**Monoliths washcoated with AuCu catalysts for CO removal in an ethanol fuel processor:
effect of CeO₂-SiO₂ dual support on the catalytic performance and reactor cost**

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Abstract

Monoliths washcoated with AuCu/CeO₂-SiO₂ catalysts were evaluated in the CO removal from a syngas, using a single catalytic unit. Initially, powder catalysts of AuCu supported on mixed CeO₂-SiO₂ oxides with several SiO₂ loadings (0, 25, 50, 75 and 100 mol%) were assessed. SiO₂ addition into AuCu/CeO₂ increased the surface area of catalysts by up to 3.4 times and reduced its cost by up to 60 %, but also impacts CO conversion. However, structured catalysts were most effective to remove CO compared to powder samples. Computational fluid dynamics simulations of the monoliths showed that the improvement in heat diffusion and an intimate contact between the reactant gases and the catalytic monolith walls contribute to their high activity. Moreover, stability tests in on/off cycles at 220 °C for 100 h confirmed that outlet CO concentrations from monoliths washcoated with AuCu/CeO₂ (CO < 0.2 %) and AuCu/CeO₂-SiO₂ with 75 mol% of SiO₂ (CO < 3.6 %) is adequate to feed high temperature fuel cells. Besides, the cost of the Au/CeO₂-SiO₂ monolith (14 USD/g_{cat}) is 36 % lower compared to the AuCu/CeO₂ monolith, paving the way to the development of compact and economic systems to remove CO in bioethanol fuel processor units.

Keywords: CO cleanup; CO oxidation; H₂ oxidation; Structured catalysts; WGS.

1. Introduction

Hydrogen (H_2)-based technologies are promising to supply power to homes, industrial plants, vehicles, and small devices [1,2]. H_2 production in large-scale centralized facilities from non-renewable resources, such as natural gas [3], is well standardized. However, obtaining H_2 from renewable resources is a key point for the development of sustainable energy systems.

Furthermore, difficulties in H_2 delivery and storage have sparked interest in on-site production systems [3], where H_2 is produced using existing fuels, favoring decentralized energy production, even in places that are not connected to the electrical network or in remote installations [1]. The growth of biorefineries to produce biofuels, such as bioethanol and biodiesel [4], that can be used as a starting point to produce H_2 [5,6], offers an opportunity to implement sustainable energy models using H_2 .

Power production based on H_2 on-site systems is carried out in compact devices known as fuel processors units (FPU) [7,8], in which syngas (gas containing mainly H_2 and CO) is produced from a liquid fuel and subsequently purified to obtain H_2 suitable for fuel cells (FC) [9]. FC fed with H_2 (H_2 -FC) produce electricity, heat and water, without pollutants [10]. Recently, technoeconomic evaluations of FPU fed with bioethanol (B-FPU) have shown that these devices allow to produce H_2 economically competitive to current prices for H_2 -powered car refueling stations [3,11]. Figure 1 shows the steps involved in a B-FPU (i.e., syngas production by ethanol reforming and CO removal from the syngas). Ethanol reforming has been extensively studied [12,13], including the assessment of catalysts structured in foams [14], pellets [15] and monoliths [7,16]. However, CO removal still presents several challenges for catalysis and engineering process design.

Figure 1. Strategies to remove CO in a bioethanol fuel processor unit according to the type of fuel cell used. HT-WGS: high temperature water gas shift, LH-WGS: low temperature water gas shift, CO-SMET: CO selective methanation, CO-PROX: CO preferential oxidation, PSA: pressure swing adsorption.

Figure 1 shows that the steps to remove CO in the syngas depend on the type of H₂-FC to which the B-FPU will be connected. For FC with low CO tolerance, such as proton-exchange membrane FC (PEMFC), a low CO content (< 50 ppm [17]) in the syngas is required. Figure 1 shows that to ensure a low CO concentration two approaches have been proposed: (i) a traditional approach [18], where a series of catalytic reactions are carried out, including a reactor for a high temperature water gas shift (HT-WGS), followed by a reactor for a low temperature water gas shift (LH-WGS) and, finally, a reactor for CO selective methanation (CO-SMET) and/or CO preferential oxidation (CO-PROX). The advantage of the traditional approach is that

it ensures low CO concentrations (< 20 ppm [19]). However, the use of several units increases the volume and cost of the B-FPU, constraining its use in some compact applications. Alternative (ii) is based on the use of a pressure swing adsorption (PSA) unit [3] or selective membranes [20,21] after the WGS reactor. These processes significantly reduce the volume of B-FPU, but they are usually expensive.

The emergence of a new generation of more CO-tolerant H_2 -FC, such as high-temperature PEMFC (HT-PEMFC) that withstands up to 5 % of CO [22], has encouraged the development of new approaches to design simpler B-FPU [23]. Therefore, envisioning an early commercialization of CO-tolerant FC, we have worked on the development of a B-FPU that contains a single catalytic unit for CO removal. Firstly, we developed an active catalyst of RhPt/CeO₂-SiO₂ for stable syngas production from actual bioethanol (i.e., obtained from fermentation of residual biomass) [6,24]. Secondly, we identified an Au-Cu catalyst (with an Au/Cu molar ratio = 1 [25]) supported on nanoparticles of CeO₂ [26] as promising to perform CO removal from an actual syngas in a single unit. We chose CeO₂ as support among other alternatives (i.e., CeO₂, SiO₂, ZrO₂, Al₂O₃, La₂O₃, Fe₂O₃, CeO₂-SiO₂, CeO₂-ZrO₂ and CeO₂-Al₂O₃ [27]) due to its greater activity to oxidize CO; CeO₂ morphology was also studied, finding that a polyhedra nano-shape is an active and stable support for CO removal over a AuCu/CeO₂ system [26]. Now, our intention is to structure the AuCu/CeO₂ catalyst to favor the development of a compact B-FPU [3].

Recently, monolith reactors washcoated with powder catalysts supported on CeO₂ have been shown as promising for H₂-cleanup. Lacoste et al. [28] tested CuO-CeO₂/SBA-15 catalysts

deposited over cordierite monoliths in the CO-PROX suggesting that the macropores of cordierite walls conferred mechanical resistance to catalysts, contributing to high stability of the structured system. González-Castaño et al. [29] evaluated monoliths washcoated with a Pt/CeO₂/Al₂O₃ catalyst for WGS, reporting that the structured system favors water diffusion on metal-support interface, which could be a relevant point in the actual WGS process intensification. Landi et al. [30] studied monoliths washcoated with a CuO/CeO₂ catalyst for CO-PROX, showing that coated monoliths provided both conversion and selectivity higher than the reference powder catalyst. Then, cordierite monoliths washcoated with catalysts based on CeO₂ are attractive to develop a compact technology for the CO removal in syngas streams.

Most economic assessments of B-FPU have focused on the bioethanol reformer [11], finding few reports on the cost associated with cleaning H₂ through catalytic systems. In general, the use of noble metals such as Au is controversial in the CO removal process: some authors recommend avoiding Au due to its high cost [31], while others suggest that the high performance of noble metals translates into a most cost-effective catalyst [32]. Also, the cost of the catalyst associated with the support goes into the background. However, the high demand of CeO₂ for environmental applications and industrial processes [33] has increased its price. Figure 2a shows that the average cost of CeO₂ doubles other supports used in CO removal, such as ZrO₂, Al₂O₃, FeO₂ and SiO₂ [27]. Likewise, considering the overall price of the catalyst (i.e., active metals plus support), the AuCu/CeO₂ has a cost 73 % higher when compared to the other options (Figure 2b). The higher cost of CeO₂ has led us to look for alternatives to reduce its amount in the structured catalyst, seeking to decrease the cost of the catalytic system without significantly impacting its catalytic performance.

Figure 2. Cost of (a) metal oxides and (b) AuCu based catalysts commonly used for CO removal in a B-FPU. Values obtained from Sigma Aldrich (www.sigmaaldrich.com), Merck (www.merckmillipore.com), Fisher Scientific (www.fishersci.com) and Alfa Aesar (www.alfa.com) in February 2020 for presentations between 50-1000 g and purity > 99 %.

Figure 2a shows that SiO₂ is the cheapest support. Besides, in a preliminary study [27] it was identified that although the inclusion of a second metal oxide (i.e., ZrO₂, Al₂O₃ and SiO₂) in the CeO₂ matrix decreases its activity in CO removal, this effect is less significant in the CeO₂-SiO₂ system. The evaluation was carried out by fixing a Ce/Si molar ratio of 1 in the catalysts. Thus, prior to catalyst structuring, an evaluation of the effect of SiO₂ inclusion into the AuCu/CeO₂ catalyst over both the cost and the catalytic performance may be required.

In this contribution, CO removal from syngas was evaluated using a monolith reactor washcoated with AuCu-based catalysts, seeking to identify the potential of this catalytic system to be integrated in a B-FPU. Firstly, the effect of dual supports of CeO₂-SiO₂ with several SiO₂

loadings over the cost and activity of powder Au-Cu catalysts was determined. Then, activity and selectivity of structured catalysts were compared to powder samples. Also, a computational fluid dynamics (CFD) simulation of the monolithic reactors was carried out to identify profiles of temperature and concentration of chemical species throughout the channels of monolithic reactors. Finally, the stability of monoliths washcoated with AuCu/CeO₂ and AuCu/CeO₂-SiO₂ catalysts in the CO removal from a syngas was assessed. The study also included the use of characterization techniques such as high-resolution transmission electron microscopy (HR-TEM), UV-visible diffuse reflectance spectroscopy (UV-vis), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Raman spectroscopy, BET analysis, ultrasonic pulse test and thermal shock test.

2. Experimental

2.1 Synthesis of powder catalysts

Polycrystalline CeO₂ nanoparticles were obtained by the hydrothermal method as described in [26]. A solution 0.3 M of NaOH (Merck, Germany) was mixed slowly with an aqueous solution of Ce(NO₃)₃·6H₂O (Sigma Aldrich, USA), stirring at 500 rpm for 1 h. Then, the mixing was passed to an airtight container and heated at 100 °C for 24 h. The obtained slurry was filtered, washed with abundant water and calcined at 500 °C for 2 h. Formation of nanoparticles of CeO₂ was confirmed by HRTEM. CeO₂ occurs as polyhedral particles with an average diameter of 9±2 nm (Figure S-1 in Supplementary Material).

Afterwards, the dual supports of CeO₂-SiO₂ with several contents of SiO₂ (i.e., 0, 25, 50, 75 and 100 mol%) were prepared. For this, nanoparticles of CeO₂ were added into a slurry of SiO₂

(Merck, Germany). The mixing was dried at 80 °C for 12 h, carefully crushed in a mortar and calcined at 500 °C for 2 h. This preparation method was selected based on initial tests (Method 1, Figure S-2 and Table S-1 in Supplementary Material), where several alternatives to obtain the dual supports of CeO₂-SiO₂ were assessed. CeO₂-SiO₂ samples were labeled as CeSi-X, where X indicates the SiO₂ percent content in the support (X = 25, 50 and 75 mol% SiO₂).

1 wt% Au and 1 wt% Cu were impregnated onto the CeO₂-SiO₂ supports by deposition-precipitation and incipient wetness impregnation methods, respectively, using the procedure described in [25]. HAuCl₄·3H₂O (Sigma Aldrich, USA) and Cu(NO₃)₂·3H₂O (Sigma Aldrich, USA) were used as precursors of active metals. Catalysts were calcined at 500 °C for 4 h and sifted using a 140-mesh sieve. Before reaction, an activation pretreatment was performed in all catalyst samples [25], which consisted in a reduction at 300 °C with 8 % H₂/Ar stream for 1 h, followed by a purge with pure Ar stream for 30 min and ended by a stabilization in 10 % air/Ar stream for 30 min. AuCu/CeO₂-SiO₂ samples were labeled as “Activated” catalysts.

2.2 Preparation of catalytic monoliths

Cordierite monoliths (Corning Inc.) with 400 CPSI (cells per square inch) and 2 cm long were used. Monoliths were washcoated by repetitive immersion in a slurry of powder catalyst (25 wt% of catalyst in the slurry), followed by drying at 105 °C for 1 h under continuous rotation (60 rpm), and calcination in muffle at 500 °C for 4 h. Polyvinyl alcohol (PVA) was used as a binder with a proportion of 0.6 g_{PVA}/g_{cat}. A net catalyst loading of 3.3 mg_{cat}/cm² in the monoliths was achieved. Before reaction, the washcoated monoliths were activated using the same procedure described for powder samples. Stability of monolith coatings was assessed by ultrasonic pulses.

In particular, washcoated monoliths were submerged into acetone in a ultrasonic bath (Fisher Scientific, USA) for 10 s, then dried at 70 °C for 1 h and weighted [34]; the procedure was repeated to achieve 100 s. Adhesion of the washcoat was assessed by a thermal shock test [7]. For this, monoliths were heated at 700 °C for 1 h and then quickly cooled down with abundant N₂ (500 mL/min). The procedure was repeated three times, determining catalyst losses in each cycle. The data of all characterization tests are available at the website [data set] [35].

2.3 Activity and stability tests

Powder samples of AuCu supported on dual oxides of CeO₂-SiO₂ were evaluated in CO removal with a syngas containing H₂ (19.9±0.3 mol%), CO (6.3±0.1 mol%), CO₂ (5.2±0.5 mol%), O₂ (5.6±0.3 mol%), H₂O (7.8±0.2 mol%) and N₂ (55.2±0.6 mol%). Syngas composition was defined in preliminary tests where a cordierite monolith washcoated with a RhPt/CeO₂-SiO₂ catalyst was evaluated in the ethanol steam reforming. Besides, an excess oxygen factor (λ) of 1.8 was fixed, which was optimized in a previous work [25]. Channeling and back mixing through the catalyst bed were avoided using a ratio of 50 between the catalyst bed height (L) and catalyst particle size (D_p), and a ratio of 60 between the reactor internal diameter (D) and D_p [36,37]. 0.200 g of catalyst with 0.200 g of ground quartz as a diluent were used in all tests, achieving a space velocity (SV) of 5.6 ± 0.3 L/g_{cat}*min. Species at the outlet stream of the catalytic system were continuous monitored, using a Clarus 580 gas chromatograph (GC, Perkin Elmer, USA) equipped with a Carboxen 1010 plot column (30 m, 0.53 mm, Restek, USA) connected to a thermal conductivity detector (TCD), using N₂ (20 mL/min) as internal reference. An isothermal method at 60 °C was used in the GC unit.

CO removal was also assessed over monoliths washcoated with AuCu/CeO₂ and AuCu/CeO₂-SiO₂ (75 mol% of SiO₂), using a syngas with the same composition described in the evaluation of powder samples. Activity was tested between 100 to 300 °C and stability was evaluated in on/off tests at 220 °C. The species at the outlet stream were quantified online, using a 490 micro-GC (Agilent Technologies, USA) equipped with three columns connected with several TCD. N₂ (60 mL/min) was used as internal reference and isothermal method at 60 °C was used. Elemental balances between the inlet and the outlet streams of the reactor were quantified in all tests, achieving balances of C, H and O > 90 %.

Conversion (x_i) of CO and H₂, and the molar composition (y_i) of outlet streams were calculated by Eq. 1 and 2, respectively.

$$x_i = \frac{N_{inlet} - N_{outlet}}{N_{inlet}} * 100 \quad \text{Eq. 1}$$

$$y_i = \frac{N_{j,outlet}}{\sum_0^n N_{j,outlet}} * 100 \quad \text{Eq. 2}$$

Where N_{inlet} is the flow (mol/min) of CO or H₂ inlet into the reactor, N_{outlet} is the flow (mol/min) of CO or H₂ leaving the reactor, and $N_{j,outlet}$ is the flow (mol/min) of species j (i.e., H₂, CO, CO₂, O₂ and N₂) leaving the reactor. The data of activity and stability tests are available at the website [data set] [35].

2.4 Catalysts characterization

HRTEM micrographs of CeO₂ nanoparticles were obtained in a Tecnai F20 Super Twin unit (FEI, USA). UV-vis spectroscopy was carried out using a UV-VIS-NIR 3600 spectrophotometer

(Shimadzu, Japan) equipped with PMT, InGaAs, PbS light detectors and an ISR-3100 accessory. The spectra were recorded at room temperature in the wavelength range of 200–800 nm with 0.1 nm of resolution. Barium sulphate was used as a reflectance standard. XPS spectra of catalysts were obtained using a SPECS system (SPECS group, Germany) equipped with a XR-50 X-ray source and a Phoibos 150 EP hemispherical energy analyzer with MCD-9 detector. The binding energy (BE) values were obtained with a precision of 0.1 eV, maintaining the analysis chamber below 10^{-7} Pa. XPS data was processed in CasaXPS software, adjusting the adventitious C 1s line at 284.8 eV. XRD was conducted in a D5000 diffractometer (Siemens, Germany) using Cu K α radiation (45 kV, 35 mA). Profiles were collected in 2θ at range of 20 to 100°, using a step of 0.02° and 1 s/step. The lattice parameter and the average crystallite size of CeO₂ were determined by a Rietveld refinement of diffraction patterns in FullProf suite software (2019 version, France), ensuring a Chi-square test (χ^2) < 2.0 and a R-weighted pattern (R_{wp}) < 30 %. Raman spectroscopy was carried out in a RE 0.4 in Via Qontor confocal microscope (Renishaw, UK) equipped with a 532.1 ± 0.3 nm laser. Spectra were collected using an exposure time of 2 s, 1 % of laser power and 48 accumulated scans. Surface area of powder samples was determined by BET method in a ChemBET Pulsar unit (Quantachrome Instruments, USA). 0.1 g of sample was degassed at 120 °C for 2 h in inert gas (N₂, 20 mL/min). BET surface area was determined with a 30 % N₂/He stream in a liquid N₂ bath.

2.5 CFD simulation

CFD simulation of the catalytic system, considering the actual dimensions of the monoliths, was carried out in COMSOL Multiphysics commercial software (V5.5), according to methodology detailed in [38]. A mesh independence test was performed to ensure an accurate numerical

solution, identifying that more than 12,000 elements are enough for the CFD model.

Thermodynamic and transport assumptions for reactive gas and monolith are summarized in Table S-2, Supplementary Material. Table 1 shows the governing equations (Eq. 3 to 6), kinetic model (Eq. 7 and 9), and chemical reactions (Eq. 10 to 12) considered in the CFD model. Kinetic models based on power law (Eq. 7 in Table 1) are widely accepted for the CO removal on Au and Cu catalysts [39–41]. Thermodynamic and transport properties were modelled by polynomial approximations, using NASA coefficients [42].

Table 1. Governing equations, kinetic model and reaction network involved in CFD simulations

Equation/Reaction ^a	Description	
$\nabla(\rho_f \cdot u) = 0$	Continuity equation	Eq. 3
$-\nabla p + \nabla \cdot (\mu(\nabla u + (\nabla u)^T)) - \frac{2}{3}\mu(\nabla \cdot u)I + F = 0$	Momentum balance	Eq. 4
$\rho_f C_p u \cdot \nabla T + \nabla \cdot (-k_{con} \nabla T) = Q + Q_r$	Energy balance	Eq. 5
$\nabla \cdot (-D_i \nabla c_i + u c_i) = R_i$	Convection-diffusion equation	Eq. 6
$r_n = k_n \sum c_i^{\gamma_i} - \frac{k_n}{K_n} \sum c_i^{\gamma_i}$	Power law equation	Eq. 7
$k_n = k_{\infty_j} e^{-\frac{E_{aj}}{RT}}$	Arrhenius equation	Eq. 8
$K_n = e^{-\frac{\Delta G^\circ}{RT}} \prod \left(C_t \frac{P^\circ}{P} \right)^\gamma$	Chemical equilibrium	Eq. 9
$\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$	WGS reaction	Eq. 10
$\text{CO(g)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$	CO oxidation	Eq. 11
$\text{H}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(g)}$	H ₂ oxidation	Eq. 12

^a ρ_f = density, u = velocity vector, p = pressure, I = identity matrix, μ = dynamic viscosity, F = external forces, C_p = heat capacity, T = temperature, k_{con} = thermal conductivity, Q = external heat, Q_r = reaction heat, D_i = diffusion coefficient, i = species (i.e., CO, H₂O, CO₂, O₂ or H₂), c_i = molar concentration, R_i = species surface rate, r_n = reaction rate, n = chemical equation (i.e., WGS, CO oxidation or H₂ oxidation), k_n = reaction rate constant, γ_i = stoichiometric coefficient, K_n = reaction rate constant of equilibrium, k_{∞_j} = pre-exponential factor, E_{aj} = activation energy, R = universal gas constant, ΔG° = Gibbs free energy (including formation terms), C_t = sum of all concentration species, P° = standard pressure.

3. Results and discussion

3.1 Relationship between cost and activity of the powder catalysts

Table 2 shows the total price of catalysts (1 wt% Au and 1 wt% Cu) supported on several CeO₂-SiO₂ supports. Costs were calculated according to the information detailed in Table S-3 (Supplementary Material), considering the losses during the synthesis of catalysts and actual market prices of each reagent. The cost associated with active metals (Cu + Au) is ~3.5 USD/g_{cat} for all samples. Thus, the catalysts cost associated to the support would range between 21 and 84 %, depending mainly on the CeO₂ content. The high cost of CeO₂ is the result of its high market price (Figure 2a) and the losses during its synthesis to ensure homogeneous nanoparticles; cheaper CeO₂, namely, without a homogeneous and well-defined morphology, would lead to a rapid deactivation, as shown in [26]. Therefore, inclusion of SiO₂ in AuCu/CeO₂ have a positive effect in terms of the cost of the catalysts, achieving a price up to 1.6 times lower for AuCu/CeSi-75 compared to AuCu/Ce.

Table 2. Price of catalysts and the minimum CO concentration obtained in the outlet stream of the reactor

Catalyst	Total price (USD/g _{cat})	Cost associated with the support (%)	T (°C)	CO concentration achieved (mol%)
AuCu/Ce	21	84	220	0.4
AuCu/CeSi-25	19	82	220	0.6
AuCu/CeSi-50	17	80	220	1.7
AuCu/CeSi-75	13	73	260	1.1
AuCu/Si	4	21	260	4.0
Monolith washcoated with AuCu/Ce	22	82	260	0.2
Monolith washcoated with AuCu/CeSi-75	14	71	300	0.3

Figure 3. CO conversion obtained over (a) bare supports and (b) supported AuCu catalysts.

CeO₂-SiO₂ supports were labeled as CeSi-X, where X indicates the SiO₂ percent content (X = 25, 50 and 75 mol% SiO₂). Syngas feed: H₂ (19.9±0.3 mol%), CO (6.3±0.1 mol%), CO₂ (5.2±0.5 mol%), O₂ (5.6±0.3 mol%), H₂O (7.8±0.2 mol%), and N₂ (55.2±0.6 mol%). Reaction conditions: SV of 5.6 ± 0.3 L/g_{cat}*min and 0.35 g of the catalytic bed.

Figure 3 shows the CO conversion from a syngas stream over the bare supports and supported AuCu catalysts. Volcano type curves [34] are observed for the CO conversion over both bare supports (Figure 3a) and AuCu catalysts (Figure 3b). Inclusion of active metals (Au and Cu) improves CO conversion; however, the activity of catalysts decreases with the SiO₂ content in the support. Notwithstanding, most of AuCu catalysts (except AuCu/CeSi-50 and AuCu/Si) favor a CO conversion > 85 % (Figure 3b). While highly active catalysts are desirable, complete CO removal is not required for a B-FPU connected to a FC with high CO tolerance, as recent

research has allowed for the development of HT-PEMFC that resist up to 5 % of CO in the cleaned H₂ stream [22]. Table 2 shows the minimum CO concentration in the outlet stream obtained with each sample. Most catalysts (except AuCu/Si) ensured CO concentrations < 5 %, paving the way to carry out CO removal from syngas using a single catalytic unit. Despite being the most active, the cost of AuCu/Ce is 9 % higher than that of AuCu/CeSi-25 and 61 % higher than AuCu/CeSi-75. Therefore, AuCu/CeO₂-SiO₂ catalysts show promising features in terms of cost and activity to be integrated into a B-FPU to produce H₂ streams adequate for HT-PEMFC.

The effectiveness of the AuCu system to promote CO oxidation has been well documented by other researchers [43–45]. Additionally, in previous studies [25,27] we identified that Au contributes to the formation of CO* intermediates while Cu provides reactive oxygen on the catalytic surface, and this combined effect favors the CO conversion on AuCu/CeO₂ catalysts, as seen in Figure 3b. However, dilution of CeO₂ with a second support as SiO₂ impacts its ability to convert CO [27]. Nevertheless, AuCu/CeSi-75 sample shows a CO conversion higher than that of AuCu/CeSi-50 (Figure 3b), indicating that the SiO₂ inclusion in the AuCu/CeO₂ system could alter several properties of the catalysts. Consequently, to understand the effect of the presence of SiO₂ in the catalyst, several characterization tests were carried out on the powder samples before monolith evaluation.

3.2 Effect of SiO₂ on the surface and structure of AuCu/CeO₂-SiO₂ catalysts

3.2.1 UV-vis spectroscopy

Catalyst surface of the activated samples of AuCu catalysts was assessed by UV-vis spectroscopy. Figure 4a shows the UV-vis spectra of the AuCu catalysts. Catalysts based on CeO₂ show the typical absorptions for O²⁻→Ce⁴⁺ charge transfer (277 nm) and cerium inter-band transitions (347 nm) [46]. However, the presence of a second oxide as SiO₂ can alter the optical absorption of CeO₂, favoring a slight shift in wavelength [47]. Moreover, absorption with $\lambda \geq 470$ nm confirms the presence of active metals (Au and Cu [48,49]). The intensity and width of the bands are usually related to the size and shape of the active particles on the catalyst surface. Signal related to spherical Au particles ($\lambda \sim 528$ nm) can present a red-shift towards higher wavelength due to changes in particle size and morphology of Au [49]. Similarly, bands associated with Cu⁺ (472 nm) and Cu²⁺ (692 nm) are susceptible to a red-shift due to changes on the interaction of Cu with the support [48]. AuCu/Ce-50 and AuCu/CeSi-75 catalysts show wider and less intense bands than the other samples (Figure 4a), indicating the formation of active particles of several morphologies and sizes on the catalytic surface. Thus, SiO₂ is likely producing a change in the distribution of active particles on the catalyst surface, which promotes variations in the activity of AuCu catalysts (Figures 3b). Consequently, the catalytic surface was also studied by XPS (*vide infra*).

Figure 4. (a) UV-vis spectra for activated samples of Au-Cu catalysts. (b) Correlation of the lattice parameter and the average crystallite size of CeO₂ obtained by a Rietveld refinement of XRD patterns of Au-Cu catalysts. CeO₂-SiO₂ supports were labeled as CeSi-X, where X indicates the SiO₂ percent content (X = 25, 50 and 75 mol% SiO₂).

3.2.2 XPS

The surface composition of AuCu catalysts was studied by XPS. Figure 5 shows the XPS spectra for Au, Cu and Ce, and Table 3 shows the surface concentration of Au and Cu. The amount of Au and Cu exposed decreases with the SiO₂ content in the support, indicating that SiO₂ could favor the adsorption of active metals towards the bulk of the support or the formation of larger particles [37], which would confirm the presence of particles of Au and Cu with several morphologies, as proposed in the UV-vis spectroscopy section.

Table 3. Atomic surface content, Auger parameter, $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio, TO/ F_{2g} index and BETsurface area of AuCu/ CeO_2 - SiO_2 catalysts

Catalyst	Surface content (at%) ^a		Auger parameter ^a	$\text{Ce}^{3+}/\text{Ce}^{4+}$ ^a	TO/ F_{2g} index (10^2) ^b		BET surface area ($\text{m}^2/\text{g}_{\text{cat}}$) ^c
	Au	Cu			Activated	Used	
AuCu/Ce	1.7	5.0	1849.4	0.21	7.3	6.9	81
AuCu/CeSi-25	1.1	4.0	1849.0	0.18	5.5	5.3	115
AuCu/CeSi-50	1.4	3.2	1849.6	0.18	4.0	3.9	160
AuCu/CeSi-75	1.0	2.4	1849.1	0.18	2.9	2.8	275
AuCu/Si	0.6	2.2	1849.4	N/A	N/A	N/A	453

A: activated; U: Used; N/A: Not applicable. ^ameasured by XPS; ^bmeasured by Raman spectroscopy; ^cmeasured by N_2 adsorption.

Figure 5. XP spectra for (a) Au 4f, (b) Cu $2p_{3/2}$ and (c) Ce 3d in activated samples of AuCu catalysts supported on CeO_2 - SiO_2 with several SiO_2 loadings. CeO_2 - SiO_2 supports were labeled as CeSi-X, where X indicates the SiO_2 percent content ($X = 25, 50$ and 75 mol% SiO_2).

Figure 5a shows the XPS spectra for Au 4f_{5/2} and 4f_{7/2}. The characteristic peak at 83.8 eV shows the presence of only Au⁰ species [50], which act as CO adsorption sites [25,51]. Also, Figure 5b shows the XPS spectra for Cu 2p_{3/2}. The well-known Cu²⁺ satellites around 940 eV confirm the presence of oxidized Cu species (CuO), which is in line with previous reports [25,44]. However, the identification of reduced Cu species (i.e., Cu⁰ and Cu⁺), associated with the 932.6 eV peak, is difficult or impossible only by the Cu2p XPS spectra [52]. For this, we used the Cu LMM Auger spectra to identify the presence of reduced Cu species. Table 3 shows the modified Auger parameters for the AuCu catalysts. Most of the samples has an Auger parameter corresponding to the Cu⁺ species (1849.2 to 1849.8 eV [52]). No evidence of the presence of Cu⁰ (~1851.2 eV [52]) was identified. Both Cu²⁺ and Cu⁺ species have been associated with the enhancement of CO oxidation during H₂ cleanup [25,53]. Then, the alteration in the concentration of Au and Cu in the catalytic surface by SiO₂ presence could favor changes on the activity of catalysts (Figure 3b).

The oxidation state of Ce is frequently used to determine the interaction of active metals with CeO₂ [51]. Figure 5c shows the XPS spectra for Ce 3d_{5/2} and 3d_{3/2}, where the five pairs of spin-orbit doublets are observed (V₀, V, V', V'' and V''' for Ce 3d_{5/2} and U₀, U, U', U'' and U''' for Ce 3d_{3/2}) [25,54]. The peaks V₀, V', U₀ and U' are associated with the presence of reduced species (Ce³⁺), and the rest of peaks correspond to Ce⁴⁺ species [55]. Formation of Ce³⁺ species is favored by interaction between CeO₂ and cations such as Cu²⁺ [56,57]. Table 3 shows that the Ce³⁺/Ce⁴⁺ ratio, related to the formation of oxygen vacancies [25,55], decreases by about 14 % in AuCu catalysts supported on mixed oxides (i.e., AuCu/CeSi-25, AuCu/CeSi-50 and AuCu/CeSi-75) with respect to the AuCu/Ce sample (Table 3). The decrease in the Ce³⁺/Ce⁴⁺

ratio suggests that SiO₂ alter oxygen vacancies of CeO₂, decreasing the CO oxidation capacity of catalysts [58].

3.2.3 XRD

The crystal structure of CeO₂ in the activated samples of supported AuCu catalysts was evaluated by XRD (see Figure S-3, Supplementary Material). Figure 4b correlates the lattice parameter and the average CeO₂ crystal size obtained by a Rietveld refinement. The CeO₂ lattice size decreases in the AuCu/CeO₂ sample compared to the bare CeO₂. A decreasing in lattice size has been associated with the replacement of Ce⁴⁺ ions by CuO species [59,60], which favors the formation of oxygen vacancies [56]. Likewise, as the SiO₂ content increases in the AuCu/CeO₂ system, the lattice parameter of CeO₂ increases, indicating a lower CuO-CeO₂ interaction, probably because of the new interaction between Cu and SiO₂. Also, the average crystal size of CeO₂ does not change significantly by the presence of SiO₂, obtaining a size of 14.4 ± 0.4 nm for all AuCu catalysts. Therefore, the reduction of oxygen vacancies observed by XPS could be associated with an additional interaction between Cu and SiO₂, without affecting the CeO₂ structure.

3.2.4 Raman spectroscopy

The CeO₂ structure in the activated and used samples of AuCu catalysts was studied by Raman spectroscopy. Figure 6 shows the Raman spectra for Au-Cu catalysts containing CeO₂. In all the samples, CeO₂ shows the typical F_{g2} mode at 464 cm⁻¹ and two satellite bands at 240 (transverse optical mode, TO) and 600 cm⁻¹ (longitudinal optical mode, LO), related to oxygen vacancies in CeO₂ [61,62]. Table 3 contains the TO/F_{g2} index that allows comparing the number of defects in

the lattice associated with oxygen vacancies in CeO₂. The results in Table 3 show that the higher the SiO₂ content, the lower the TO/F_{g2} index value, in agreement with the XPS results, where a decrease in the Ce³⁺/Ce⁴⁺ ratio was also observed in AuCu catalysts supported on dual oxides.

Figure 6. Raman spectra for (a) activated and (b) used samples of supported AuCu catalysts. CeO₂-SiO₂ supports were labeled as CeSi-X, where X indicates the SiO₂ percent content (X = 25, 50 and 75 mol% SiO₂).

The variation in the TO/F_{g2} index (Table 3) between activated and used samples was less than 5 %. Additionally, no signal was identified in mode G (1590 cm⁻¹, associated with stable carbon deposits) and D (1350 cm⁻¹, associated with amorphous carbon) of carbon, indicating that carbon formation would not be a relevant aspect on AuCu catalysts supported on mixed CeO₂-SiO₂ oxides [27]. Thus, the characterization tests presented here and those previously reported in [26,27] show that the AuCu/CeO₂-SiO₂ supported catalysts appear not to be susceptible to

significant changes during CO removal in a single unit, which could be beneficial for long term operations.

3.2.5 BET surface area

Table 3 shows the surface area of the AuCu catalysts. The surface area of the catalysts increases with the SiO₂ content, but not linearly. For example, the increase in the surface area of AuCu/CeSi-25 is 1.4 times greater than that of AuCu/Ce, but for the AuCu/CeSi-50 and AuCu/CeSi-75 the increase is 2.0 and 3.4 times, respectively. As presented above, inclusion of SiO₂ in AuCu/CeO₂ system decreases oxygen vacancies of CeO₂, impacting oxidation capacity of catalysts. However, SiO₂ interacts also actively with active metals and promotes an increase in surface area of AuCu catalysts, which are key characteristics to favor CO adsorption on catalytic surface during CO removal [26,34]. Therefore, we speculate that with a 75 mol% of SiO₂ in the support of the AuCu/CeO₂ system, the increase in surface area mitigates the impact of the reduction of oxygen vacancies, favoring AuCu/CeSi-75 to have a higher activity than AuCu/CeO₂-50 (Figure 3b).

3.3 Monolith evaluation

In this section, monolithic reactors were evaluated in the CO removal from a syngas in a single catalytic unit. The most active catalyst (i.e., AuCu/Ce) and the most economical one (i.e., AuCu/CeSi-75) that ensured CO concentrations < 5 % (Table 2) were used to prepare the monolith catalysts.

3.3.1 Washcoating assessment

Physical stability and adhesion of the catalyst were evaluated with ultrasonic and thermal shock tests. Figure S-4 (Supplemental Material) shows the catalyst weight loss corresponding to the ultrasonic and thermal shock cycles. The monolith washcoated with the AuCu/CeSi-75 catalyst showed about 50 % less loss of coating in both tests, suggesting that the presence of SiO₂ favors a better adherence of the catalyst to the monolith walls. Tiscornia et al. [34] evaluated monoliths of cordierite washcoated with a CuO/CeO₂/SiO₂ catalysts, reporting that Aerosil (fumed silica) particles anchored to the macroporous walls of the cordierite contribute to a high mechanical stability. That is, the inclusion of SiO₂ in the AuCu/CeO₂ system reduces the price of the catalyst (Table 2) and improves the adhesion of the catalyst coating to the walls of the monolithic reactor.

3.3.2 Catalytic activity of monoliths

Honeycomb monoliths present an opportunity to structure catalysts for CO removal from a syngas because they reduce the volume of the reactor, which is a critical factor for the implementation of H₂-based technology in compact applications [34]. Figure 7 shows the conversion of CO and H₂ obtained with the monoliths washcoated with AuCu/Ce and AuCu/CeSi-75, where the results using powder samples were included for comparison purposes. Over 240 °C, monolithic reactors are more effective in CO removal compared to their equivalent powder samples, which could be associated with an improvement in the transfer of mass and heat into the monoliths, as discussed later. Also, both monoliths washcoated with AuCu/Ce and AuCu/CeSi-75 have similar activity at high temperatures (> 260 °C), achieving CO conversion > 95 % and H₂ loss < 10 %. As presented in Table 2, the price of the washcoated monolith is only slightly higher than the powder samples due to the low price of cordierite. Therefore, cordierite

monoliths offer an increased activity at higher temperatures with similar cost compared to non-structured samples.

Figure 7. Conversion of (a) CO and (b) H₂ obtained in the CO removal from a syngas over powder catalysts and monoliths washcoated with AuCu/Ce and AuCu/CeSi-75 samples. Suffixes P: powder and M: monolith. Syngas feed: H₂ (19.9±0.3 mol%), CO (6.3±0.1 mol%), CO₂ (5.2±0.5 mol%), O₂ (5.6±0.3 mol%), H₂O (7.8±0.2 mol%), and N₂ (55.2±0.6 mol%). Reaction conditions: SV = 5.6 ± 0.3 L/g_{cat}*min.

Table 4 compares the activity of several structured catalysts in cordierite monoliths for CO removal. In general, it is possible to obtain a high CO conversion (> 95 %) using monolithic reactors. There were no previous reports on the CO removal of a syngas coming directly from an ethanol reformer in a single unit. That is why we reported an initial CO concentration > 6 mol%, with a H₂/CO of 3.1, which is the outlet condition of the syngas coming from a reformer. These

conditions are more severe than those evaluated over monolithic reactors at CO-PROX conditions after several previous pre-cleaning units (i.e., $\text{CO} < 2 \text{ mol\%}$ and $\text{H}_2/\text{CO} \gg 10$). All the works reported in Table 4 used the traditional way to remove CO in fuel reformers (i.e., $\text{HT-WGS} \rightarrow \text{LH-WGS} \rightarrow \text{CO-SMET/CO-PROX}$, Figure 1), with higher H_2/CO ratios [19], which favors CO conversion during the final stage of CO-SMET and/or CO-PROX [63]. Thus, despite that they were evaluated under more severe conditions, AuCu/Ce and AuCu/CeSi-75 show similar performance to previous reports for CO removal over structured catalysts. Therefore, structured AuCu/Ce and AuCu/CeSi-75 catalysts are promising to remove CO in a single catalytic unit, showing higher activity than powder samples at temperatures higher than 240 °C. A CFD simulation was carried out to find an explanation of the observed high performance of the structured catalysts.

Table 4. Comparison of several structured catalysts for CO removal

Coating of monolith	Gas composition in the inlet stream	Reaction	T (°C)	CO conversion (%)	Ref.
Pt/CeO ₂ /Al ₂ O ₃	H ₂ (50 mol%), CO (7 mol%), CO ₂ (7 mol%), H ₂ O (30 mol%) and N ₂ as balance.	WGS	310	~100*	[29]
CuO-CeO ₂ /SiO ₂	H ₂ (40 mol%), CO (1 mol%), O ₂ (1 mol%) and He as balance.	CO-PROX	160	99	[34]
CuO/CeO ₂	H ₂ (50 mol%), CO (0.5 mol%), O ₂ (0.9 mol%) and N ₂ as balance.	CO-PROX	150	~100*	[30]
Ru/TiO ₂	H ₂ (60 mol%), CO (1.0 mol%), CO ₂ (20 mol%), H ₂ O (15 mol%) and N ₂ as balance.	CO-SMET	220	100	[17]
PtCu/Al ₂ O ₃	H ₂ (40 mol%), CO (1 mol%), O ₂ (1 mol%) and He as balance.	CO-PROX	110	100	[64]
CuO/CeO ₂	H ₂ (50 mol%), CO (0.5 mol%), O ₂ (0.9 mol%) and N ₂ as balance.	CO-PROX	150	99	[65]

AuCu/CeO ₂ - SiO ₂	H ₂ (19.9±0.3 mol%), CO (6.3±0.1 mol%), CO ₂ (5.2±0.5 mol%), O ₂ (5.6±0.3 mol%), H ₂ O (7.8±0.2 mol%) and N ₂ as balance.	WGS, CO- PROX	260	95	This work
AuCu/CeO ₂	H ₂ (19.9±0.3 mol%), CO (6.3±0.1 mol%), CO ₂ (5.2±0.5 mol%), O ₂ (5.6±0.3 mol%), H ₂ O (7.8±0.2 mol%) and N ₂ as balance.	WGS, CO- PROX	300	96	This work

*Values obtained from graphical estimation

3.3.3 CFD model

CO removal from syngas over washcoated monoliths was modeled by CFD, seeking to explain the improvement of catalytic activity in monoliths compared to powder samples at temperatures higher than 240 °C (Figure 7). Figure S-5 (Supplementary Material) shows the excellent agreement between the experimental CO, H₂, CO₂ and O₂ flows at the outlet stream of the monolithic reactors and the results obtained in COMSOL Multiphysics. Then, CFD allows to model simultaneously mass and heat transfer and kinetics of the process [38]. Kinetic parameters obtained by non-linear regression of power law model (Eq. 7, Table 1) are presented in Table S-4 (Supplementary Material). Parity plots (Figure S-6 in Supplementary Material) show that CFD models adequately fit the experimental data, ensuring a deviation < 10 % in most of the values, which indicates that the models correctly predict the product distribution in both AuCu/Ce and AuCu/CeSi-75 monolithic reactors.

The temperature profile in the monoliths was also studied with the CFD simulation. Figure 9 shows that the temperature on the external walls of the monolith (which is the same as the furnace) is lower than the temperature in the internal channels of the monoliths. Actually, WGS ($\Delta H = -42$ kJ/mol), CO oxidation ($\Delta H = -283$ kJ/mol) and H₂ oxidation ($\Delta H = -241$ kJ/mol) are

exothermic reactions [66], which favor the increase in the temperature of the internal channels of the reactors. The temperature gradient can be up to 80 °C when the furnace operates at 300 °C. For non-reversible reactions, as CO oxidation, temperature favors an increase in reaction rate [67]. Therefore, increased temperature in internal channels could be associated with improved activity to CO removal over monolithic reactors compared to powder samples (Figure 7). In addition, the temperature increase is greater at the entrance of the monolith, since the CO conversion occurs mainly at the first 5 mm of the channels, as shown Figure 9. A high CO conversion in the initial section of the channels also shows that the reactive gas interacts easily with catalyst adhered to the walls. Landi et al. [30] proposed that washcoated monoliths prevent the intra-particle mass transfer limitation (typically observed in powder samples), favoring CO oxidation during CO-PROX. Consequently, structured monoliths promote improvements in mass and heat transfer favoring an increase in activity, which match with previous reports [29,30,34,64]. Then, stability of structured catalysts (i.e., monoliths based on AuCu/Ce and AuCu/CeSi-75 catalysts) was evaluated in intermittent operation tests.

Figure 8. Temperature profiles for cross section of (a) a monolith washcoated with AuCu/Ce catalysts operating at 200 °C, (b) a monolith washcoated with AuCu/CeSi-75 catalysts operating at 200 °C, (c) a monolith washcoated with AuCu/Ce catalysts operating at 300 °C and (d) a monolith washcoated with AuCu/CeSi-75 catalysts operating at 300 °C.

Figure 9. Molar concentration of CO at several temperatures vs. channel length of monoliths washcoated with (a) AuCu/Ce and (b) AuCu/CeSi-75 catalysts.

3.3.4 Stability of monoliths in on/off test

Thinking in a future implementation in fixed or mobile applications, stability of FPU is commonly evaluated by on/off stability tests (also called start-up/shutdown cycling) [7,32]. Figure 10 shows the conversion of CO and H₂ and the distribution of products obtained in an on/off test with monoliths washcoated with AuCu catalysts. Monolithic reactors were evaluated at 220 °C to prevent complete CO conversion, favoring the identification of deactivation phenomena [68]. The monolith washcoated with AuCu/Ce (Figure 10a) shows a stable conversion of CO (92 ± 2 %) and H₂ (11 ± 2 %), while the monolith washcoated with AuCu/CeSi-75 (Figure 10b) loses about 6 % of its initial CO activity (73 %). However, H₂ conversion decreases on the AuCu/CeSi-75 monolith, which is a beneficial effect, achieving only a ~4 % H₂ loss at the end of the test. Also, Figures 10c and d show that despite not being evaluated at the maximum CO conversion temperature, but at 220 °C, both AuCu/Ce (CO ≤ 0.2 %) and AuCu/CeSi-75 (CO ≤ 3.6 %) systems ensure a clean H₂ stream with a CO concentration < 5 %. In addition, it is expected that at higher temperatures (260 to 300 °C), the monoliths based on AuCu catalysts favor a high conversion of CO (> 95 %), achieving CO concentrations < 1 %. Therefore, monoliths based on AuCu catalysts are promising to be used in a compact B-FPU connected to a HT-PEMFC.

Figure 10. (a and b) Conversion of CO and H₂ and their corresponding product distribution (c and d) obtained in the CO removal over monoliths washcoated with AuCu/Ce and AuCu/CeSi-75 catalysts. Syngas feed: H₂ (19.9±0.3 mol%), CO (6.3±0.1 mol%), CO₂ (5.2±0.5 mol%), O₂ (5.6±0.3 mol%), H₂O (7.8±0.2 mol%), and N₂ (55.2±0.6 mol%). Reaction conditions: 220 °C, 3.3 g_{cat}/cm².

4. Conclusions

The effect of the addition of SiO₂ in the AuCu/CeO₂ system over both the cost and the catalytic performance for the CO removal from a syngas using only one catalytic unit was evaluated. It was identified that > 80 % of the catalyst cost relies on CeO₂, while the use of a noble metal (Au)

would contribute with $< 20\%$. However, the inclusion of SiO_2 in the support could decrease the catalyst cost until 60% compared to AuCu/CeO_2 . Moreover, the $\text{AuCu/CeO}_2\text{-SiO}_2$ catalysts achieved conversion $> 80\%$ of the initial CO in the syngas.

On the other hand, the most active catalyst (AuCu/Ce) and the cheapest (AuCu/CeSi-75) one that ensured adequate CO concentrations to be used in HT-PEMFC (i.e., $< 5\%$), were washcoated on monoliths of cordierite. At temperatures higher than $240\text{ }^\circ\text{C}$, monolithic reactors were found to be more efficient to remove CO and have a similar cost compared to powdered catalysts. A CFD simulation showed that the improvement in the activity of the structured catalysts is related to enhancements in heat diffusion in the internal channels of the monolith and the easy contact between reactive gas and catalyst in the walls of monoliths. Thus, both structured catalytic systems (i.e., AuCu/Ce and AuCu/CeSi-75) allowed obtaining a syngas with concentrations of $\text{H}_2 > 65\%$ and $\text{CO} < 5\%$. Moreover, the monolith based on AuCu/CeSi-75 is 38% cheaper, has greater adhesion to the monolith walls and favors less H_2 losses (only 4% of H_2 is lost), which makes it promising to be used in a compact B-FPU coupled to an HT-PEMFC.

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CRedit author statement

Bernay Cifuentes: Conceptualization, Methodology, Validation, Formal analysis, Writing - Original Draft, Visualization; **Alejandro Cifuentes:** Software, Methodology, Validation, Investigation, Writing - Review & Editing, Visualization; **Felipe Bustamante:** Resources, Methodology, Writing - Review & Editing, Supervision; **Lluís Soler:** Formal analysis, Validation, Investigation, Writing - Review & Editing; **Jordi Llorca:** Formal analysis, Methodology, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition; **Martha Cobo:** Resources, Methodology, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

Conflict of Interest

All authors have no conflict of interest to report.

References

- [1] H. Mohammed, A. Al-Othman, P. Nancarrow, M. Tawalbeh, M. El Haj Assad, Energy (2019) 207–219.
- [2] U. Lucia, Renew. Sustain. Energy Rev. 30 (2014) 164–169.
- [3] T.S. Moraes, H.N. Cozendey da Silva, L.P. Zotes, L.V. Mattos, L.E. Pizarro Borges, R. Farrauto, F.B. Noronha, Int. J. Hydrogen Energy 44 (2019) 21205–21219.
- [4] J.B. Heo, Y.-S. Lee, C.-H. Chung, Biotechnol. Adv. 37 (2019) 107422.
- [5] V.L. Pachapur, S.J. Sarma, S.K. Brar, Y. Le Bihan, G. Buelna, M. Verma, Biofuels 9

- (2018) 129–138.
- [6] N. Sanchez, R.Y. Ruiz, B. Cifuentes, M. Cobo, *Waste Manag.* 98 (2019) 1–13.
 - [7] T.S. Moraes, L.E.P. Borges, R. Farrauto, F.B. Noronha, *Int. J. Hydrogen Energy* 43 (2018) 115–126.
 - [8] L. Salemme, L. Menna, M. Simeone, *Energy* 57 (2013) 368–374.
 - [9] J. Holladay, E. Jones, D.R. Palo, M. Phelps, Y.H. Chin, R. Dagle, J. Hu, Y. Wang, E. Baker, *Mater. Res. Soc. Symp. - Proc.* 756 (2003) 429–434.
 - [10] N.P. Brandon, Z. Kurban, *Philos. Trans. R. Soc. London A Math. Phys. Eng. Sci.* 375 (2017) 1–17.
 - [11] R. Roldán, *Int. J. Hydrogen Energy* 40 (2015) 2035–2046.
 - [12] J. Llorca, V.C. Corberán, N.J. Divins, R.O. Fraile, E. Taboada, *Renew. Hydrog. Technol. Prod. Purification, Storage, Appl. Saf.* (2013) 135–169.
 - [13] N. Sanchez, R. Ruiz, V. Hacker, M. Cobo, *Int. J. Hydrogen Energy* 45 (2020) 11923.
 - [14] V. Palma, C. Ruocco, A. Ricca, *Int. J. Hydrogen Energy* 41 (2016) 11526–11536.
 - [15] R. González-Gil, C. Herrera, M.A. Larrubia, F. Mariño, M. Laborde, L.J. Alemany, *Int. J. Hydrogen Energy* 41 (2016) 16786–16796.
 - [16] A. Casanovas, C. de Leitenburg, A. Trovarelli, J. Llorca, *Catal. Today* 138 (2008) 187–192.
 - [17] C.B. Lee, S.H. Cho, D.W. Lee, K.R. Hwang, J.S. Park, S.H. Kim, *Energy* 78 (2014) 421–425.
 - [18] M. Ouzounidou, D. Ipsakis, S. Voutetakis, S. Papadopoulou, P. Seferlis, *Energy* 34 (2009) 1733–1743.
 - [19] I. Rossetti, M. Compagnoni, M. Torli, *Chem. Eng. J.* 281 (2015) 1036–1044.

- [20] R. Koch, E. López, N.J. Divins, M. Allué, A. Jossen, J. Riera, J. Llorca, *Int. J. Hydrogen Energy* 38 (2013) 5605–5615.
- [21] E. López, N.J. Divins, J. Llorca, *Catal. Today* 193 (2012) 145–150.
- [22] R.E. Rosli, A.B. Sulong, W.R.W. Daud, M.A. Zulkifley, T. Husaini, M.I. Rosli, E.H. Majlan, M.A. Haque, *Int. J. Hydrogen Energy* 42 (2017) 9293.
- [23] J.D. Arévalo, Á. Martínez-Hernández, J.C. Vargas, L.F. Córdoba, J.D. Arévalo, Á. Martínez-Hernández, J.C. Vargas, L.F. Córdoba, *Tecciencia* 13 (2018) 55–64.
- [24] B. Cifuentes, M. Hernández, S. Monsalve, M. Cobo, *Appl. Catal. A Gen.* 523 (2016) 283–293.
- [25] B. Cifuentes, F. Bustamante, J.A. Conesa, L.F. Córdoba, M. Cobo, *Int. J. Hydrogen Energy* 43 (2018) 17216–17229.
- [26] B. Cifuentes, F. Bustamante, D.G. Araiza, G. Diaz, M. Cobo, *Appl. Catal. A, Gen.* 598 (2020) 117568.
- [27] B. Cifuentes, F. Bustamante, M. Cobo, *Catalysts* 9 (2019) 852–877.
- [28] A.M. Lacoste, I.S. Tiscornia, A. V. Boix, *Int. J. Hydrogen Energy* 43 (2018) 14238–14251.
- [29] M. González-Castaño, S. Ivanova, O.H. Laguna, L.M. Martínez T., M.A. Centeno, J.A. Odriozola, *Appl. Catal. B Environ.* 200 (2017) 420–427.
- [30] G. Landi, P.S. Barbato, A. Di Benedetto, L. Lisi, *Appl. Catal. B Environ.* 181 (2016) 727–737.
- [31] L.M. Martínez T, O.H. Laguna, C. López-Cartes, M.A. Centeno, *Mol. Catal.* 440 (2017) 9–18.
- [32] T. Tabakova, *Front. Chem.* 7 (2019) 1–43.

- [33] F. Le Normand, L. Hilaire, K. Kili, G. Krill, G. Maire, J. Phys. Chem. 92 (1988) 2561–2568.
- [34] I.S. Tiscornia, A.M. Lacoste, L.E. Gómez, A. V. Boix, Int. J. Hydrogen Energy 45 (2020) 6636–6650.
- [35] B. Cifuentes, A. Cifuentes, F. Bustamante, L. Soler, J. Llorca, M. Cobo, Mendeley Dataset (2020) DOI: 10.17632/rw8drwgv8p.2.
- [36] D.R. Sahoo, S. Vajpai, S. Patel, K.K. Pant, Chem. Eng. J. 125 (2007) 139–147.
- [37] B. Cifuentes, M.F. Valero, J. a. J. Conesa, M. Cobo, Catalysts 5 (2015) 1872–1896.
- [38] A. Cifuentes, R. Torres, J. Llorca, Int. J. Hydrogen Energy (2019) In Press-10.1016/j.ijhydene.2019.11.034.
- [39] H.C. Lee, D.H. Kim, Catal. Today 132 (2008) 109–116.
- [40] E. Quinet, L. Piccolo, F. Morfin, P. Avenier, F. Diehl, V. Caps, J.L. Rousset, J. Catal. 268 (2009) 384–389.
- [41] G. Yi, H. Yang, B. Li, H. Lin, K.I. Tanaka, Y. Yuan, Catal. Today 157 (2010) 83–88.
- [42] Bonnie J. McBride, Michael J. Zehe, Sanford Gordon, NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species: National Aeronautics and Space Administration, 2002.
- [43] X. Li, S.S.S. Fang, J. Teo, Y.L. Foo, A. Borgna, M. Lin, Z. Zhong, ACS Catal. 2 (2012) 360–369.
- [44] P. Destro, S. Marras, L. Manna, M. Colombo, D. Zanchet, Catal. Today 282 (2017) 105–110.
- [45] S. Najafshirtari, R. Brescia, P. Guardia, S. Marras, L. Manna, M. Colombo, ACS Catal. 5 (2015) 2154–2163.

- [46] D. Kang, X. Yu, M. Ge, Chem. Eng. J. 330 (2017) 36–43.
- [47] C. Zhang, J. Lin, Phys. Chem. Chem. Phys. 13 (2011) 3896–3905.
- [48] Z. Ren, F. Peng, J. Li, X. Liang, B. Chen, Catalysts 7 (2017) 48–60.
- [49] A.S.A. Al-Sherbini, J. Nanomater. 2010 (2010) 1–6.
- [50] X. Liu, A. Wang, L. Li, T. Zhang, C.Y. Mou, J.F. Lee, J. Catal. 278 (2011) 288–296.
- [51] J.A. Hernández, S.A. Gómez, T.A. Zepeda, J.C. Fierro-González, G.A. Fuentes, ACS Catal. 5 (2015) 4003–4012.
- [52] T.M. Ivanova, K.I. Maslakov, A.A. Sidorov, M.A. Kiskin, R. V. Linko, S. V. Savilov, V. Lunin, I.L. Eremenko, J. Electron Spectros. Relat. Phenomena 238 (2020) 146878.
- [53] G. Marbán, I. López, T. Valdés-Solís, Appl. Catal. A Gen. 361 (2009) 160–169.
- [54] L. Soler, A. Casanovas, A. Urrich, I. Angurell, J. Llorca, Appl. Catal. B Environ. 197 (2016) 47–55.
- [55] A. Abd El-Moemen, A.M. Abdel-Mageed, J. Bansmann, M. Parlinska-Wojtan, R.J. Behm, G. Kučerová, J. Catal. 341 (2016) 160–179.
- [56] J.L. Ayastuy, E. Fernández-Puertas, M.P. González-Marcos, M.A. Gutiérrez-Ortiz, Int. J. Hydrogen Energy 37 (2012) 7385–7397.
- [57] H. Jin, R. You, S. Zhou, K. Ma, M. Meng, L. Zheng, J. Zhang, T. Hu, Int. J. Hydrogen Energy 40 (2015) 3919–3931.
- [58] Y. Xie, J. Wu, G. Jing, H. Zhang, S. Zeng, X. Tian, X. Zou, J. Wen, H. Su, C.-J.J. Zhong, P. Cui, Appl. Catal. B Environ. 239 (2018) 665–676.
- [59] A. Martínez-Arias, A.B. Hungria, M. Fernandez-Garcia, J.C. Conesa, G. Munuera, A. Martí, A.B. Hungri, J. Phys. Chem. B (2004) 17983–17991.
- [60] D.G. Araiza, A. Gómez-Cortés, G. Díaz, Catal. Today 282 (2017) 185–194.

- [61] S.T. Hossain, E. Azeeva, K. Zhang, E.T. Zell, D.T. Bernard, S. Balaz, R. Wang, Appl. Surf. Sci. 455 (2018) 132–143.
- [62] L. Ilieva, P. Petrova, G. Pantaleo, R. Zanella, L.F. Liotta, V. Georgiev, S. Boghosian, Z. Kaszkur, J.W. Sobczak, W. Lisowski, A.M. Venezia, T. Tabakova, Appl. Catal. B Environ. 188 (2016) 154–168.
- [63] R.J.B. M. J. Kahlich, H.A. Gasteiger, Journal New Mater. Electrochem. Syst. 1 (1998) 39–46.
- [64] L.E. Gómez, B.M. Sollier, A.M. Lacoste, E.E. Miró, A. V. Boix, J. Environ. Chem. Eng. 7 (2019) 103376–103386.
- [65] P.S. Barbato, A. Di Benedetto, G. Landi, L. Lisi, Top. Catal. 59 (2016) 1371–1382.
- [66] D.G. Oliva, J.A. Francesconi, M.C. Mussati, P.A. Aguirre, J. Power Sources 182 (2008) 307–316.
- [67] O.P. Klenov, N.A. Chumakova, S.A. Pokrovskaya, A.S. Noskov, Chem. Eng. Sci. 205 (2019) 1–13.
- [68] F. Schüth, M.D. Ward, J.M. Buriak, Chem. Mater. 30 (2018) 3599–3600.