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CO preferential oxidation reaction aspects in a nanocrystalline CuO/CeO_2 catalyst



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ABSTRACT

CuO/CeO₂ catalysts were prepared by the Pechini method and applied in the CO preferential oxidation (CO-PROX). The CuO content effects on the catalysts and the presence of H_2O and CO_2 in the reaction stream on the catalytic performance were investigated. The catalyst with 1.0 wt.% CuO presented the highest conversion and selectivity in the COPROX in the temperature range 100–250 °C. It was observed that the catalytic system is sensitive to the dispersion of the active phase and, independently of the copper content, the high activity of the CuO/CeO₂ catalysts is closely related to the finely dispersed CuO species strongly interacting with CeO₂ support. In the long-term stability test under the real CO-PROX condition with 10 mol% H_2O and 15 mol% CO_2 in the reactant stream, about 90% CO conversion can be maintained even at low temperature (150 °C) with 95% selectivity.

1. Introduction

It is growing the interest in proton exchange membrane fuel cells (PEMFC) due to the increase in demand for clean energy. The hydrocarbons steam reforming typically generates the hydrogen rich stream used as a fuel for PEMFC. However, the reformed gas stream contains significant amounts of carbon monoxide that leads to the deactivation of the PEMFC platinum electrocatalyst. Hence, its concentration should be reduced below 100 ppm in the hydrogen-rich current that is tolerated by the Pt catalyst of the fuel cell membrane [1–3].

The reformed gas is purified in two reactional steps. In the first step, the water-gas shift reaction (WGSR) reduces the CO about 2.5-5.0% by volume. However, only with the subsequent step, the CO-PROX, the amount of carbon monoxide can reach the level of up to 10 ppm [4–7].

An ideal catalyst for CO-PROX must be active and selective for CO oxidation (Eq. (1)), avoiding significant amounts of water formation through the hydrogen oxidation (Eq. (2)). In addition, the catalyst must exhibit thermal stability over long reaction periods [6–8].

$$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2 \quad \Delta H_{298K} = -283 \frac{kJ}{mol}$$
(1)

$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O \ \Delta H_{298K} = -242 \frac{kJ}{mol}$$
 (2)

Cerium oxide (CeO₂) has been widely applied as a catalyst support

because of its ability to store and liberate oxygen under oxidation and reduction conditions that can be adjusted by appropriate doping with metals [9,10]. Copper supported on ceria is widely used in PROX-CO reaction because of its physicochemical properties and low cost compared to noble metals [1].

The CuO/CeO₂ system performance depends on the method of preparation, since this has an influence in its physicochemical characteristics, affecting the Cu(I)/(II) and Ce(III)/(IV) redox couples that have large influence on the activity [11,12]. The superior performance of CeO₂/CuO catalysts in CO-PROX has been attributed to the combination of strong metal-support interaction with the following factors: (i) the facilitation of redox interplay between Cu^{2+}/Cu^+ and Ce^{3+}/Ce^{4+} redox couples; (ii) the presence of oxygen vacancies; (iii) superior reducibility of mixed CuO/CeO₂ composites as compared to that of individual counterparts; (iv) the geometric or ligand effects induced by the interaction of metal-support and (v) the interfacial reactivity [13–17].

Therefore, in this work it was investigated the catalytic performance of CuO/CeO₂ prepared by Pechini citrate method in CO-PROX reaction at low temperatures (100–250 °C) as well as the H₂O and CO₂ influence in a 24-h stability test with a reaction stream containing 10 mol% H₂O and 15 mol% CO₂.

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2. Experimental

2.1. Synthesis of catalysts

The catalysts with nominal metal loadings of 1.0 and 5.0 wt.% was prepared by the Pechini method [18] with aqueous solution (1.0 M) of the following reagents: citric acid $[C_6H_8O_7]$, ethylene glycol $[C_2H_4(OH)_2]$, copper nitrate $[Cu(NO_3)_2.3H_2O]$ and cerium nitrate [Ce $(NO_3)_2.6H_2O]$. Emulsifying agents were added in a molar ratio of 3:1. The catalysts synthesis were carried out at 50 °C under constant stirring for 30 min followed by stirring at 100 °C for 48 h. The obtained solids were mechanically milled and dried at 100 °C overnight. Finally, they has been calcined at 500 °C for 5 h in an oven with flowing synthetic air. The catalysts synthesized with 1.0 and 5.0 wt.% copper were named as 1CuCe and 5CuCe, respectively.

2.2. Catalytic activity measurements

2.2.1. Ideal CO-PROX

CO-PROX reactions have been carried out in a glass tubular fixedbed reactor (5 mm i.d.) operating under atmospheric pressure. Samples (400 mg) have been reduced *in-situ* with pure H₂ at 300 °C for 2 h, under flow of 30 cm³ min⁻¹. Gases mixture of 4.0% CO, 2.0% O₂, 50% H₂ and N₂ has been prepared by adjusting the rates of flow mass controllers (MKS Instruments 247, with four channels). The tests have been carried out by decreasing the temperature from 300 °C to 100 °C in steps of 50 °C. The reactor temperature has been monitored by a thermocouple and controlled by a FLYEVER FE50RP temperature controller. Gas chromatography analyses (GC) have been carried out in triplicate at each temperature step, in order to allow the reaction system to stabilize.

2.2.2. Real CO-PROX

The effects of addition H_2O and CO_2 in the reactor feed stream have been evaluated by adding of 10 mol% H_2O and 15 mol% CO_2 to the feed gas in order to simulate the effluent's real stream composition in the steam-reforming reactor. Activation conditions identical to the used in ideal CO-PROX reaction H_2O and CO_2 was utilized in that test. Longterm stability test (24-h) has been achieved with real CO-PROX conditions at 150 °C.

The reactor effluents of ideal and real PROX-CO was analyzed in an in-line chromatograph (GC 3800-VARIAN), with two thermal conductivity detectors, Porapak N and 13X molecular sieves packed columns. The CO conversion (X_{CO}) and the selectivity towards CO₂ (S_{CO_2}) have been calculated as shown in Eqs. (3) and (4):

$$X_{CO}(\%) = \frac{CO^{Input} - CO^{Output}}{CO^{Input}} \times 100\%$$
(3)

$$S_{CO_2}(\%) = 0.5 \times \left[\frac{CO^{Input} - CO^{Output}}{O_2^{Input} - O_2^{Output}} \right] \times 100\%$$
(4)

2.3. Catalysts characterization

2.3.1. Conventional X-ray powder diffraction – XPD

Conventional X-ray powder diffraction (XPD) patterns of calcined catalysts have been obtained with a Rigaku Multiflex powder diffractometer with Cu K α radiation and the crystalline phases was identified by comparison with the patterns recorded in JCPDS. The average size of the crystallites has been determined by the Scherer's equation.

2.3.2. In-situ X-ray powder diffraction – in-situ XPD

Time-resolved diffraction data have been carried out on the XPD-D10B of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil) in the reflection mode at 20 from 20° to 80°, with an angular velocity equal to 0.02° /s and wavelength equal to 1.54987 Å. The powders have been placed in the sample-holder provided with a thermocouple to read the sample temperature during the experiments. The set up allows putting the sample inside a reactor with controlled heating and gas-flow lines. Analyzes have been carried out under condition of ideal and real CO-PROX. In the ideal CO-PROX, the catalysts have been tested with 4.0% CO, 2.0% O₂, 50% H₂ and N₂ gas feed, simulating the condition of a stream free of other gases such as CH₄, H₂O and CO₂. In the real CO-PROX, the catalysts have been tested with 4.0% CO, 2.0% O₂, 50% H₂ and 5.0% CO₂, simulating the gas stream out of methane steam reforming. The catalysis samples have been previously reduced *in-situ* with H₂ at 300 °C for 30 min. After the reduction step, the temperature has been raised to 100 °C under N₂ flow, the gases were switched and the reaction was started.

2.3.3. N₂ physisorption analysis

The catalysts surface area has been measured by N_2 -adsorption – BET method – in a Quantachrome Nova 1200 surface analyzer.

2.3.4. Temperature-programmed reduction – H_2 -TPR

The oxide species reducibility information have been obtained by temperature-programmed reduction (TPR) in a Micromeritics Pulse Chemisorb 2705 instrument, at a heating rate of 10 °C min⁻¹. The temperature has been raised from room temperature up to 1000 °C, with a mixture of 5.0% H₂/N₂ flowing at 30 cm³ min⁻¹. Temperature-programmed reduction (H₂-TPR) and oxidized surface reduction (s-TPR) measurements has been collected. The s-TPR measurements allow us to calculate the copper dispersion (D_{Cu}) and average copper size (AV) by reduction with 5.0% H₂/N₂ mixture, followed by Cu° surface reoxidation under mild conditions with N₂O, at 60 °C. Finally, the reduction with 5.0% H₂/N₂ mixture, as described in an earlier study for this system [3,19].

2.3.5. Transmission electron microscopy - TEM

The morphology and the crystal shape of the prepared catalysts particles have been examined by transmission electron microscopy (TEM) with a Philips CM120 transmission electron microscope operated at 200 kV, equipped with an energy dispersive X-ray spectrometer (EDS).

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Conventional X-ray powder diffraction - XPD

The 1CuCe and 5CuCe XDP patterns are shown in Fig. 1. The CeO_2 characteristic peaks at 28.6°, 33.4°, 47.8° and 56.7° – corresponding to the reflections in the (111), (200), (220) and (311) crystalline planes of the fluorite-type cubic phase (JCPDS 34-0394) – can be clearly observed in the XPD results of both catalysts. However, none of the copper species diffraction peaks has been detected, implying that these species



Fig. 1. XRD patterns of CuO/CeO₂ catalysts.

Table 1

1CuCe and 5CuCe catalysts textural properties.

Catalyst	CeO ₂ crystallite	BET surface	CuO nominal	CuO Amount –
	size	Area	amount	EDS
	(nm)	(m ² g ⁻¹)	(% molar)	(% molar)
1CuCe	8.09	92.0	1.00	1.30
5CuCe	12.6	53.0	5.00	4.80

have been highly dispersed or are forming a solid solution with the ceria. These results indicate that the preparation method resulted in solids with the desired structure and small particle size with highly dispersed metallic phase [11,20–26].

The corresponding crystallite dimensions have been calculated according to the (111) plane by the Scherrer's equation and are tabulated in Table 1. The particle size of the 5CuCe catalyst is higher than in the 1CuCe catalyst, confirming that the copper dispersion is higher in the catalyst with lower copper content [11,20–26].

3.1.2. Energy dispersive X-ray spectrometry - EDS

Table 1 shows the results of semi-quantitative chemical analysis by EDS. The EDS analysis results are in agreement with the CuO nominal values used in the catalysts synthesis. Therefore, the Pechini method has been efficient to obtain the proposed catalytic system.

3.1.3. N₂ physisorption analysis

The catalysts surface area has been measured by N_2 physisorption analysis and the results are shown in Table 1. The 1CuCe has a larger surface area compared to 5CuCe catalyst. The higher surface area presented by the 1CuCe catalyst is due to the smaller particle size and the greater dispersion of the active phase on the support, as observed in the conventional XPD results.

3.1.4. Temperature-programmed reduction $-H_2$ -TPR

Fig. 2 shows that the 1CuCe and 5CuCe H₂-TPR profiles of catalysts are similar, both exhibiting reduction peaks in two temperature ranges: one peak between 150–200 °C and another one between 400–1000 °C. According to the literature, the ceria reduction with hydrogen only begins above 350 °C. Therefore, the reductions below this temperature are related to the CuO species reduction. These CuO peaks in Fig. 2 are named α , β and γ , while the δ and ϵ refers to bulk ceria [2,3].

As reported in the literature [2,3,7,27–29], the α reduction peak has been assigned to the isolated Cu²⁺ ions that can strongly interact with the support and these Cu²⁺ ions which have close contact with each other, that are highly dispersed and strongly interacted with the support. The β reduction peak has been assigned to the small amorphous clusters, which do not appear in XRD patterns (Fig. 1) [2,27–29]. Finally, the γ reduction peak has been assigned to the large three-dimensional clusters and bulk CuO phase have characteristics and properties identical to those of pure CuO powder [2,27–29].



Fig. 2. H₂-TPR profiles of CuO/CeO₂ catalysts.



Fig. 3. CO conversion and CO_2 selectivity versus temperature under ideal CO-PROX: (a) 1CuCe and (b) 5CuCe.

3.2. Catalytic performance

3.2.1. Ideal and real PROX

Fig. 3 shows the catalytic performance of the 1CuCe and 5CuCe catalysts under ideal CO-PROX conditions, i.e. reagent stream containing 4.0% CO, 2.0% O_2 , 50% H_2 and N_2 balance. The temperature range of effective CO removal is defined as the CO conversion > 99.5% [2]. With 1CuCe, the most active catalyst, the temperature range of effective CO removal is in the range of 150–200 °C, whereas with the 5CuCe catalyst the range is 200–250 °C. At 200 °C, the CO conversion of 1CuCe catalyst is 100%, whereas the obtained with the 5CuCe catalyst, at the same temperature, is 94.3%. At 100 °C the CO to CO₂ conversion rates are 87.8% with1CuCe and 69% with 5CuCe. In addition, both catalysts exhibit CO-PROX selectivity higher than 95%, indicating that there was no hydrogen oxidation in considerable amounts.

Fig. 4 shows the catalysts results referred to the real CO-PROX condition. They are qualitatively similar to those of Fig. 3, with the 1CuCe catalyst exhibiting the best performance. Water and CO_2 addition did not caused a significant change in the behavior of the catalysts. At 200 °C, the CO conversion with 1CuCe catalyst was 96.8%, and with the 5CuCe catalyst, it was 94.4%. The selectivity was not significantly altered either. Thus, the results indicate that the system is not very sensitive to H_2O and CO_2 in the reaction medium, meaning that no prior purification steps are required.

In both CO-PROX reaction conditions, the O_2 conversion was 100% with both catalysts and throughout temperature range.

3.2.2. Textural properties influence

The dispersion and metallic area of copper are shown in Table 2. The higher 1CuCe surface area favors the copper species dispersion. High dispersion in turn favors the copper-support strong interaction [30–33]. This strong interaction implies the interface spots formation,



Fig. 4. CO conversion and CO_2 selectivity versus temperature under real CO-PROX: (a) 1CuCe and (b) 5CuCe.

Table 2

Metallic area and dispersion of the catalysts.

Samples	Metallic area $(m^2/g_{cat})^*$	Dispersion (%)
1CuCe	144.0	67.00
5CuCe	105.0	58.00

* $g_{cat} = gram of catalyst.$

which are more favorable to the reaction due to the greater surface oxygen availability and consequently greater reduction potential [31–33]. Therefore, the 1CuCe catalyst showed higher activity in the CO-PROX reaction than the 5CuCe catalyst.

The influence of the metal-support interaction on catalytic activity is still controversial. The most accepted hypothesis is that the oxide can modify the electronic properties of the metal. For example, acidic supports attract electrons from the metal particles, leaving them deficient in electrons, whereas basic supports can increase the electronic density of the metal [31]. Another possible explanation for the effect of the metal-support interaction on the catalytic activity is associated with the charges transport due to the formation of a Schottky barrier between the metal and the semiconductor oxide [31,32].

3.2.3. CuO content influence

The higher the copper amount in the catalyst, the greater the CuO bulk formation. These bulk copper species are reduced only after all copper surface had participated in the reaction. In addition, the cationic structure sub-network represents a major barrier to penetration into the bulk metal [30]. Therefore, the catalyst with higher copper content (5CuCe) has presented lower activity in the CO-PROX reaction.



Fig. 5. Isothermal stability test for 1CuCe catalyst at 150 °C.

3.2.4. Long-term stability test

The 1CuCe catalyst has been selected for isothermal stability test due to its higher activity in the CO-PROX reaction under real and ideal conditions. Fig. 5 shows the results at 150 °C under the real CO-PROX conditions. Only a decrease in the CO conversion rate of approximately 7.88% throughout the reaction has been observed. The catalyst selectivity also remained stable in the 97–100% range over the entire reaction period.

3.3. Used catalyst microstructural characterization

3.3.1. In-situ XPD

Fig. 6 shows the *in-situ* XPD patterns under ideal and real CO-PROX conditions of the 1CuCe catalyst after 30 min reaction. There are no peaks related to the CuO, only fluorite phase peaks are present. These peaks remain present even after the ideal and real CO-PROX conditions, indicating no segregation of the active phase under the applied reaction conditions, favoring the interaction support-metal, responsible for the good catalyst performance in the CO-PROX reaction.

3.3.2. Transmission electronic microscopy - TEM

TEM analysis has been performed to verifying the morphology of the catalyst before and after the ideal and real CO-PROX. Fig. 7 shows that in the 1CuCe catalyst the particle sizes are of the nanometric order, agreeing with the conventional XPD results (Table 1). The active site for CO-PROX reaction in Cu–O–Ce catalysts are in the metal-support interface. The nanosize order of particles favors a strong metal-support electronic interaction, improving interface performance. In addition, the metal-oxide bonding interactions can also modify the oxide properties, generating new active sites. Hence, both metal and oxide properties can be drastically altered at the interface, resulting in a unique interfacial activity [1].



Fig. 6. *in-situ* XPD results for 1CuCe catalyst: (a) before CO-PROX reactions, (b) after 30 min in ideal CO-PROX and (c) after 30 min in real CO-PROX.







(c)

Fig. 7. TEM images of the 1CuCe catalyst: (a) before CO-PROX reactions, (b) after ideal CO-PROX and (c) after real CO-PROX.

4. Conclusions

The catalysts 1.0 mol% CuO (1 CuCe) and 5.0 mol% CuO (1 CuCe) have been prepared by the Peccini citrate method and applied in the CO preferential oxidation reaction. The results of the microstructural characterization (surface area, XPD and H₂- TPR) and catalytic performance agree with each other, and show that the 1CuCe is the better catalyst in both in the real and ideal CO-PROX. The best performance of the 1CuCe relative to the 5CuCe catalyst is due to the greater dispersion of the active phase on the support, which facilitates the CuO species reduction.

The 1CuCe remained stable in the 24 h test at 150 °C, with no

modifications in its microstructure, confirming its high performance.

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