternative one, according to which a mixed phase Cu/Ce with a perovskite-type structure is formed [16, 17].

Results of our analyses allow no appreciation of significant variations in the unit cell parameter. The absence of such a phenomenon, if not attributable to the insufficient sensitivity of the apparatus, could be attributed to the fact that in our samples prepared by impregnation, the amount of the eventual mixed phases or solid solutions should not be relevant.

Figure 1 reports the results of activity tests carried out over a 5 CuO/CeO₂ catalyst sample for the preferential oxidation of CO in a mixture containing 0.5 vol % CO, 0.5 vol % O₂, 50 vol % H₂ in N₂. The catalyst exhibits high oxidation capacity at a temperature as low as 70°C (Fig. 1a) and high selectivity towards CO oxidation (Fig. 1d). One-hundred-percent CO selectivity is visible until 100°C, in accordance with conversion of CO of 40% (Fig. 1a); this highest value of selectivity was detected by measuring stoichiometric O₂ consumption



Fig. 1. (a) CO conversion and O₂ selectivity to CO as functions of temperature on 5 wt % CuO/CeO₂. (b) O₂ and H₂ conversion as functions of temperature on 5 wt % CuO/CeO₂. Test conditions: [CO] = 0.5 vol %; $\lambda = 2$; [H₂] = 50 vol % and W/F = 0.03 (g s)/cm³.

for the conversion of carbon monoxide alone. At higher temperatures, the oxidation of hydrogen also begins, yielding a higher O_2 conversion; the CO conversion increases with increased temperature, but only up to 150°C, where a maximum is observed. Indeed, at higher temperature, carbon monoxide conversion starts to decrease (whereas the consumption of O_2 is quite complete).

The presence of a maximum for CO conversion with temperature is frequently observed in the CO PROX tests [9]; its origin could be due either to the thermodynamic limit imposed on CO conversion by the reverse water gas shift reaction or to a different dependence on temperature of the kinetics of the two reactions of hydrogen and CO oxidation (different activation energies).

However, the evidence that O_2 is completely consumed when the conversion of CO is maximum suggests that the oxidation of hydrogen, whose kinetics is negligible at the lowest temperatures investigated, becomes faster and not negligible at the highest ones. Moreover, some experimental tests were performed in order to verify the capability of CuO/CeO₂ to catalyze the reaction of reverse water gas shift (WGS) reaction.

In order to understand whether the reverse WGS reaction is catalyzed by the catalyst in the temperature range of interest (50–170°C), experiments were performed feeding only hydrogen (50 vol %) and CO₂ to the reactor and measuring the amounts of CO eventually produced. Figure 2 shows the results of two different series of such tests. On the one hand, the activity of catalyst has been tested under conditions as close as possible to those of PROX experiments: 1 vol % CO₂ and 50 vol % H₂ (diluted by nitrogen). On the other hand, the eventual production of CO has been verified, also under more favorable conditions for the reverse WGS reaction, with a larger concentration of CO₂ employed (20%).

In Fig. 2 the limit values of CO concentration expected by thermodynamics have been plotted. Results of such experiments show that the time scale of

the reverse water gas shift is probably much larger than that of the oxidation of CO, since under the same contact time involved in the CO PROX tests, the conversion of CO₂ to CO is negligible, although the thermodynamic limit is not very strict under the operating conditions of interest. Actually, the conversion of CO₂ becomes measurable only at temperatures higher than 200°C, i.e., outside the range of interest for the process of CO removal in H₂ streams to fuel cells. This means in principle that the catalyst is not prevented to promote the complete oxidation of CO to CO₂, up to reduce its concentration to few ppm and that the volcano-shaped curve of CO conversion as function of temperature must be explained by other phenomena than the proceeding of the reverse WGS reaction.

In order to investigate this phenomenon, we have also carried out parallel tests of CO and H_2 oxidation on the same catalyst and in the same experimental conditions of CO PROX tests, but by feeding one reactant at



Fig. 2. CO outlet concentration as a function of temperature on 5 wt % CuO/CeO₂ in the reverse WGS reaction. Tests conditions: $[CO_2] = 1$ vol % (1) or 20 vol % (2) $[H_2] =$ 50 vol %; balance N₂. *W/F* = 0.03 (g s)/cm³. Equilibrium conditions represented by the dashed line for $[CO_2] = 1$ vol % (3) and continuous line for $[CO_2] = 20$ vol % (4).



Fig. 3. (a) CO conversion as functions of temperature on 5 wt % CuO/CeO₂ for the CO oxidation (\circ) and CO-PROX (\bullet) reactions. (b) H₂ conversion as functions of temperature on 5 wt % CuO/CeO₂ for H₂ oxidation (\bullet) and CO-PROX (\bullet) reactions. (c) Oxygen conversion as a function of temperature in the CO oxidation (\circ), H₂ oxidation (\bullet), and CO-PROX (\bullet) reactions. Tests conditions: CO oxidation CO/O₂/N₂ = 0.5/0.5/99 (vol %); H₂ oxidation H₂/O₂/N₂ = 50/0.5/49.5 (vol %); CO-PROX CO/H₂/O₂/N₂ = 0.5/50/0.5/49 (vol %). *W/F* = 0.03 (g s)/cm³.

a time. Two different gas mixtures were used as the reactor feed: one containing 0.5 vol % CO and 0.5 vol % O₂ and the other containing 50 vol % H₂, 0.5 vol % O₂ in N_2 . Figure 3 shows that the light-off temperature for the oxidation of CO is significantly lower than for the oxidation of H₂: the difference can be quantified in about 40°C, thus showing that the CuO/CeO₂ catalyst exhibits an intrinsically higher capability in converting CO (light-off temperature at $<70^{\circ}$ C, Fig. 3a) rather than H₂ (light-off at about 100°C, Fig. 3b), even if the concentration of CO is significantly lower than that of H₂. Moreover, it seems that the activation energy for the oxidation of CO is lowered by the catalyst to values much lower than for the oxidation of hydrogen and, consequently, with increasing temperature, the difference between the two reaction rates tends to diminish, since the derivative of H_2 oxidation rate is higher (being proportional to the activation energy) up to make the two reactants competing each other for the reaction with oxygen. In this way, the conversion of CO reaches a maximum, because it is limited by the consumption of O_2 due to H_2 oxidation.

Moreover, by comparing the conversion plots of both CO and H_2 in the two cases of simple feeding of one reactant at time or in the CO-PROX tests (namely, when both reactant are fed to the reactor), it is evident that the oxidation of the two compounds are very weakly influenced by the simultaneous presence of both. In particular, the conversion of hydrogen appears quite unaffected by the presence of CO, even though carbon monoxide reacts with oxygen in a faster way and reduces O_2 concentration in the reactor. The conversion of CO is instead weakly lowered by the presence of H_2 , but a difference of about 30°C in the lightoff temperatures between the two reactions is still evident.

Finally, when CO and H_2 are both present in the reaction mixture, it is possible to confirm that the oxi-

dation of CO starts at lower temperatures and exhibits a 100% selectivity until the hydrogen oxidation reaction starts (in the range from 70 to 100°C). On the other hand, when the hydrogen oxidation starts, it subtracts oxygen from the reaction environment, thus limiting the CO conversion, which can decrease even with increasing temperature.

If all this is true, the selectivity of the process should basically depend on the reaction temperature and very poorly or not at all on the CO/H_2 ratio in the reaction mixture, unless a very large difference exists between the kinetic laws of the two competitive reactions. For example, in the case of Pt catalyst for CO PROX such a consideration does not apply, since the selectivity towards the preferential oxidation of CO rather than of H_2 lies in the strong adsorption of carbon monoxide on the catalyst which in the range of optimal temperatures of the process largely cover the catalyst surface and prevents hydrogen to reach the active centers [3, 6]. Thus, selectivity is strongly dependent on the CO/H₂ ratio and decreases when the concentration of CO becomes too low. In order to test such behavior, we carried out CO-PROX tests at constant temperature and variable contact times.

In such experiments, it is possible to measure the selectivity of the process while changing the CO/H_2 ratio without varying the temperature.

The results reported in Fig. 4 show that at low temperature (82°C), where selectivity is still 100% (namely, H₂ is not converted at all), the conversion of CO increases with increasing contact time, leaving the selectivity of the process at a constant level (namely, H₂ remains unconverted also when the H₂/CO ratio becomes much larger). Moreover, a similar behavior is also observed at 122°C, where selectivity is lower (about 80%) and conversion much higher (close to 100%): in such conditions, selectivity still remains constant with increasing contact time, while the conversion of CO increases.

For this purpose, we have reported the amount of unconverted carbon monoxide, since the conversion is too high and variations are not very easily appreciable.

In these latter experimental conditions (relatively high temperature and very high CO conversion) similar results were obtained by Ratnasamy et al. [18], who confirmed that the selectivity is constant with changing contact time.

Anyway, the main requirement for the CO-PROX step in the fuel processor is to decrease the CO concentration in the gas mixture to the PEMFC tolerance limit (~10 ppm) sacrificing as little fuel as possible (H₂). The main goals of the copper–ceria catalyst in the CO-PROX reaction compared to gold- and platinum-based ones are the highest oxygen selectivity, also at high CO conversion, and the possibility of achieving a deep abatement level by only increasing the contact time, since the selectivity only depends on temperature.

The catalytic activity of copper-ceria systems has been investigated by changing the support: the same amount of CuO (5 wt %) has been impregnated on two different CeO_2 -ZrO₂ supports (ceria/zirconia = 85/15; 60/40 wt %). The comparison among the activity of the different samples is reported in Table 2 in terms of light-off temperatures (T_0) and of 50% CO conversion (T_{50}) . It is evident that the catalyst supported on ceria exhibits better catalytic performance than those supported on ceria-zirconia, in agreement with Ratnasamy [18], who compared the activity of two CuO supported catalysts, one on pure ceria, the one on 50/50 wt % ceria-zirconia. In particular, the higher the zirconium content in the support the higher the T_{50} . Actually, these differences cannot be explained by the higher surface area of the sample supported on pure ceria. On the contrary, as reported in Table 1 and already discussed above, the mixed ceria-zirconia oxides, being characterized by lower values of the crystalline mean size and a more defective structure, typically show higher values of surface area than pure ceria. Moreover, Table 2 also reports the value of the selectivity towards the oxidation of CO into CO₂ in the CO-PROX tests, as measured at 50% CO conversion. Results show that at equal CO conversion, the selectivity decreases with increasing Zr content as well, thus suggesting that the use of zirconium as a promoter of the OSC properties of the support does not have a favorable effect in this process.

Opportune tests of CO and H_2 oxidation as reported in Fig. 3 have been also performed for catalyst samples supported on mixed ceria–zirconia (not reported here). They demonstrated that the increased surface area (as well as the increased reducibility of the active phase) does not significantly enhance the activity towards CO, while producing an increment in the H_2 oxidation rate, consequently lowering the overall process selectivity.

In addition, the search for an optimal catalyst composition for the CO-PROX reaction must necessarily



Fig. 4. CO conversion (1) at 82°C, unconverted CO (2) and O₂ selectivity to CO₂ (3) at 122°C as functions of contact time. Catalyst: 5 CuO/CeO₂; Tests conditions: [CO] = 0.5 vol %; $\lambda = 2$; [H₂] = 50 vol % in N₂.

involve study of the effect of copper concentration, since CuO is the active component of the system. By comparison of the activity of three different copperbased catalysts characterized by different amounts of CuO (2, 5, 8 wt %), the effect of copper concentration on CO-PROX activity has been investigated on ceria supported samples. Results of the activity tests are reported in Fig. 5.

Among the catalysts tested, 5 CuO/CeO_2 exhibits the best performance for the CO-PROX reaction in terms of activity and selectivity towards the CO oxidation. As the copper concentration is increased from 2 to 5 wt %, the activity and the selectivity increase, while another increase in copper concentration from 5 to 8 wt % lowers both the activity and the selectivity of the catalyst.

It is known that only the copper species well-dispersed on the support are active towards CO oxidation in CuO/CeO₂ catalysts, while bulk CuO cannot adsorb CO and contributes only a little to the activity [20]. For a copper concentration lower than 5 wt % in catalysts supported on CeO₂ and prepared by wet impregnation, no visible CuO crystal phases could be observed [20]. From our XRD analysis, the characteristic signal of CuO is evidenced only in 8 wt % CuO/CeO₂ catalyst,

Table 2. Light-off temperature (T_0), T_{50} , and CO selectivity for 5 wt % CuO/CZ (100/0; 85/15; 60/40) catalysts. Feed composition: CO/O₂/H₂/N₂ = 1/1/50/48 (vol %); *W/F* = 0.03 (g s)/cm³

CATALYST CODE	T_0 , °C	<i>T</i> ₅₀ , °C	$S_{50}^{ m CO}$, %
5 CuO/CeO ₂	50	109	100
5 CuO/CZ (85/15)	50	116	100
5 CuO/CZ (60/40)	60	165	70
2 CuO/CeO ₂	60	146	100
8 CuO/CeO ₂	50	110	100



Fig. 5. Activity test on 2 wt % CuO/CeO₂ (1); 5 wt % CuO/CeO₂ (2); 8 wt % CuO/CeO₂ (3). (a) CO conversion versus temperature, (b) O₂ conversion versus temperature; (c) O₂ selectivity to CO₂ versus CO conversion. Reaction condition: [CO] = 1 vol %; $\lambda = 2$; [H₂] = 50 vol % at *W/F* = 0.03 (g s)/cm³.



Fig. 6. (a) CO conversion as a function of the temperature and (b) oxygen selectivity as a function of the CO conversion for 5 wt %CuO/CeO₂ catalysts. Feed composition: (*I*) CO/O₂/H₂/N₂ = 0.5/0.5/50/49 vol %; (2) CO/O₂/CO₂/H₂/N₂ = 0.5/0.5/15/50/34 vol %; (3) CO/O₂/H₂O/H₂/N₂ = 0.5/0.5/1.4/50/47.6 vol %; (4) CO/O₂/CO₂/H₂O/H₂/N₂ = 0.5/0.5/15/1.4/50/33.6 vol %. *W/F* = 0.03 (g s)/cm³.

meaning that in all other cases the copper species should be well integrated in the support structure. Thus, an increase in catalytic activity in CO-PROX reaction when copper concentration increases from 2 to 5 wt % could correlate to the increased number of CuO particles dispersed in the support, while a further increase in copper content (from 5 to 8 wt %) could induce the formation of inactive copper species that, on the contrary, could decrease the selectivity of CO oxidation in favor of the conversion of H₂. Moreover, we have also seen that the active phase is more dispersed and reducible when supported on CeO₂ than on CeO₂–ZrO₂ supports, thus explaining the superior activity/selectivity of the CuO/CeO₂ sample.

In addition, as we pointed out in the introduction section, since the actual effectiveness of a catalytic system is closer to CO-PROX reaction conditions, activity tests must be carried out in the presence of CO_2 and

H₂O. Results of such tests are reported in Fig. 6, where it shows the effect of the presence of 15 vol % CO₂ and/or 1.4 vol % H₂O in the standard feed containing CO (0.5 vol %), O₂ (0.5 vol %) and H₂ (50 vol %) (N₂ is used as diluting compound). In the presence of CO₂, the catalyst activity is depressed, as can be seen by the CO conversion curves shifting to a higher temperature than in the absence of carbon dioxide. The selectivity of O₂ to CO appears changed by the presence of CO₂, even apparently increasing, as shown by comparison of the values at equal temperatures.

However, if a more correct comparison in terms of O_2 to CO at equal CO conversion is carried out (Fig. 6b), the presence of carbon dioxide proves not very relevant in changing the intrinsic selectivity of the process, meaning that both reactions, the oxidations of CO and H₂, are depressed by the presence of CO₂, and in a similar way.



Fig. 7. TPR of CO (1) and H₂ (2). The plot represents the consumption of the reductant as a function of time (in the isothermal part at 30°C and at 400°C), or as a function of temperature (when the sample is heated).

Likewise, the addition of 1.4 vol % of H₂O $(CO/O_2/H_2/H_2O/N_2 = 0.5/0.5/50/1.4/47.6)$ also produces a decrease in catalyst activity, but without relevant variations in the dependence of O₂ to CO selectivity on CO conversion and finally, by the simultaneous addition of CO₂ and H₂O (CO/O₂/H₂/H₂O/CO₂/N₂ = 0.5/0.5/50/1.4/15/33.6), the catalyst activity is still more depressed, being the two effects addictive. Both effects can be explained in similar way by assuming that CO_2 and H_2O are adsorbed on the same active site of the reaction. The competitive adsorption between reactants and these two additional compounds also exists when they are not present in the feed, as they are always formed as reactions products. Carbon dioxide, as has been demonstrated in individual TPD tests (not reported here), can be still very strongly adsorbed at temperatures relatively higher than 200°C, while water is known to strongly interact with copper.

To investigate the selectivity shown by copperbased catalysts towards CO oxidation rather than H_2 , TPR analysis has been performed using H_2 or CO as a reducing agent (Fig. 7).

TPR of CO exhibits four reduction peaks, the first of which at ambient temperature, prior to imposing the heating ramp of the sample. The total amount of CO consumed in the experiment is in a CO/Cu ratio of about 2, suggesting that not only copper but also ceria is reduced in the range of temperatures investigated, as generally proposed for the strong metal-support interaction between reducible transition metals and the supporting ceria [13, 21]. On the other hand, the hydrogen TPR shows three peaks in the range 120–200°C, the first two at the same temperature and in the same amount with respect to the TPR of CO. The total amount of H₂ consumed in the experiment is in a ratio H₂/Cu of about 1.5, meaning that ceria is reduced in H₂ TPR as well.

However, according to the literature [13, 21, 22], ceria shows two reduction peaks, the first at a temperature of about 500°C and corresponding to the reduction of surface ceria, and the second at about 800°C and related to the reduction of bulk ceria. Both peaks appear hence in a range of temperatures not investigated in the present tests, but it is also known that doping the ceria structure with transition metal oxides enhances the reducibility of surface cerium. Such a "strong metalsupport interaction" is responsible for the higher consumption of CO and H₂ in the corresponding TPR with respect to the expected ideal value if only copper is involved in the reduction process. Moreover, TPR tests also confirm an intrinsic higher tendency of this catalyst to be reduced by CO rather than by H₂. Not only is the overall CO consumption higher, but also the temperatures at which reduction with carbon monoxide occurs, are lower. Even at ambient temperature, the catalyst is reduced by CO, as already demonstrated by Martinez-Arias et al. [17]. Probably, the exact 0.5 ratio measured for CO consumed per Cu atom in the ambient temperature peak would suggest that all of the copper is present in the Cu⁺ state in the catalyst, also under reaction conditions, notwithstanding the presence of a small amount of oxygen.

CONCLUSIONS

CuO/CeO₂ catalysts shows very high activity towards the oxidation of CO in a hydrogen-rich environment in a range of relatively low temperatures (70–170°C). The oxidation of CO rather than of H₂ is strongly favored in the low temperature region (70–120°C), while at higher temperatures, the oxidation of hydrogen starts to take place and assumes a more relevant role, decreasing the overall selectivity of the process and causing a maximum of CO conversion plot with increasing temperature.

The very high selectivity of these catalysts, which is specific feature of such systems in comparison with noble metals, is consequently a unique function of temperature, probably due to the different activation energy of the two competitive reactions, and does not depend on the CO conversion and hence on the CO/H₂ ratio in the reacting mixture. Actually, if the contact time is increased, it is potentially possible to achieve a complete abatement of CO without a decrease in the selectivity. The presence of ZrO_2 in the support is not beneficial for catalyst performance, while an optimal content of CuO supported on pure ceria at about 5 wt % has been found.

Finally, good resistance to the presence of reformate species (carbon dioxide and water) in concentrations close to those of practical interest has been verified.

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