CuO/CeO₂ supported on Zr doped SBA-15 as catalysts for preferential CO oxidation (CO-PROX)

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**Abstract**

The application of the catalytic system CuO/CeO₂ supported on Zr doped SBA-15 mesoporous silica to the preferential oxidation of CO on hydrogen streams (CO-PROX) suitable to be used to feed PEM fuel cells, has been studied. A loading of 20% (wt.) Ce and 6% (wt.) Cu was found optimal for the CO-PROX reaction. The influence of the presence of CO₂ and H₂O in the gas feed was also studied in order to simulate the real operation conditions of a PEMFC feed stream generated by alcohol steam reforming. The catalysts were characterized by XRD, adsorption–desorption of N₂ at −196 °C, TEM, –H₂-TPR and XPS. The system reducibility was found modified by the incorporation of zirconium in the support, with improvement of both the conversion and selectivity of the catalytic system, compared to the same material without Zr.

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**1. Introduction**

Hydrogen suitable to feed proton exchange membrane fuel cells (PEMFCs) can be produced by reforming of alcohols or hydrocarbons, in case followed by water–gas shift reaction. The reformed gas obtained still contains variable amounts of CO, which will decrease the energy efficiency of the fuel cell because CO-induced poisoning of the Pt anode catalyst. There are several methods to eliminate CO from the hydrogen rich gas stream, such as selective CO methanation, selective diffusion through membranes, but preferential oxidation of CO (CO-PROX) is the most economical and efficient approach both for static and mobile applications to reduce CO to the desired level without excessive hydrogen consumption [1–7].

Several catalytic systems based on supported very expensive noble metals (Au, Pt, Ru) have been proposed but CuO/CeO₂ based oxide systems seem to be a selective, thermally stable and low cost alternative catalyst [8–11]. The particular ability of these CO-PROX catalysts was essentially attributed to the synergistic redox properties of copper–ceria interfacial sites [12–18]. This system has been studied by different authors finding that the preparation methods and the Cu loading are determinant for the performance of the CuO/CeO₂ catalysts [13,21]. The presence of Zr was found to modify the redox properties of the Cu/ Ce pair, improving the catalytic results [11]. The presence of CO₂ and H₂O in the feed stream decreases the formation of Cu⁺–carbonyls, indicative of CO oxidation [19]. Recently it was observed that the segregation of Cu and the formation of metallic Cu are involved in the partial deactivation of CO-PROX catalysts [20].

In this work a CuO/CeO₂ system supported on different mesoporous silica doped with zirconium is studied. The materials were characterized before and after the CO-PROX reaction, by XRD, adsorption–desorption of N₂ at −196 °C, TEM, H₂-TPR and XPS in order to find possible correlations between composition, structure and catalytic performance.

**2. Experimental**

2.1. Catalyst preparation

The mesoporous Zr doped SBA-15 silica (SBAZr10) was prepared according to the method proposed by Szczodrowski et al. [22] with Si/Zr atomic ratio = 10. Besides, a SBA-15 sample (SBA) was prepared following the synthetic method described by Gómez-Cazalla et al. [23]. An additional support material (SBAZrO₂) was prepared by incipient wetness impregnation of a pure silica SBA-15 using a zirconium(IV) acetate solution, with an atomic ratio Si/Zr = 10, and then calcined for 6 h at 550 °C with a heating ramp of 1 °C min⁻¹. The active phase was incorporated...
by incipient wetness impregnation using an aqueous solution of copper(II) and cerium(III) acetates. The loading of copper was 6 wt.% and cerium was 20 wt.%. Due to the limited solubility of the salts used, the impregnation was made in several steps until the total incorporation of the salts. All samples were dried 12 h at 60 °C and then calcined at 550 °C for 4 h with a heating ramp of 1 °C min⁻¹. The catalysts were labeled YCe20Cu6, where Y denoted the used support (SBAZr10Ce20Cu6, SBACe20Cu6, SBAZrO210Ce20Cu6 respectively).

2.2. Catalytic tests

Catalytic activity tests were carried out in a laboratory flow apparatus, with a fixed bed reactor operating at atmospheric pressure. The catalysts (0.100 g), with a defined particle size (0.050–0.110 mm) were introduced into a tubular Pyrex glass reactor (5 mm i.d.), and placed inside an aluminum heating block.

Before the catalytic experiments, the samples were heated in situ at 400 °C under flowing air for 1 h. The contact time W/F was 0.18 g s cm⁻² (GHSV = 22 000 h⁻¹). The reaction mixture composition was 1.25% CO, 1.25% O₂, 50% H₂, balanced with He. The effect of CO₂ and H₂O was examined in separate runs with the addition of 15 vol.% CO₂ and 10 vol.% H₂O. An ice-cooled cold finger was used to trap the excess of oxygen factor (λ) is defined as (Eq. (4)):

\[ \lambda = 2 \times \frac{n_{\text{O}_2}^{\text{in}}}{n_{\text{CO}}^{\text{in}}} \]

The selectivity towards CO₂ was calculated by (Eq. (3)):

\[ \text{Sel}_{\text{CO}_2} = \frac{n_{\text{CO}_2}^{\text{out}}}{2(n_{\text{O}_2}^{\text{in}} - n_{\text{CO}_2}^{\text{in}})} \times 100 \]

and the excess of oxygen factor (λ) is defined as (Eq. (4)):

\[ \lambda = 2 \times \frac{n_{\text{O}_2}^{\text{in}}}{n_{\text{CO}}^{\text{in}}} \]

In all the catalytic tests, λ = 2 was used, because this value was previously found optimal for preferential oxidation of CO [10–12].

2.3. Characterization methods

X-ray diffraction (XRD) patterns were obtained with a Philips CM200 microscope working at 10 kV. The measurements of X-ray dispersive energy were registered using an EDAX CM200ST probe based in a detector SiLi. The samples were dispersed in 2-propanol and dropped over a Ni grid to avoid interferences in the Cu measurements.

Temperature-programmed reduction of H₂ (H₂-TPR) experiments were carried out using ~0.1 g of freshly calcined catalyst placed in a U shaped quartz reactor inside of a tubular oven. In order to remove contaminants, the powders were pre-treated with helium (50 cm³ min⁻¹) to 150 °C for 1 h. After cooling to ambient temperature, TPR experiments were carried out in 10 vol.% H₂/Ar (30 cm³ min⁻¹) increasing the temperature from room temperature to 600 °C with a heating ramp of 10 °C min⁻¹, by a temperature programmable controller. The water produced in the reduction was eliminated using a isopropanol–liquid N₂ trap. The hydrogen consumption was calibrated versus CuO and registered using a TCD mounted in a GC Shimadzu 14-B.

X-ray photoelectron spectroscopy (XPS) studies were realized by a Physical Electronic PHI 5700 spectrometer using non monochromatic Mg K radiation (300 W, 15 kV, 1253.6 eV) for the analysis of the core level signals of C 1s, O 1s, Si 2p, Cu 2p, Zr 3d and Ce 3d with a hemispherical multichannel detector. The spectra of powdered samples were registered with a constant pass energy values at 29.35 eV, using a 720 μm diameter circular analysis area.

The X-ray photoelectron spectra obtained were analyzed with PHI ACESS ESCA-V6.0F software and processed using Multipak 8.2B package. The binding energy values were referenced to C 1s signal (284.8 eV). Shirley type background and Gauss–Lorentz curves were used to determine the binding energy. Short acquisition times (<10 min) were used in order to avoid photoreduction of copper and cerium species [25].

3. Results and discussion

3.1. Catalytic tests

The gas stream of the three studied samples was initially fixed to 1.25% CO, 1.25% O₂, 50% H₂ balanced with He. As found in previous works [10–12], the carbon balance showed a good correlation between CO₂ formed and CO consumed. Reverse water gas shift (rWGS) and methanation reactions were found negligible in our experiments.

The gas stream of the three studied samples was initially fixed to 1.25% CO, 1.25% O₂, 50% H₂ balanced with He. As found in previous works [10–12], the carbon balance showed a good correlation between CO₂ formed and CO consumed. Reverse water gas shift (rWGS) and methanation reactions were found negligible in our experiments and only CO and H₂ oxidations are the reactions considered in these catalytic tests.

The evolution of the conversion of CO and selectivity towards CO₂ curves of the studied catalysts are presented in Fig. 1. All samples showed a good catalytic performance, reaching conversions near 100% at 140 °C. The incorporation of Zr into the support, increases the conversion of CO and the selectivity to CO₂ in comparison with the sample without Zr, labeled as SBACe20Cu6. Both SBAZr samples show a CO conversion of 95% with high selectivity towards CO₂. In the case of SBAZr10Ce20Cu6, the selectivity towards CO₂ appears to remain close to 100% up to 160 °C. The selectivity loss is caused by the occurrence of the oxidation of hydrogen to water, more thermodynamically favorable at high temperatures.

Since CO₂ and H₂O can be present in significant quantities in reformed gases, the influence of these compounds was evaluated on the best performing sample, SBAZr10Ce20Cu6. The influence of the addition of 15 vol% CO₂ to the feed stream is shown in Fig. 2. As expected and as found previously [12], the addition of CO₂ highly decreases the conversion at reaction temperatures <140 °C. Only at this temperature the conversion reaches the value of 95%. A better
approximation to the real operation conditions of a PEMFC feeding system can be studied when both 15% CO2 and 10% H2O were added to the feed stream. Both conversion and selectivity fall down drastically, but at 165 °C the sample exhibits a good performance with a conversion of 87% and selectivity towards CO2 of 72%.

3.2. Characterization

3.2.1. XRD studies

Phase identification was realized on the XRD patterns of both fresh and used samples. The diffractograms of the supports prepared with the Zajáč method [22] do not present any peak associated to ZrO2 phases, while SBAZrO210 shows the diffractions peaks of the tetragonal ZrO2 (JCPDS #072949) due to the postsynthesis incorporation of that phase at 2θ = 30.1, 50.2, 50.6, 59.6 and 60.0°. The diffraction patterns of the studied catalyst are shown in Fig. 3. All fresh catalysts show peaks associated to cubic CeO2 (cerianite phase, JCPDS #072155) at 2θ = 28.5, 33.4, 47.5 and 56.5° and monoclinic CuO (tenorite phase, JCPDS #043179) at 2θ = 35.5 and 38.7° wit weak intensities in the samples with SBA and SBAZr10 supports. After the catalytic test, new peaks appeared, associated to metallic Cu, with 2θ = 43.5 and 50.4°. If all the intensities of these peaks are compared, the XRD profile of the catalyst based on the SBAZr10 support shows peaks with weaker intensities due to lower reduction degree in comparison to the other studied samples.

Crystallites size of the active phases can be estimated by measuring the contributions to peak broadening using Rietveld methodology to fit the experimental diffractogram with the reference patterns of the detected phases. Average particle sizes for each crystalline phase are summarized in Table 1, showing good values of Rwp and particles with nanometric size. The particle size of the crystalline active phases varies with the support. The sizes of cerianite and tenorite are smaller in the case of the pristine SBA-15. With the incorporation of Zr the sizes of the actives phases parti-
cles increase, being bigger in the case of the support SBAZrO$_2$10. In any case nanometric crystallites are obtained, ruling out the formation of solid solutions between phases, in accordance with lattice parameters of cerianite phase, showed in Table 1, and compared with the CeO$_2$ reference value.

3.3. Surface and textural properties

The specific surface area of the supports and fresh catalysts were studied using the data obtained from adsorption–desorption isotherms of N$_2$ at $-196\ ^\circ\mathrm{C}$. All materials show the typical type IV isotherm, according with the IUPAC classification. In Fig. 4, the isotherms of SBAZr10Ce20Cu6 catalyst are graphically presented, showing a H1 hysteresis cycle, according with the behavior of these materials.

The pore size graph, also presented in Fig. 4, shown a narrow distribution centered on the 4–5 nm, corresponding to the mesopores range, typical of SBA-15 based materials. BET area, pore volume and average pore size calculated by the BJH method of all supports and catalysts are summarized in Table 2. All the supports have high specific surface area, typical of these mesoporous materials. The incorporation of the active phase into the supports decreased the specific surface area, while the average pore size remained similar to that of the supports.

The surface data and the information obtained by XRD can be corroborated using TEM. The micrography presented in Fig. 5 shows the morphology of these materials. Clear areas are visible, where must probably SBA-15 hexagonal pores are present and dark areas where a high Cu/Ce ratio was detected by EDX. In the clear areas, the signals associated with the presence of Cu and Ce are less intense than those observed in the dark areas.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Lattice parameter (Å)</th>
<th>$D_i$ (nm)</th>
<th>$\varepsilon$ (%)</th>
<th>$R_{wp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBAZr10Ce20Cu6</td>
<td>Cerianite</td>
<td>5.415(4)</td>
<td>14.1</td>
<td>0.16</td>
<td>5.56</td>
</tr>
<tr>
<td>SBAZr10Ce20Cu6</td>
<td>Tenorite</td>
<td>59.0</td>
<td></td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>SBAZr10Ce20Cu6</td>
<td>Zirconia</td>
<td>22.1</td>
<td></td>
<td>0.67</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_p$ (cm$^3$ g$^{-1}$)</th>
<th>$D_{p,BJH}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBAZr10</td>
<td>536</td>
<td>0.53</td>
<td>4.2</td>
</tr>
<tr>
<td>SBAZr10Ce20Cu6</td>
<td>147</td>
<td>0.17</td>
<td>3.8</td>
</tr>
<tr>
<td>SBA</td>
<td>455</td>
<td>0.47</td>
<td>4.0</td>
</tr>
<tr>
<td>SBAZr10Ce20Cu6</td>
<td>139</td>
<td>0.16</td>
<td>3.8</td>
</tr>
<tr>
<td>SBAZrO$_2$10</td>
<td>330</td>
<td>0.35</td>
<td>4.2</td>
</tr>
<tr>
<td>SBAZrO$_2$10Ce20Cu6</td>
<td>215</td>
<td>0.27</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Fig. 3. X-ray diffraction patterns of the samples, fresh and after catalytic test (with $-U$ suffix).

Fig. 4. N$_2$ adsorption–desorption isotherm at $-196\ ^\circ\mathrm{C}$ and, in the inset, BJH pore size distribution of the sample SBAZr10Ce20Cu6.

Fig. 5. TEM image of the sample SBAZr10Ce20Cu6.
3.3.1. \( \text{H}_2 \)-TPR and XPS – redox behaviour

The redox behavior of catalysts can be studied with \( \text{H}_2 \)-TPR and XPS techniques. The CO-PROX reaction was studied by several authors [26–29] and a Mars-Van Krevelen type reaction mechanism is widely accepted and a correlation between redox and catalytic properties is strongly suggested. These properties are attributed to the interactions between CeO\(_2\) and CeO\(_2\)-ZrO\(_2\) interfaces, as previously discussed [20]. \( \text{H}_2 \)-TPR studies showing the reducibility of metallic species were widely used in catalyst characterization, especially when metallic oxides are involved in the active phase. The profiles of the samples are shown in Fig. 6 and compared with a CuO reference using the equivalent amount of copper.

The reduction of CeO\(_2\) and ZrO\(_2\) [10–12] cannot occur in the studied temperature range. The reduction of CuO supported on CeO\(_2\) and CeO\(_2\)-ZrO\(_2\) was observed to start at a much lower temperature (>50°C) than bulk CuO. All the consumption of hydrogen in these samples is associated to the reduction of copper species [8]. The TPR curve of the CuO reference shows a \( \text{H}_2 \) consumption peak at 232°C. The incorporation of high dispersed ZrO\(_2\) on the surface of the support increases the dispersion of Cu and Ce species, giving rise to a shift of the maximum of the TPR curve at a lower temperature (225°C) and a shoulder at 211°C. Finally, when Zr is incorporated in the structure of the support (SBAZr10) the temperature of the maximum of the curve decreases to 204°C.

XPS was used to study the chemical state of the elements and their relative abundance at catalyst surface. Ce 3d and Cu 2p signals were of special interest to know the chemical state of the active phase of the fresh and used catalysts.

\( \text{Cu} \) 2p core levels spectra for fresh and used catalysts are shown in Fig. 7. A broad \( \text{Cu} \) 2p\(_{3/2}\) signal composed of two contributions at 932.8 and 934.8 eV with a shake-up satellite in the 940–945 eV region were observed for all the catalysts. The high binding energy contribution (934.8 eV) could be ascribed to the presence of CuO particles [8]. The second contribution at 932.8 eV can be assigned to reduced copper or small clusters of copper interacting with the support or with ceria. These observations are confirmed by XRD (Fig. 3) and TPR-\( \text{H}_2 \) (Fig. 6) by the presence of the shoulder at low reduction temperature.

After reaction, all the catalysts show a similar behavior, the partial reduction of copper species are highly denoted and could be estimated by the ratio between the intensity of the shake-up satellite peak and the main \( \text{Cu} \) 2p\(_{3/2}\) peak, with a significant reduction of this ratio for used catalyst. All fresh catalysts show a \( \text{I}_{\text{sat}}/I_{\text{mp}} \) value lower than that observed for CuO (0.55), indicating the presence of partially reduced copper species [8,12] formed by the interaction with ceria species [19,20]. These ratios are summarized in Table 3, showing a lower reduction degree in the catalyst with the SBAZr10 support.

Fig. 8 shows the Ce 3d core level spectra for the fresh and used SBAZr10Ce20Cu6 catalyst as an illustrative example. The core level Ce 3d signal is composed by several contributions and was early studied by Burroughs et al. [30], and several authors [31–33] used the nomenclature initially proposed. The core level of Ce 3d signal of ceria is composed by six contributions \( \nu_0, \nu_1, \nu_2 \) (Ce 3d\(_{5/2}\)) and \( \nu_0', \nu_1', \nu_2' \) (Ce 3d\(_{3/2}\)) that correspond to Ce\(_{3+}\) 3d final states and four peaks \( \nu_0, \nu_1, \nu_2 \) (Ce 3d\(_{5/2}\)) and \( \nu_0', \nu_1', \nu_2' \) (Ce 3d\(_{3/2}\)) corresponding to Ce\(_{3+}\) 3d final states. These final states are caused by the hybridization between the Ce 4f levels and O 2p states. Although the Ce 3d core level spectra are complex, an easy relation (Eq. (5)) can be used to estimate the amount of surface Ce\(_{3+}\):

\[
\text{Ce}^{3+}(\%) = \frac{S(\nu_1')}{S(\nu_1') + S(\nu_2')} \times 100 \tag{5}
\]

Fig. 8 shows the deconvolution of Ce 3d core level signal for the fresh and used SBAZr10Ce20Cu6 catalysts. The contribution of \( \nu_0 \) and \( \nu_0' \) corresponding to Ce\(_{3+}\) 3d\(_{5/2}\)/O\(_2\)\(_{5/2}\) final state at 880.5 and 989.8 eV are not considered due to low intensities of Ce 3d signal. Both Ce\(_{3+}\) and Ce\(_{4+}\) species are present before and after PROX reaction for all the catalysts. The Ce\(_{3+}\) percentages are summarized on Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zr/Ce</th>
<th>Cu/Ce</th>
<th>%Ce(_{3+})</th>
<th>Cu(<em>{\text{hot}})/Cu(</em>{\text{tot}})</th>
<th>(I_{\text{sat}}/I_{\text{mp}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBAZr10Ce20Cu6</td>
<td>0.6</td>
<td>1.0</td>
<td>21.5</td>
<td>0.23</td>
<td>0.45</td>
</tr>
<tr>
<td>SBAZr10Ce20Cu6U</td>
<td>0.3</td>
<td>0.9</td>
<td>22.0</td>
<td>0.68</td>
<td>0.25</td>
</tr>
<tr>
<td>SBAZr10Cu6</td>
<td>0</td>
<td>0.7</td>
<td>17.5</td>
<td>0.26</td>
<td>0.45</td>
</tr>
<tr>
<td>SBAZr10Ce20Cu6U</td>
<td>0</td>
<td>0.6</td>
<td>25.8</td>
<td>0.69</td>
<td>0.19</td>
</tr>
<tr>
<td>SBAZrZr10Ce20Cu6U</td>
<td>3.1</td>
<td>1.6</td>
<td>16.5</td>
<td>0.20</td>
<td>0.48</td>
</tr>
<tr>
<td>SBAZrZr10Ce20Cu6U</td>
<td>3.2</td>
<td>1.9</td>
<td>15.6</td>
<td>0.73</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Table 3: Redox parameters of fresh and used catalysts, calculated using data of Cu 2p, Zr 3d and Ce 3d regions.
showing a increase of Ce$^{3+}$ after reaction due to partial reduction of the catalyst. If all the percentages are compared the catalyst with SBAZr10 support shows a lower reduction degree after reaction and the best catalytic performance.

The presence of surface carbonates was detected at 288.8 eV in the C 1s core level signal close to the reference signal of adventitious carbon at 284.8 eV. The presence of surface carbonates is always observed on the surface of lanthanide oxides. The O 1s core level spectra show an asymmetric peak that can be decomposed in two contributions at 529.8 and 532.7 eV assigned to the metal-oxide and to silica, respectively. Si 2p and Zr 3d$^{5/2}$ core levels spectra have maxima at 103.0 eV and 182.3 eV, assigned to silica and Zr$^{4+}$, respectively. These XPS data in addition to the XRD data confirm that the catalysts are quite stable in catalytic operative conditions.

4. Conclusions

Zirconium doped SBA-15 appear to be good supports for the catalytic system CuO$_x$–CeO$_2$ to be used in the CO-PROX, due to the possible synergic effect of the dispersion of the active phases and their reducibility, as demonstrated by H$_2$-TPR and XPS studies. Most probably the organized surface of the support helps to provide a high dispersion of the nanometric size active phases, improving the contact between the particle interfaces, which were archived as active sites.

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