

INHIBITING EFFECT OF CO₂ ON THE CO-PROX ACTIVITY OF CuO/CeO₂ CATALYSTS

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Abstract.

The inhibiting effect of CO₂ on the performance of CuO/CeO₂ catalysts towards CO-PROX reaction has been investigated. CO₂ reduces catalytic activity up to 160°C, its effect being negligible at higher temperatures. The CO₂ coverage of both ceria support and active phase was determined by CO₂ TPD tests and the distribution of adsorbing sites was modeled. Two sites for CeO₂ (one modified by the copper addition and assigned to strong interacting Ce-Cu sites) and an additional site associated to less interacting copper for CuO/CeO₂ catalysts were identified by the model. The sites present in larger amount rapidly desorb CO₂ at temperatures below 160°C, especially after copper addition, suggesting that these centres are the active sites for CO oxidation.

Introduction

The polymeric membrane fuel cell (PEMFC) represents an attractive technological solution for the generation of power at small scale due to the compactness, modularity, efficiency and environmental impact.

The hydrogen stream feeding the fuel cell can still contain carbon monoxide with concentration up to 1 vol.%, causing the poisoning of the Pt anode catalyst. The CO concentration should be reduced to 10 – 50 ppm. A promising solution is based on the catalytic preferential oxidation of CO (CO-PROX) [1–4].

Copper/ceria based catalysts have been proposed as alternative systems to noble metals for CO-PROX reaction since they show performances even higher than those reported for the more expensive noble metals [5–6].

The inhibiting role of both H₂O and CO₂ over CuO–CeO₂ catalysts have been shown [5–8] and cannot be related to the activation of WGS and/or r-WGS. As a consequence, chemical/physical interactions of CO₂ and H₂O with the catalyst are responsible for their inhibiting effect.

Park et al. [9] reported a comparison between catalytic activity and CO₂ and H₂O TPD results. They suggested that CO₂ and H₂O compete with CO for the adsorption on the same active sites. CO₂ TPD experiments have been also reported by Avgouropoulos and Ioannides [10]; in their experiments CO₂ is desorbed giving a tailed peak up to 300–400°C related to carbonates decomposition.

In this work the role of CO₂ on the activity and selectivity was assessed; in particular, the extent of adsorption of CO₂ over a CeO₂-supported copper oxide catalyst

has been quantified.

The results of catalytic tests performed at different temperatures have been correlated to CO₂ temperature programmed desorption (TPD) runs performed on both the support (CeO₂) and the catalyst (CuO/CeO₂).

Materials and methods

Commercial CeO₂ (Grace) was used as support. The CuO/CeO₂ catalysts were prepared by wet impregnation of the support with copper acetate ((CH₃COO)₂Cu•H₂O). The sample was then dried overnight at 120°C and subsequently calcined at 450°C under dry air flow (5Nl/h) for 3h. Catalysts with nominal CuO weight percentage equal to 0.5, 4 and 8 were prepared. The values of surface area were determined by BET method adsorbing N₂ at 77K using a Quantachrome Autosorb 1-C.

CO₂ TPD experiments were carried out using a Micromeritics Autochem II 2020 analyzer equipped with a TC detector. About 100 mg sample was pre-treated 1h at 450°C in flowing air and then contacted for 45 min at room temperature with a 15% CO₂/He mixture. After 30 min He purging the sample was heated 10°C min⁻¹ up to 300 °C.

The lab-scale set-up used for CO-PROX experiments has been described elsewhere [11]. The powder catalyst (300 mg) with a particle size of 200-400 μm was placed in a tubular quartz reactor, provided with a thermocouple for the measurement of the catalyst temperature. The reactor is externally heated by an electric tubular furnace. Catalytic tests were conducted at fixed flow rate (20 l(STP)/h) corresponding to a contact time of 0.054 g•s•cm⁻³. Hydrogen, carbon monoxide and oxygen concentrations were fixed at 50 vol.% , 0.5 vol.% and 0.9 vol.% respectively, while two carbon dioxide (0 vol.% and 15 vol.%) concentrations were used. Reaction temperature was varied between 60°C and 220°C.

In order to get insights into the nature of the catalytic sites involved in the CO₂ adsorption/desorption, we developed a model of CO₂ TPD.

It is based on the kinetic model on the Polanyi-Wigner equation under the Redhead approximation which states that the catalytic sites do not interact. From the TPD signals of the materials three peaks establish. We then assumed that CO₂ adsorb over three catalytic sites.

The unsteady balance equations on the fraction (θ_1 , θ_2 and θ_3) read:

$$\frac{d\theta_1}{dt} = -k_1^d \exp\left(-\frac{E_{des1}}{RT}\right) \theta_1^{n_1}$$

$$\frac{d\theta_2}{dt} = -k_2^d \exp\left(-\frac{E_{des2}}{RT}\right) \theta_2^{n_2}$$

$$\frac{d\theta_3}{dt} = -k_3^d \exp\left(-\frac{E_{des3}}{RT}\right) \theta_3^{n_3}$$

The overall CO₂ mass balance and the corresponding initial conditions (not reported) complete the mathematical model solved by means of a Runge-Kutta method.

Results

A significant surface area reduction with respect to that of the support (Table 1) can be noticed only at high copper loading when formation of small CuO crystallites was detected [12].

In figure 1 the CO conversion and selectivity are reported as a function of the catalyst temperature as obtained in the absence and in the presence of CO₂ (15 % vol.). From these results two different operating regimes may be distinguished.

In the low temperature range ($T < 160$ °C; Regime A) both CO conversion and selectivity are affected by the CO₂ feeding, while at higher temperature (Regime B) the performance of the catalyst does not appear affected by CO₂. Catalysts with different copper content show the same qualitative behavior (not reported).

Table 1 – BET surface area and amount of CO₂ desorbed in the TPD experiments.

Sample	Surface area (m ² g ⁻¹)	desorbed CO ₂ (μmol g ⁻¹)	desorbed CO ₂ (μmol m ⁻²)
CeO ₂	56	300	5.36
0.5 % CuO/CeO ₂	56	324	5.79
4 % CuO/CeO ₂	50	296	5.92
8 % CuO/CeO ₂	47	325	6.91

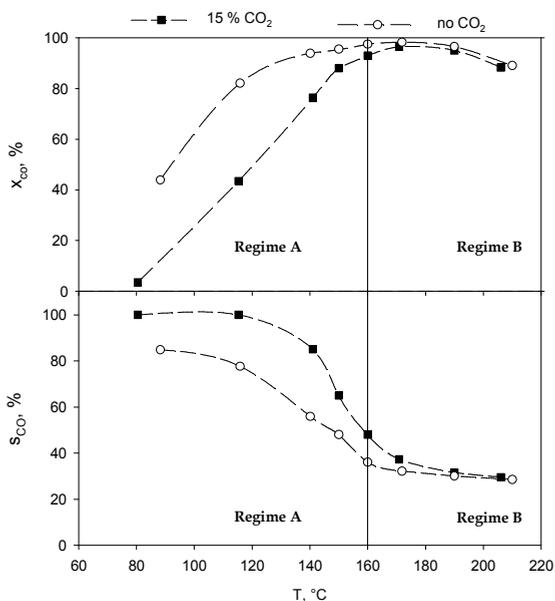


Figure 1. Effect of CO₂ addition on CO-PROX performance of 4%Cu/CeO₂ catalysts: CO conversion (top); CO selectivity (bottom).

In order to get insights into the reasons of this behavior, CO₂ temperature programmed desorptions (TPD) over the CeO₂ support and CuO/CeO₂ catalysts were

carried out and a model of CO₂ desorption was developed.

In Table 1 the amount of CO₂ desorbed from all samples is reported. For all samples, support included, a CO₂ amount of about 300 μmol g⁻¹ was obtained. If the released CO₂ is ratioed to the surface area, it increases with CuO loading, thus suggesting that copper provides additional adsorption sites.

CO₂ desorbs from the catalyst in the temperature range of 80-300 °C (figure 2), coincident with the range in which the CO-PROX reaction is active.

In all cases a dominant CO₂ desorption signal is peaked at 120-135 °C, with a smaller peak at about 250 °C, more evident for the support.

It must be underlined that the most part of CO₂ is released in the gas phase at temperature below 180 °C, thus confirming that in the Regime B CO₂ does not affect the catalyst performance.

In figure 2 the model curves are also shown for each sample together with the experimental TPD profiles. The agreement is quite good up to about 230 °C, i.e. in the temperature range interesting for the CO-PROX reaction.

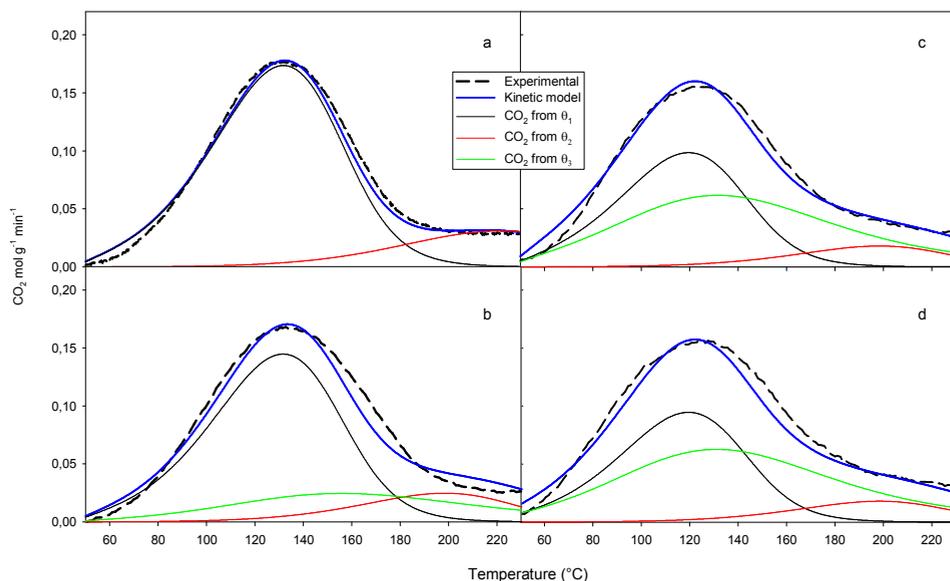


Figure 2. Experimental (dashed lines) and modeling (solid lines) TPD of CO₂ over CeO₂ (a) and CuO/CeO₂ at different values of CuO content (b): 0.5 wt.%; (c): 4 wt.%; (d): 8 wt.%). Carrier He, flow rate = 50 cc/min. Model CO₂ desorption curves from θ_1 , θ_2 and θ_3 sites are also reported.

In the case of the support (CeO₂) TPD profile can be reproduced with only two sites (θ_1 and θ_2), while in the case of the copper catalyst (CuO/CeO₂) an additional one (θ_3) is needed. From our results, the activation energy of the CO₂ desorption from θ_1 sites is affected by copper addition (E_{a1} : 48920 J/mol K for the support; 47320 J/mol K for the catalysts). All the other kinetic parameters are not affected

by both CuO addition and amount. This suggests that these sites are related to highly dispersed copper strongly interacting with the support, which are claimed as active sites for CO-PROX reaction [13-14].

In Figure 2 the desorption peaks of each site as calculated by the model are also plotted for all the samples. On increasing the CuO content, the contribution of site θ_1 decreases while the contribution of site θ_3 significantly increases. The high temperature contribution (θ_2) remains almost unaffected by the CuO amount.

According to the above considerations, sites θ_1 can be related to the activation of carbon monoxide, while site θ_3 are responsible of the hydrogen combustion. As a consequence, the temperature range corresponding to the last part of the Regime A (Figure 1) can be identified as an optimal operating zone in the case of CO₂ co-feeding. As a matter of fact, under these conditions sites θ_3 are still significantly occupied by CO₂, while the most part of sites θ_1 are free.

Conclusions

The inhibiting effect of carbon dioxide on the CuO/CeO₂ activity towards CO-PROX reaction has been explained in terms of its interaction with the catalyst surface. Catalytic tests revealed that CO₂ feeding negatively affected the catalytic activity but increases the CO selectivity at temperatures below 160°C; on the other hand, at higher temperatures catalytic performance are unaffected by CO₂. By TPD experiments, it clearly appears that CO₂ is chemisorbed onto both the ceria support and copper oxide active phase. As a consequence, the effect of CO₂ on the catalytic performance is due to the formation of stable surface species. Two adsorption sites on the ceria support and an additional one when copper is added were identified.

The low temperature site is modified by copper addition; according to our results these sites are those responsible for CO activation. CO₂ is completely removed from these sites at about 160°C, thus confirming that these species are those involved in the selective CO conversion. Conversely, sites related to copper oxide not strongly interacting with ceria show CO₂ desorption at temperatures slightly higher and are mainly active towards H₂ oxidation.

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