

## Article

## Development of suitable CuO-based materials supported on Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub> and ZrO<sub>2</sub> for Ca/Cu H<sub>2</sub> production process

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**ABSTRACT**

Functional materials for the sorption enhanced reforming process for H<sub>2</sub> production coupled to a Cu/CuO chemical loop have been synthesized. The performance of CuO-based materials supported on Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub> and ZrO<sub>2</sub> and synthesized by different routes has been analyzed. Highly stable materials supported on Al<sub>2</sub>O<sub>3</sub> or MgAl<sub>2</sub>O<sub>4</sub> synthesized by co-precipitation and mechanical mixing with sufficient Cu loads (around 65 %wt.) have been successfully developed. However, it has been found that co-precipitation under these conditions is not a suitable route for ZrO<sub>2</sub>. Spray-drying and deposition precipitation did not provide the best chemical features to the materials. As the Ca/Cu process is operated in fixed bed reactors, the best candidates were pelletized and their stability was again assessed. Pellets with high chemical and mechanical stability, high oxygen transport capacity and good mechanical properties have been finally obtained by co-precipitation. The good homogeneity that provides this route would allow an easy scaling up.

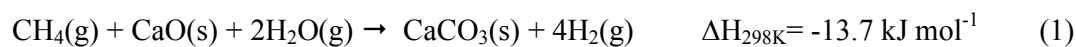
**Keywords:** H<sub>2</sub> production, CO<sub>2</sub> capture, Ca-Cu looping process, CuO-based materials

## 1. INTRODUCTION

Hydrogen is an essential raw material used in chemical and refining industries for the manufacture of commodity chemicals like ammonia, methanol and fuels. H<sub>2</sub> can also be used as a clean source of energy to replace conventional fossil fuels in electricity generation. The demand of H<sub>2</sub> required from chemical and energy industries is increasing progressively<sup>1</sup>. On the other hand, greenhouse gases as CO<sub>2</sub>, produced mainly in fossil fuel combustion, have increased their concentration in the atmosphere during the last decades and they are the main cause of the global warming. Therefore, it is necessary to develop new CO<sub>2</sub> capture technologies to mitigate the CO<sub>2</sub> emissions from large scale power plants and industrial processes in order to fulfill strict forthcoming environmental regulations<sup>1,2</sup>.

Steam Methane Reforming (SMR) is the most widely used technology to produce H<sub>2</sub> at commercial scale, producing around 50 % of the H<sub>2</sub> worldwide<sup>3,4</sup>, but at the expense of significant CO<sub>2</sub> emissions (9,1 - 8,9 kg CO<sub>2</sub> per kg H<sub>2</sub>). The modern H<sub>2</sub> production plant is a stepped process where the reforming reactor is followed by a High Temperature Shift (HTS) reactor to maximize CO conversion and H<sub>2</sub> production<sup>5,6</sup>. Finally, a pressure swing adsorption (PSA) unit is also needed when H<sub>2</sub> purities higher than 95 %vol.<sup>7,8</sup> are pursued. At this point, hydrogen production combined with CO<sub>2</sub> capture and permanent CO<sub>2</sub> storage is presented as one of the potential routes to decarbonize the energy and industrial sectors. Although there are well-established routes to capture CO<sub>2</sub> in a concentrated form suitable for geological storage, the development of new technologies that allows the CO<sub>2</sub> capture cost to be reduced is also needed. In this context, the sorption enhanced methane reforming (SER) is a novel process of H<sub>2</sub> production that combines a reforming catalyst with a CO<sub>2</sub> sorbent (usually CaO) aiming

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3 at removing the CO<sub>2</sub> as soon as it is formed<sup>9</sup>. Eq. (1) expresses the global reaction for  
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5 the SER process using CH<sub>4</sub> as fuel and CaO as CO<sub>2</sub> sorbent. According to Le  
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7 Chatelier's principle, the presence of the CO<sub>2</sub> sorbent shifts the equilibrium to the right  
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9 achieving practically complete methane and CO conversions which leads to a higher  
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11 hydrogen yield at relatively mild conditions of pressure and temperature. In addition,  
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13 the final reaction is slightly exothermic because it combines one very endothermic  
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15 reaction (steam reforming) with two exothermic reactions (shift and carbonation  
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17 reactions).



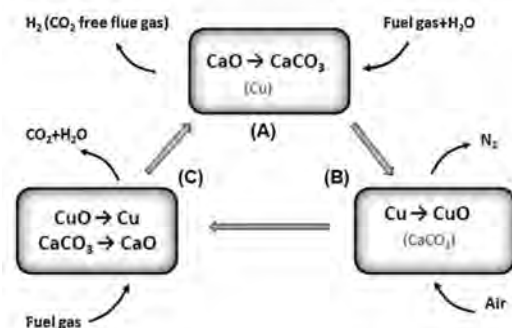
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26 Multicycle operation of SER process requires the continuous regeneration of the sorbent  
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28 by calcining the CaCO<sub>3</sub>, Eq. (2), into CaO and CO<sub>2</sub>. This is a highly endothermic  
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30 reaction ( $\Delta H_{298\text{K}} = 178.5 \text{ kJ mol}^{-1}$ ) and it has to be performed in a CO<sub>2</sub> rich environment  
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32 if the process aims at capturing the CO<sub>2</sub>. In this way, an additional energy input is  
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34 needed to reach the calcination temperature imposed by the equilibrium<sup>9</sup>. Among  
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36 different alternatives proposed in the literature to reduce the energy penalty due to the  
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38 sorbent regeneration<sup>10-15</sup>, a new process known as Ca/Cu looping process was proposed  
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40<sup>16</sup>. This process makes use of a Cu/CuO chemical loop to solve the endothermic CaCO<sub>3</sub>  
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42 calcination and to generate a CO<sub>2</sub> concentrated stream suitable for further purification  
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44 and storage. At the same time, the process produces pressurized H<sub>2</sub> from CH<sub>4</sub> by steam  
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46 reforming in presence of a CaO-based sorbent<sup>7,9</sup>. The key point of this new technology  
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48 lies in the fact of using the exothermic reaction of CuO reduction with additional CH<sub>4</sub> or  
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50 other fuel gas to supply the energy for CaCO<sub>3</sub> calcination. In this way, the gas stream  
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3 that leaves the calciner will be ideally comprised of CO<sub>2</sub> and H<sub>2</sub>O which can be easily  
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5 separated by condensation.  
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7 The basic Ca-Cu looping process consists of a sequence of three reaction steps (see  
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9 Figure 1), which are adiabatically carried out in fixed-bed reactors operating in parallel.

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11 In the first stage (stage A), an enriched stream of H<sub>2</sub> is produced by the sorption  
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13 enhanced reforming of methane in the presence of a reforming catalyst, a CaO-based  
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15 sorbent and a copper-based solid (that acts as inert in this stage). This takes place at 600  
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17 °C - 750 °C, steam-to-carbon molar ratios between 2.5 and 5, and pressures between 10  
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19 bar and 35 bar in order to achieve high H<sub>2</sub> production yields with high CO<sub>2</sub> capture  
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21 efficiencies <sup>17</sup>. In the next stage (stage B), the copper-based material is oxidized with  
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23 diluted air at high pressure. A low oxygen concentration in the feed moderates the  
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25 increase of temperature during the oxidation of Cu to CuO, thereby avoiding the  
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27 decomposition of CaCO<sub>3</sub> by partial calcination <sup>18</sup>. In the following reaction stage (stage  
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29 C), the calcination of the CaCO<sub>3</sub> formed during the SER is accomplished by means of  
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31 the simultaneous reduction of CuO with a gaseous fuel at atmospheric pressure. A  
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33 suitable CuO/CaCO<sub>3</sub> molar ratio in bed composition has to be selected to ensure that the  
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35 heat released during CuO reduction is sufficient to completely decompose the CaCO<sub>3</sub>  
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37 without any external energy supply <sup>19-21</sup>.  
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41 A detailed conceptual design of the process based on literature data was carried out by  
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43 Fernández et al. <sup>9</sup>. In this work, simple reaction models served to define a range of  
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45 operation conditions for the process in terms of Cu/Ca ratios and suitable operation  
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47 pressures and temperatures for the different process stages.  
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**Figure 1.** General scheme of the novel Ca/Cu reforming process.

A general layout of a complete H<sub>2</sub> production plant based on this process was designed by Martínez et al.<sup>21</sup> and promising results in terms of H<sub>2</sub> equivalent efficiencies were predicted by the model. Recently, experimental results in a pseudo-adiabatic fixed bed reactor were reported and confirmed the feasibility of supporting the calcination reaction of CaCO<sub>3</sub> with the exothermic reduction of CuO with H<sub>2</sub><sup>22</sup>. Moreover, a relevant number of papers have been published describing in detail the different stages of the process<sup>23-28</sup>.

A key aspect for the future development of the process is to have materials with optimum properties for cyclic operation<sup>21</sup>. With respect to the reforming catalyst, in principle, a commercial Ni-based catalyst has been proposed in the works by Fernández et al.<sup>9, 23, 24</sup> although more active materials currently under development could also be considered. The ratio Cu/Ca in the process will be determined by the requirements in the calcination step<sup>7</sup>, and in order to reduce the thermal ballast of the inert fractions comprising the materials, it is necessary to maximize the active phase content of both the CaO based and the Cu-based materials<sup>7, 9</sup>. Some recent works are oriented to the development of composite materials containing CaO and CuO<sup>29-34</sup> and/or CaO and Ni acting as reforming catalyst<sup>35-39</sup>. With respect to the CaO-CuO composites, the results indicate that the progress of the carbonation reaction in the combined material might

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3 affect negatively the kinetics of the oxidation reaction of Cu<sup>31</sup>. In addition, recent  
4 studies<sup>30</sup> produced mixed pellets with a Cu content around 50%wt. finding that the  
5 content of Cu/CuO has a significant influence on the cyclic performance of the CaO.  
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7 The authors observed that the composites showed good reactivity for CuO but loss in  
8 CO<sub>2</sub> capture capacity after cycling. Moreover, the mechanical stability of the composite  
9 materials might be affected along cycling<sup>34</sup>. In general, these materials are still  
10 immature with respect to the use of individual pellets and important efforts on their  
11 development are required.  
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20 Focusing exclusively on CuO-based materials, a number of authors have published their  
21 results about CuO-based materials tested in Chemical Looping Combustion (CLC)<sup>40-52</sup>,  
22 Chemical Looping with Oxygen Uncoupling (CLOU)<sup>52-59</sup>, Chemical Looping  
23 Reforming (CLR)<sup>60, 61</sup> and Ca/Cu looping<sup>22, 29, 34, 62</sup> processes. Most of the work has  
24 focused on the development of oxygen carriers for CLC processes. The CLC technology  
25 has been confirmed by Lyngfelt et al.<sup>63</sup> that can be operated in a number of different  
26 units from 0.3 to 120 kW, with more than 4000 hours of operation using different  
27 oxygen carriers and wide variety of CuO-based oxygen carriers for CLC applications  
28 has been summarized in a review prepared by Adánez et al.<sup>64</sup>. The materials were  
29 prepared by different synthesis routes like freeze granulation, impregnation, extrusion,  
30 spray-drying, co-precipitation or mechanical mixing. The majority of the published  
31 works has referred to the use of Al<sub>2</sub>O<sub>3</sub> as support<sup>40, 41, 50, 53, 62, 65-69</sup>. Several authors have  
32 recently developed high loaded CuO-based particles (around 70%wt. of Cu) by co-  
33 precipitation<sup>50, 68</sup> and they discovered that pH and the precipitating agent have a strong  
34 influence on the chemical structure of the materials<sup>50</sup>. They have tested their materials  
35 under 25 cycles and the results suggested that CuO reacted with Al<sub>2</sub>O<sub>3</sub> to form fully  
36 reducible CuAl<sub>2</sub>O<sub>4</sub><sup>49, 50</sup>. Other promising results with materials onto Al<sub>2</sub>O<sub>3</sub> has  
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3 obtained by Song et al.<sup>51</sup> that have reported a synthesis method based on layered double  
4 hydroxides (LDHs) precursors that improve the reactivity and stability of the materials  
5 achieving the homogeneous mix of the elements at molecular level. Mainly in order to  
6 avoid the formation of intermediates, other alternative support materials have been  
7 reported in the literature as  $\text{MgAl}_2\text{O}_4$ <sup>54, 65, 66</sup>,  $\text{ZrO}_2$ <sup>59, 65, 70</sup>,  $\text{CeO}_2$ <sup>52, 71</sup>,  $\text{TiO}_2$ <sup>72</sup>,  $\text{SiO}_2$ <sup>60,</sup>  
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65 and combined metal oxides like  $\text{CuO-Fe}_2\text{O}_3$ <sup>73</sup>. Regarding to the use of  $\text{MgAl}_2\text{O}_4$  as support, Imtiaz et al.<sup>58</sup> has analyzed the effect of cycles on materials with Cu contents until 72%wt. and they found stable and close to the theoretical values for oxygen transport capacities during 25 cycles.

Since the Ca/Cu looping process is a relatively new concept, there are not many works published so far about Cu materials specifically designed and tested in fixed bed reactors. Most of the research has been developed in lab scale packed bed reactors using a mixture of CaO and existing commercial pellets of a Cu based material<sup>22</sup>. Although this work has shown promising results for the Ca/Cu looping process, additional efforts on the development of the pellets with high chemical and mechanical stability are still needed. In general, these new materials should have a high CuO load because the calcination enthalpy is considerably higher than the CuO reduction enthalpy. In agreement with the mass and energy balances of the process<sup>9</sup> materials with Cu loads between 55 to 70%wt. would be suitable candidates for the process. Therefore the development of highly stable CuO-based materials in pellet form that can be successfully adapted to reducing and oxidizing conditions, keeping oxygen transport capacity and mechanical strength during long number of cycles is an essential point in order to select the optimal CuO-based materials to achieve the highest energy yields during the calcination step of the Ca/Cu looping process.

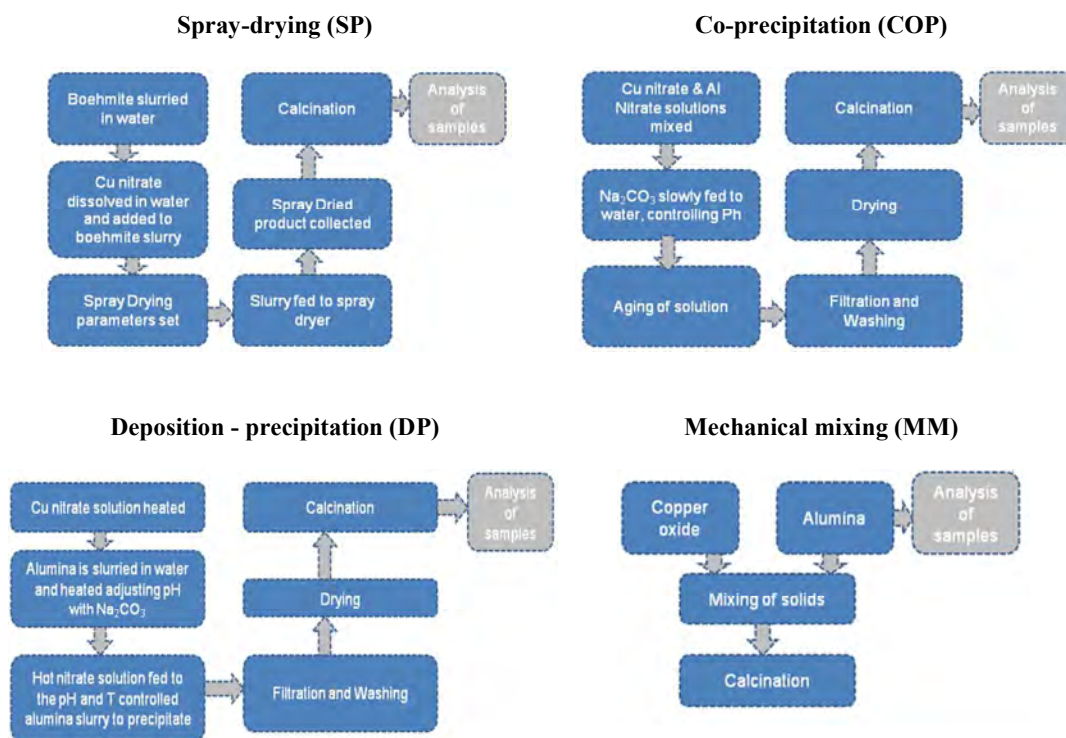
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3 Even though there are numerous studies about oxygen carriers for CLC or CLC-CLOU  
4 applications, there is still a need to evaluate how the synthesis route, the Cu load, and  
5 the particle or pellet form, might affect the performance of the materials under relevant  
6 conditions for Ca/Cu looping process. Therefore, the main objective of this paper is the  
7 development of stable CuO-based materials with suitable Cu contents for the Ca/Cu  
8 looping process. The effect that the inert support ( $\text{Al}_2\text{O}_3$ ,  $\text{MgAl}_2\text{O}_4$  and  $\text{ZrO}_2$ ), the route  
9 of synthesis and the Cu load in the material has on the stability in terms of oxygen  
10 transport capacity (OTC) of the solids along oxidation/reduction cycles has been  
11 evaluated. The materials have been tested in powder and also pellet form, the latter  
12 being the final form in which the material will be introduced in the process <sup>9</sup>. The  
13 mechanical properties of the pellets after 150 cycles have been also evaluated.  
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## 28 **2. EXPERIMENTAL**

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33 In this work, a wide range of CuO-based materials with Cu loads between 48.1 to 75.0  
34 %wt., supported on  $\text{Al}_2\text{O}_3$ ,  $\text{MgAl}_2\text{O}_4$  and  $\text{ZrO}_2$  and prepared by different synthesis  
35 routes, were analyzed. The range of Cu loads of materials has been selected in  
36 agreement with the mass and energy balances of the Ca/Cu looping process <sup>9</sup>, that  
37 suggested that materials with Cu loads between 55 to 70%wt. would be suitable  
38 candidates for the process. The performance of the materials was evaluated in powder  
39 form (with up to 100 redox cycles in a TGA apparatus) and the most promising  
40 materials were also pelletized and tested in pellet form. The materials were texturally  
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### 54 **2.1. Description of the synthesis routes**

Different synthesis routes were followed to prepare the Cu-based materials over  $\text{Al}_2\text{O}_3$ ,  $\text{MgAl}_2\text{O}_4$  and  $\text{ZrO}_2$  as inert support. The materials that use  $\text{Al}_2\text{O}_3$  as support were prepared by Johnson Matthey PLC (JM), while the rest of materials were prepared at the Instituto de Carboquímica (ICB-CSIC). Specifically, CuO-based materials were synthesized by spray-drying (JM), co-precipitation (JM and ICB), deposition-precipitation (JM) and mechanical mixing (JM). Figure 2 shows the steps followed in the synthesis routes evaluated in this research. All synthesis routes have common stages at the end of the process as for example drying and calcination steps. Specifically, regarding to the materials synthesized by ICB-CSIC via co-precipitation onto  $\text{MgAl}_2\text{O}_4$  and  $\text{ZrO}_2$ , the calcination step during synthesis was carried out at 870 °C during 2 hours using a heating rate of 50 °C/min and the drying step was carried out at 120 °C during 12 hours.



**Figure 2.** Synthesis routes of CuO-based materials.

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3 *Co-precipitation (COP):* The CuO-based materials synthesized by co-precipitation were  
4 prepared following a specific co-precipitation method to achieve Cu contents between  
5 48.1 to 75.0 %wt. Cu nitrate and Al or Mg or Zr nitrate solutions were mixed to  
6 synthesized the solids with a specific Cu load. Subsequently, the pH of the solutions  
7 was adjusted adding Na<sub>2</sub>CO<sub>3</sub>. The resulting mixture was stirred and filtered. During the  
8 filtration, the precipitate was washed several times with distilled water to remove excess  
9 nitrate and alkali ions. After that, the cake was dried and subsequently calcined in a  
10 muffle furnace. In the case of the materials synthesized by ICB-CSIC onto MgAl<sub>2</sub>O<sub>4</sub>  
11 and ZrO<sub>2</sub>, an specific amount of the Al and Mg or Zr nitrate solutions were mixed and  
12 shaken, adjusting the pH to 9,8 with Na<sub>2</sub>CO<sub>3</sub> and calcining the sample at 870 °C during  
13 2 hours.  
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18 *Spray-drying (SD):* In the solids prepared via spray-drying, the copper nitrate solution  
19 was added to boehmite slurry. Then, the slurry was fed to a spray dryer and finally the  
20 material was also calcined in a muffle furnace.  
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28 *Deposition - precipitation (DP):* By this procedure, the copper nitrate solution was  
29 initially heated. In the same way, alumina was slurried in water and also heated  
30 adjusting the pH with Na<sub>2</sub>CO<sub>3</sub>. Secondly, the hot nitrate solution was fed to the pH and  
31 temperature controlled alumina slurry to obtain a precipitate. The precipitate was  
32 washed, filtered, dried and calcined.  
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42 *Mechanical mixing (MM):* This route consists of mixing copper oxide and alumina  
43 directly in a ball mill followed by the calcination of the sample.  
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48 Table 1 compiles a list of selected materials synthesized by SD, COP, DP and MM onto  
49 the different support materials. These materials were selected to be analyzed and  
50 characterized in detail among 25 materials initially tested in the TGA.  
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Moreover, some of the most promising materials were pelletized to test the mechanical stability in long periods of operation as the Ca/Cu reforming process requires.

**Table 1:** List and physical and chemical properties of selected CuO-based materials supported on Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub> and ZrO<sub>2</sub>.

Reference	CuO- based materials							Crystal size(nm)-Fresh samples		Crystal size(nm)-Cycled samples	
	Support-Synthesis	Cu %wt.	OTC exp.*	OTC theor.	S <sub>BET</sub> m <sup>2</sup> g <sup>-1</sup>	ρ kgm <sup>-3</sup>	ε (%)	CuO	CuAl <sub>2</sub> O <sub>4</sub> , MgAl <sub>2</sub> O <sub>4</sub> or ZrO <sub>2</sub>	CuO	CuAl <sub>2</sub> O <sub>4</sub> , MgAl <sub>2</sub> O <sub>4</sub> or ZrO <sub>2</sub>
Cu75Al_SD	Al <sub>2</sub> O <sub>3</sub> -SD	75.0	0.187	0.189	6.2	5980		58.2	24.42	CuO: 27.47, Cu: 104.39, Cu <sub>2</sub> O: 3.96, CuAl <sub>2</sub> O <sub>4</sub> : 12.24	
Cu65Al_COP	Al <sub>2</sub> O <sub>3</sub> -COP	65.5	0.164	0.164	20.5	5560	60	66.09	23.09	61.3	22.3
Cu63Al_DP	Al <sub>2</sub> O <sub>3</sub> -DP	63.0	0.157	0.159	17.3	5550		106.71	23.48	CuO: 27.53, Cu: 94.63, Cu <sub>2</sub> O: 27.67, CuAl <sub>2</sub> O <sub>4</sub> : 14.51	
Cu60Al_MM	Al <sub>2</sub> O <sub>3</sub> -MM	60.4	0.151	0.151	21.4	5580		57.9	24.16	62.6	23.72
Cu70MgAl_COP	MgAl <sub>2</sub> O <sub>4</sub> -COP	69.0	0.174	0.176	12.1	5715		91.7	19.6	107.7	40.8
Cu65MgAl_COP	MgAl <sub>2</sub> O <sub>4</sub> -COP	65.0	0.163	0.163	20.9	5510	75	86.6	14.2	63.1	42.3
Cu60MgAl_COP	MgAl <sub>2</sub> O <sub>4</sub> -COP	59.7	0.151	0.151	13.7	6116		70.74	15.9	60.4	44.5
Cu72Zr_COP	ZrO <sub>2</sub> -COP	72.4	0.08	0.181	5.1	6231		130.0	72.5	144.5	112.3
Cu67Zr_COP	ZrO <sub>2</sub> -COP	67.3	0.144	0.169	4.1	6122		114.4	42.94	120.82	92.34
Cu48Zr_COP	ZrO <sub>2</sub> -COP	48.1	0.111	0.121	1.7	6116		75.75	54.33	86.54	100.94

*Methods of synthesis: SD (spray-drying), COP (co-precipitation), DP: (deposition -precipitation), MM (mechanical mixing).*

*\*OTC exp.: average of the values collected up to 100 cycles. In the case of the material Cu72Zr\_COP the values were collected until 25 cycles.*

*It is important to highlight that in the case of two cycled samples (Cu75Al\_SD and Cu63Al\_DP) it has been found the presence of CuO, Cu, Cu<sub>2</sub>O and CuAl<sub>2</sub>O<sub>4</sub> as these samples could be partially reduced.*

## 2.2. Characterization

The CuO-based fresh materials were analyzed by ICP-OES in order to determine their Cu content. The device used in these analysis was a Spectroblue apparatus of Ametek. All fresh and cycled samples were also characterized by X-ray diffraction (XRD) to identify crystalline species present in the solids and the average crystallite sizes before and after cycling. The device used for these analyses was an X-ray diffractometer Bruker AXS D8ADVANCE that employs CuK $\alpha$  radiation. The fresh materials were

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3 characterized by TPR analysis to study the main temperatures of reducible species  
4 present in each CuO-based material. The analysis was carried out in a PulseChemisorb  
5 700 supplied by Micromeritics. Specific surface area was calculated by N<sub>2</sub>  
6 physisorption applying the BET method in an Micromeritics ASAP 2020 apparatus and  
7 the solid density by He picnometry has been determined in a Micromeritics ACCUPYC  
8 II device. Also, some pictures of samples were taken after TGA cycling to show  
9 possible signs of agglomeration. Finally, the selected materials in powder and pellet  
10 form, were analyzed using SEM and EDX techniques to assess the dispersion of active  
11 phase and inert support. Scanning electron microscopy (SEM) coupled to energy  
12 dispersive X-ray (EDX) using a Hitachi S-3400 N were applied in order to determine  
13 the morphology and copper distribution in the samples. A Shimpo Dynamometer (FTS-  
14 20X) has been used to determine the horizontal crushing strength (HCS) of the selected  
15 pellets. This device measures the force needed to crush individual pellets, up to 100 N  
16 and the measurements served to calculate the average HCS value reported in the  
17 manuscript.

### 2.3. Apparatus

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19  
20 A thermogravimetric analyzer (TGA-CI Electronics Ltd.) was used to determine each  
21 material's chemical and mechanical stability under oxidizing and reducing conditions.  
22 This equipment consists of two concentrically-arranged quartz tubes located inside a  
23 furnace. Each sample was introduced in a platinum basket placed at the bottom of this  
24 device. Up to 100 oxidation/reduction cycles were performed on the materials in  
25 powder form (average particle size of 75 $\mu$ m) under isothermal conditions at 870 °C.  
26 Around 15 mg of sample in powder form of each material were loaded in the platinum  
27 basket in every test. A constant total flow of 280 ml/min of gas was fed in at the top of  
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3 the reactor, after being preheated by flowing through the external reactor tube along the  
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5 furnace with a space velocity of 0.012 m/s. Reaction temperature and gas composition  
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7 were maintained constant in each test. Reduction and oxidation cycles were performed  
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9 by a gas stream comprised of 20 vol% H<sub>2</sub> in N<sub>2</sub> and 20 vol% O<sub>2</sub> in N<sub>2</sub> respectively,  
10  
11 using a N<sub>2</sub> purge between each reduction and oxidation stage. A constant N<sub>2</sub> flow  
12  
13 passed through the head of the thermobalance to prevent any damage of the apparatus.  
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15 The materials were collected after testing to be characterized. The Cu content in each  
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17 material was calculated from the amount of oxygen reacting during successive  
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19 reduction/oxidation cycles in the TGA. These values were later corroborated by the ICP  
20  
21 data obtained in the laboratory.  
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24 The oxygen transfer capacity (OTC) and the active copper load of the materials were  
25  
26 calculated from the data obtained in the TGA by the following formulas:  
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28

$$29 \quad OTC = \left( \frac{m_{ox} - m_{red}}{m_{ox}} \right) \cdot 100 \quad (3)$$

$$31 \quad x_{red} = \frac{m_{ox} - m(t)}{m_{ox} \cdot OTC} \quad (4)$$

$$33 \quad x_{ox} = \frac{m(t) - m_{red}}{m_{ox} \cdot OTC} \quad (5)$$

34  
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36  
37 Where  $m_{ox}$  is the weight of the material completely oxidized,  $m_{red}$  is the weight of the  
38  
39 material completely reduced and  $m(t)$  is the instantaneous sample weight.  
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42 As it was mentioned before, some of the materials in powder form that presented the  
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44 best chemical behavior were pelletized in order to analyze their chemical and  
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46 mechanical stability in a long number of reaction cycles. Each pellet was tested using  
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48 the TGA and approximately 150 reduction/oxidation cycles were done at 870 °C  
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50 following the same procedure that was applied with the materials in powder form.  
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### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of oxygen carriers

Figure 3(a) shows the X-ray diffractograms of fresh and cycled samples of CuO-based materials synthesized by different routes and onto different supports. All the materials revealed that CuO is the more abundant species in the fresh material. It was also observed that a common feature of the materials supported on Al<sub>2</sub>O<sub>3</sub> is the presence of CuAl<sub>2</sub>O<sub>4</sub> in the crystalline structure. This compound was detected in all samples prepared by SD, COP and, DP. This species has been also detected by other authors that have been analyzed CuO-Al<sub>2</sub>O<sub>3</sub> materials<sup>66, 68, 74</sup>. However, in this study the formation of CuAl<sub>2</sub>O<sub>4</sub> was not observed in the materials prepared by mechanical mixing (MM). Hu et al.<sup>74</sup> studied the formation of copper aluminate spinel (CuAl<sub>2</sub>O<sub>4</sub>) and cuprous aluminate delafossite (CuAlO<sub>2</sub>) in copper-laden sludge that is thermally treated with  $\gamma$ -alumina and found four copper containing phases (CuO, Cu<sub>2</sub>O, CuAl<sub>2</sub>O<sub>4</sub> and CuAlO<sub>2</sub>) in the investigated system. It was found that CuAl<sub>2</sub>O<sub>4</sub> could be effectively formed between 850 °C and 950 °C by the  $\gamma$ -alumina precursor and CuAlO<sub>2</sub> is formed at higher temperatures (>1100 °C) in the copper-alumina system. The XRD analysis carried out by Chuang et al.<sup>67</sup> with CuO-based materials prepared by mechanical mixing, wet-impregnation and co-precipitation revealed the presence of CuO and CuAl<sub>2</sub>O<sub>4</sub> in fresh samples, but Al<sub>2</sub>O<sub>3</sub> was not detected in any case. Although most of the initial Al<sub>2</sub>O<sub>3</sub> could be forming CuAl<sub>2</sub>O<sub>4</sub> in the samples, another possible explanation could be that Al<sub>2</sub>O<sub>3</sub> was always present in its amorphous form and could not be detected by XRD<sup>40, 58</sup>. Imtiaz et al.<sup>58</sup> also observed only the presence of CuO and CuAl<sub>2</sub>O<sub>4</sub> in CuO-Al<sub>2</sub>O<sub>3</sub> solids prepared by co-precipitation. Therefore, it seems that the choice of a suitable route of synthesis of CuO based materials supported onto Al<sub>2</sub>O<sub>3</sub>, is a key aspect in order



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3 to avoid the formation of copper aluminates. In this work, it has been confirmed that  
4 MM is a suitable method of preparation of this type of materials. Some of the ways in  
5 which  $\text{CuAl}_2\text{O}_4$  can be formed from the decomposition of nitrate precursors occurs  
6 when aluminum nitrate forms amorphous alumina while heating or because the Cu and  
7 Al precursors are homogeneously mixed before heating <sup>74</sup>. In this way, the MM allows  
8 to use  $\alpha\text{-Al}_2\text{O}_3$  as a support material directly with CuO while using other type of  
9 synthesis routes the Al and Cu precursors would be practically homogeneously  
10 distributed in the sample and amorphous alumina could be formed that could react with  
11 CuO at much lower temperatures to form  $\text{CuAl}_2\text{O}_4$ . On the other hand, the presence of  
12  $\text{CuAlO}_2$ , that could limit the amount of Cu that could be recovered as CuO in an  
13 oxidation cycle <sup>69</sup>, has not been detected in any case. This means that fully CuO  
14 regeneration from  $\text{CuAl}_2\text{O}_4$  is practically achieved in all cases. Therefore, the presence  
15 of  $\text{CuAl}_2\text{O}_4$  in these samples is not a limiting step for the stability of the materials in  
16 agreement with results obtained by other authors <sup>49, 50</sup> that obtain stable reactivity for  
17 materials that also showed  $\text{CuAl}_2\text{O}_4$  after synthesis.

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19 In any case, for the CuO- $\text{Al}_2\text{O}_3$  prepared materials through SD, COP and DP, in this  
20 work, the ratio of intensity for the CuO and  $\text{CuAl}_2\text{O}_4$  peaks is maintained for the cycled  
21 samples, indicating that the proportion of species is stable along cycling. In this way, in  
22 agreement with the thermodynamic study carried out by Jacob et al. <sup>75</sup> stable  $\text{CuAl}_2\text{O}_4$   
23 can be obtained at temperatures above 800 °C.

24  
25 In contrast with the CuO onto  $\text{Al}_2\text{O}_3$  materials, no interaction was observed when  
26  $\text{MgAl}_2\text{O}_4$  was used as support. In agreement with results published in the literature <sup>40, 53,</sup>  
27 <sup>58, 73</sup> these Cu-based materials were only comprised of CuO and the spinel  $\text{MgAl}_2\text{O}_4$   
28 according to XRD analysis. The presence of alumina or magnesia was not detected in  
29 the case of  $\text{MgAl}_2\text{O}_4$  materials, indicating that all the  $\text{Al}_2\text{O}_3$  and MgO formed the

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3 MgAl<sub>2</sub>O<sub>4</sub> or existed in amorphous phases. The MgAl<sub>2</sub>O<sub>4</sub> spinel results in a very stable  
4 structure and no interference with CuO is observed.

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7 In this way, it seems that the formation of the CuAl<sub>2</sub>O<sub>4</sub> or MgAl<sub>2</sub>O<sub>4</sub> spinels,  
8 respectively, using an appropriate calcination temperature after synthesis provides the  
9 material high stability and no interaction with the CuO active phase as stable cubic  
10 ordered structures for the spinels are formed in these conditions.

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13 Regarding to the CuO-based materials with ZrO<sub>2</sub> as support, no formation of  
14 intermediate species was detected by XRD, as well as other authors that have been  
15 tested ZrO<sub>2</sub> materials<sup>73</sup>. However, we have discovered that the lattice parameters of the  
16 ZrO<sub>2</sub> phase found for these type of materials (  $a = 5.20 - 5.31 \text{ \AA}$ ,  $b = 5.20 - 5.22 \text{ \AA}$ ,  $c =$   
17  $5.14 - 5.20 \text{ \AA}$ ,  $\beta = 99^\circ$ ) correspond with the presence of monoclinic ZrO<sub>2</sub> (m-ZrO<sub>2</sub>) in  
18 agreement with the values determined for this kind of chemical structure in the literature  
19 <sup>76</sup>. The structure m-ZrO<sub>2</sub> have been identified in all fresh and cycled samples of ZrO<sub>2</sub>  
20 solids, and this structure would not be suitable to obtain highly stable materials as it has  
21 been also reported by other authors<sup>77, 78</sup>. Therefore it seems that the modification of the  
22 ZrO<sub>2</sub> structure has a direct influence on the CuO reduction, and positive results have  
23 been found for catalysts in which the tetragonal surface of ZrO<sub>2</sub> (t-ZrO<sub>2</sub>) has been  
24 identified instead of the monoclinic (m-ZrO<sub>2</sub>)<sup>78</sup>. Several authors, have studied the  
25 tetragonal to monoclinic transformation<sup>77, 79</sup> and it seems that grain size, oxygen  
26 vacancies and compressive stress are important factors. CuO-ZrO<sub>2</sub> catalysts with  
27 tetragonal ZrO<sub>2</sub> were successfully synthesized in the work published by Liu et al.<sup>80</sup>.  
28 Although their materials were prepared using a different method and lower Cu contents,  
29 the calcinations temperature during synthesis was rather low (450 °C) than the  
30 temperature used in our solids (up to 800 °C). Therefore, this elevated temperature  
31 could be related to the change from the tetragonal to the monoclinic phase of the ZrO<sub>2</sub>.  
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3 Table 1 also compiles the crystallite sizes for the different materials before and after  
4 cycling as well as the specific surface area ( $\text{m}^2 \text{g}^{-1}$ ) and true density ( $\text{kg m}^{-3}$ ). Regarding  
5 into the route of synthesis followed for the materials onto  $\text{Al}_2\text{O}_3$ , DP results in very high  
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Table 1 also compiles the crystallite sizes for the different materials before and after cycling as well as the specific surface area ( $\text{m}^2 \text{g}^{-1}$ ) and true density ( $\text{kg m}^{-3}$ ). Regarding into the route of synthesis followed for the materials onto  $\text{Al}_2\text{O}_3$ , DP results in very high CuO crystals with respect to the other procedures that showed similar CuO crystals. On the other hand, materials with similar Cu loads (65%wt.) showed different size in CuO crystals depending on the support used. Then, the CuO crystal sizes were 66.1 nm for  $\text{Al}_2\text{O}_3$ , 86.6 nm for  $\text{MgAl}_2\text{O}_4$  and 114.4 nm for materials onto  $\text{ZrO}_2$ . In addition, taking into account the materials with different Cu load prepared by the same route (COP) onto  $\text{MgAl}_2\text{O}_4$  or  $\text{ZrO}_2$ , respectively, in general an increase on the CuO crystals is related with the increase in CuO content in the material. These results are in agreement with other works in which the growth of CuO crystals with the increase of Cu load has been also observed<sup>81, 82</sup>. Then, the growth of the CuO crystals could be related with the formation of bulk CuO, instead of highly dispersed Cu species<sup>81</sup> and the decrease in the strength of the  $\text{MgAl}_2\text{O}_4$  or  $\text{ZrO}_2$  lattice associated with this increase in the Cu load. Moreover, another aspect to remark for solids onto  $\text{ZrO}_2$  by COP, is the high size of the  $\text{ZrO}_2$  crystals (42.94 nm) related with monoclinic  $\text{ZrO}_2$  with respect to the  $\text{MgAl}_2\text{O}_4$  (14.2 nm) or  $\text{Al}_2\text{O}_3$  (23.09 nm) crystals. Therefore the lowest ratios between the size of CuO and  $\text{ZrO}_2$  crystals were found for  $\text{ZrO}_2$  compounds that can be directly related with the monoclinic structure of  $\text{ZrO}_2$ , suggest clearly that the synthesis route for  $\text{ZrO}_2$  solids must be modified. Moreover, taking into account the crystal sizes of the cycled samples of the CuO- $\text{ZrO}_2$  materials that are detailed in Table 1, it has been always observed an increase in the CuO and  $\text{ZrO}_2$  crystals after cycling which could negatively affect the chemical stability of these materials.

Figure 3(b) shows the comparison between the results obtained from the TPR analysis for the materials onto the different supports. While the materials supported onto  $\text{Al}_2\text{O}_3$

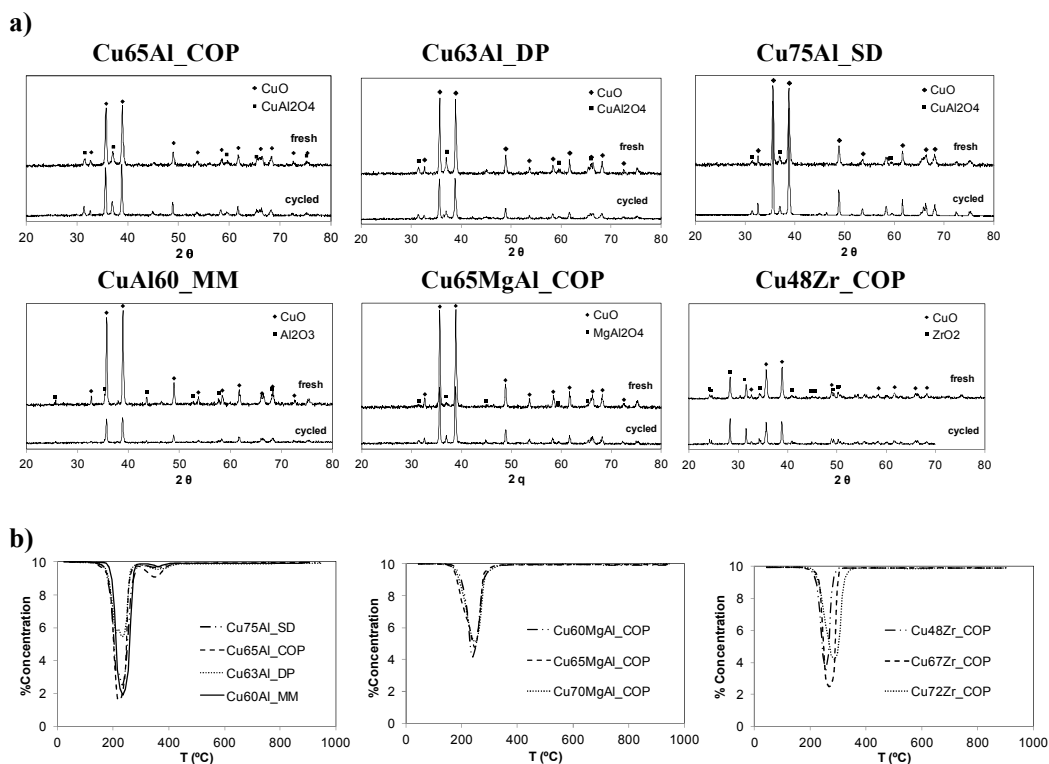
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3 present two differentiated H<sub>2</sub> uptake peaks, the materials onto MgAl<sub>2</sub>O<sub>4</sub> or ZrO<sub>2</sub> showed  
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5 an only H<sub>2</sub> consumption peak. While pure CuO shows CuO reduction peaks around 350  
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7 °C, in the case of the addition of supports to the CuO matrix, this value could be  
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9 reduced<sup>83</sup>.

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11 All the materials shows a main H<sub>2</sub> consumption peak around 275 °C and the total  
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13 consumption of H<sub>2</sub> was very similar for the materials with the same Cu load into the  
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15 different supports. However, in the case of the Al<sub>2</sub>O<sub>3</sub> materials the two peaks are  
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17 associated with the reduction of two different copper species. The main H<sub>2</sub> uptake peak  
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19 is related to the reduction of a well-dispersed CuO, and the second minor peak at  
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21 temperatures close to 400 °C is attributed to the presence of CuAl<sub>2</sub>O<sub>4</sub> in the materials.  
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25 Moreover, as it can be extracted from this figure, materials onto Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>  
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27 showed more defined peaks associated with CuO reduction than materials onto  
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29 MgAl<sub>2</sub>O<sub>4</sub> that presented wider peaks associated with this reaction. It seems that this  
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31 aspect could be related with some kind of interaction between the CuO and the  
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33 MgAl<sub>2</sub>O<sub>4</sub> that facilitates the reduction of copper species in the material<sup>84</sup>.  
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36 Comparing between synthesis routes, there are minor variations on the temperature at  
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38 which the peaks present their maximum, although similar well-defined peaks for CuO  
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40 were observed in the case of the materials prepared by COP as well as MM. It is also  
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42 important to take into account that the solid synthesized by DP presents a non-defined  
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44 peak for CuO formed by two little bends. This fact could be associated with the  
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46 reduction of Cu(II) and Cu(I) species. Regarding to the peak at higher temperature, the  
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48 MM materials presented the smallest peak, that indicates the presence of an small  
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50 amount of CuAl<sub>2</sub>O<sub>4</sub> undetected by XRD analysis. For the case of materials onto  
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52 MgAl<sub>2</sub>O<sub>4</sub> and ZrO<sub>2</sub>, there is only one reduction peak in the range 250-350 °C, that is  
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54 wider for the materials onto MgAl<sub>2</sub>O<sub>4</sub>. On the other hand, the temperature associated  
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with the reduction of  $\text{Cu}^{2+}$  of the different CuO-based materials with similar Cu contents has varied slightly depending on the support. In this way, these temperatures have been determined as 220 - 230 °C for materials onto  $\text{Al}_2\text{O}_3$ , 248 °C for materials onto  $\text{MgAl}_2\text{O}_4$  and 266 °C for materials onto  $\text{ZrO}_2$ .



**Figure 3:** a) XRD tests before and after TGA operation for solids synthesized by different techniques; b) TPR data for solids on different supports and prepared through different synthesis procedures: (left)  $\text{Al}_2\text{O}_3$  as support, (center)  $\text{MgAl}_2\text{O}_4$  as support and (right)  $\text{ZrO}_2$  as support.

Regarding to the BET surface area, Table 1 shows that the materials supported on  $\text{MgAl}_2\text{O}_4$  or  $\text{Al}_2\text{O}_3$  (synthesized by SD, COP, DP and MM) with Cu loads around 65%wt. presented similar values (close to  $20 \text{ m}^2 \text{ g}^{-1}$ ). However, the solids onto  $\text{Al}_2\text{O}_3$  prepared by SD as well as the materials supported on  $\text{ZrO}_2$  presented much lower

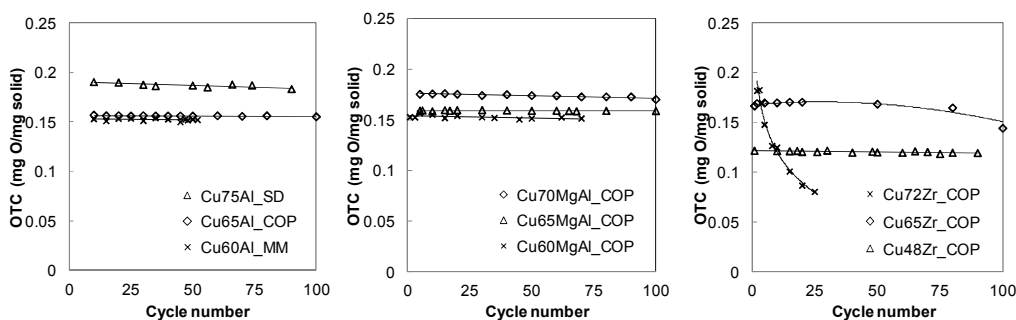
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3 (below  $7 \text{ m}^2 \text{ g}^{-1}$ ) surface areas. In the case of the SD method, the low specific surface  
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5 areas that show this kind of materials could be related with the absence of the strongly  
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7 basic sites because no adjustment of the pH was carried out during the synthesis, and  
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9 some authors have reported that the pH strongly influenced the structure of the oxygen  
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11 carriers <sup>50</sup>. Other works in the literature have shown a progressive and important  
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13 decrease in the values of the specific surface areas of CuO-ZrO<sub>2</sub> materials as the Cu  
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15 load in the materials increased <sup>85</sup>. Águila et al. <sup>81</sup> showed that an increase in the Cu load  
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17 favored the formation of large CuO particles, but the concentration of the dispersed  
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19 copper species would remain constant which indicated a stabilization of the dispersed  
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21 CuO species on some zirconia surface sites. Other published works showed an increase  
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23 of specific surface areas for Cu loads up to 30 %wt. and a decrease in the BET surface  
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25 area when the Cu content was over 50 %wt. <sup>86</sup>. The increase of surface area with an  
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27 increase in Cu content was interpreted as being due to the contribution of the copper  
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29 species to the tetragonal zirconia formation which indicates that the Cu is  
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31 monodispersely distributed on the surface of ZrO<sub>2</sub>. However, when the Cu content is  
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33 greater than a certain value, copper could be incorporated in the zirconia lattice and  
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35 amorphous composites could be obtained.  
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39 The porosity of the samples prepared by COP with similar Cu load (around 65%wt) has  
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41 been determined and high values have been obtained for the Al<sub>2</sub>O<sub>3</sub> (60%) and MgAl<sub>2</sub>O<sub>4</sub>  
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43 (75%) materials in powder form. Although the porosity of the pellets have decreased  
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45 with respect to the materials in powder form ( $P_{\text{Cu65Al\_COP\_a}} = 48\%$  and  
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47  $P_{\text{Cu65MgAl\_COP}} = 43\%$ ), this values are considered suitable for this kind of  
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49 materials. Finally, regarding to the CuO-samples density, the data obtained from He  
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51 picnometry are in the expected range for these type of materials as it can be appreciated  
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53 in Table 1 ( $5500 - 6200 \text{ kg m}^{-3}$ ).  
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### 3.2. Chemical and mechanical stability

#### 3.2.1. Materials in powder form.

The chemical stability of the synthesized materials was evaluated in the TGA apparatus described in the experimental section. Approximately, 100 reduction/oxidation cycles were performed for each CuO-based material. The materials were tested according to the routines described in the experimental section. The theoretical OTC values and the experimental OTC values for each material at cycle 100 have been added to Table 1. Highly stable OTC values were obtained for the materials synthesized by COP onto  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  with 65%wt. of Cu load or below, but a dramatic decrease in the experimental OTC values was determined for the materials onto  $\text{ZrO}_2$  with 72%wt. of Cu. In addition, Figure 4 shows the evolution of the OTC for materials with different Cu loads and onto the three supports tested in terms of the number of reaction cycles. According to this Figure, considering the materials with the highest Cu load for each support (over 70 %wt. Cu), the materials supported on  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  presented a fairly stable OTC and lost less than 5% of their initial transport capacity even after long periods of operation. In contrast a dramatic decrease in OTC nearly from the first cycle is well appreciated for the material supported on  $\text{ZrO}_2$  and it is reduced by 60 % after 25 reaction cycles. Only the reduction of the Cu load below 50 %wt. resulted in stable materials for the system CuO- $\text{ZrO}_2$  since, as previously mentioned, limited by the formation of m- $\text{ZrO}_2$ . The materials prepared by the different synthesis routes (DP, MM, COP) onto  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  with Cu contents around 65 %wt. and below, presented a highly stable oxygen transport capacity (losses below 1%).



**Figure 4.** Oxygen transport capacity (mg O transported/mg oxidized solid) in oxidation-reduction cycles: (left)  $\text{CuO}/\text{Al}_2\text{O}_3$ , (center)  $\text{CuO}/\text{MgAl}_2\text{O}_4$  and (right)  $\text{CuO}/\text{ZrO}_2$  material.

With respect to the individual conversion curves on each cycle, Figure 5a shows examples of oxidation conversion curves for cycles 20 and 100 for materials with different Cu load and onto the different supports tested. With respect to the cycle 20, slight differences appear on the slope of the oxidation conversion curve among the materials supported onto  $\text{Al}_2\text{O}_3$ . A small second slope in the oxidation conversion was observed in all the materials except in the solid synthesized by COP. The differences in materials conversion curves at cycle 100 increased, and the oxidation curves for the materials synthesized by DP and MM, although were very similar along cycles, revealed that there could be other species in the materials due to the existence of a change in the slope of the Cu conversion curve for conversions higher than 0.9. This aspect is likely associated to the formation of small quantities of  $\text{CuAl}_2\text{O}_4$  during the course of the oxidation reaction. Finally the SD material presented an important reduction on the oxidation reaction rate with cycles and the shape of the curve might indicate that diffusion phenomena might play a role during the oxidation of the material as the shape of the curve resembles the oxidation curves of the materials in which a collapse of the original chemical structure is produced. This is caused because the inert content in the material is not high enough to provide a high long-term chemical stability and mechanical stresses are caused between the active phase and the support. In the



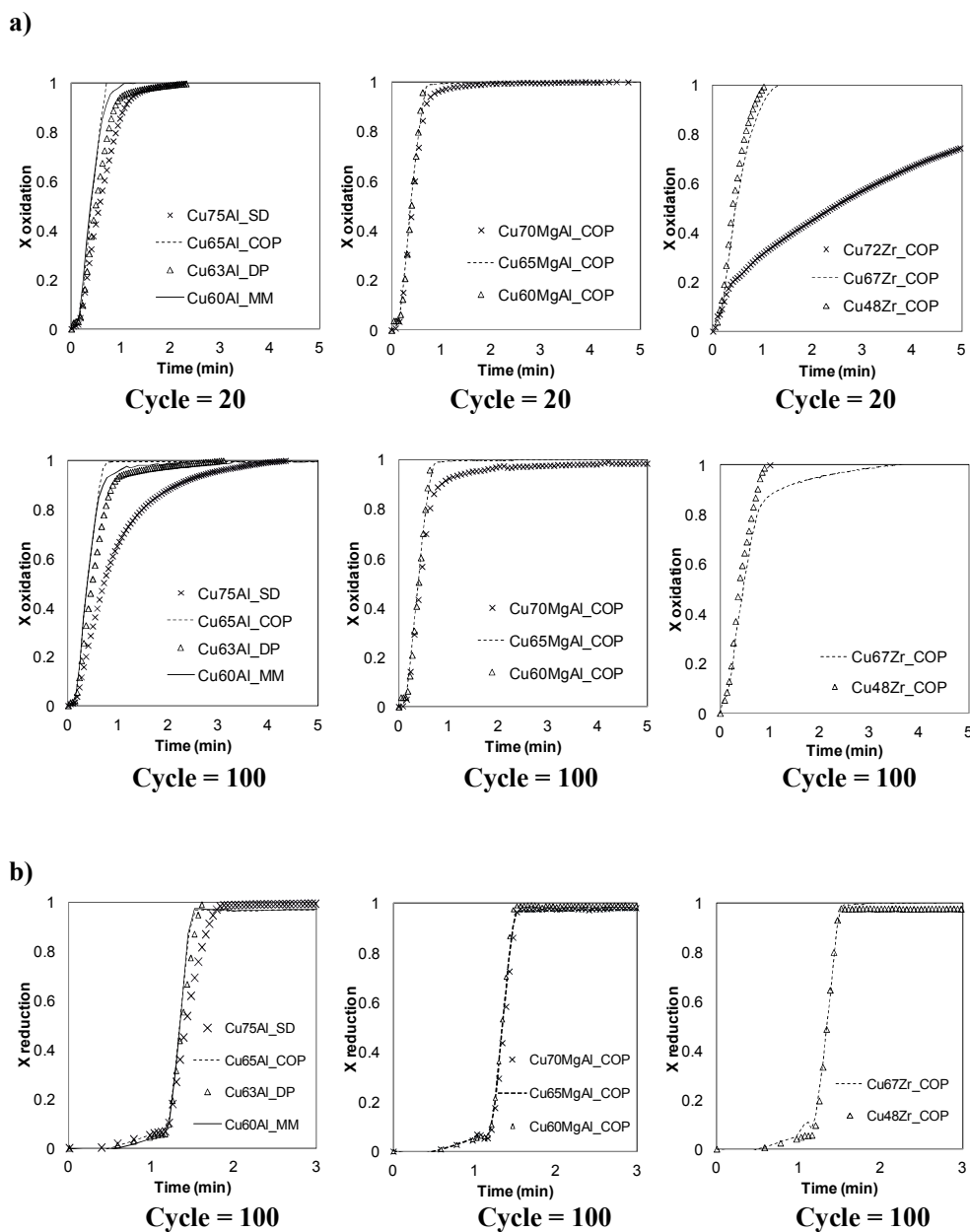
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3 past, some authors tested materials with 100%wt. of Cu load and they observed a  
4 dramatic decrease in the chemical stability with cycles<sup>40</sup>. Therefore, the morphological  
5 changes in the chemical structure of the materials with too high Cu loads after cycles,  
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7 can cause a difficulty for the O<sub>2</sub> to access to the Cu active sites and the diffusion of the  
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9 gas can become important during the oxidation reaction.  
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16 In contrast, the COP material oxidation curve is almost unaltered with respect to cycle  
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18 20. Focusing on materials that use MgAl<sub>2</sub>O<sub>4</sub> as support, materials with Cu contents up  
19  
20 to 65 %wt. presented almost identical conversion curves at cycles 20 and 100, while the  
21  
22 material with the highest Cu load (70 %wt.) presented a slight decrease in OTC. Also  
23  
24 its oxidation conversion curve at cycle 100 presented an important decrease in reaction  
25  
26 rate for conversions higher than 0.85. With respect to materials supported on ZrO<sub>2</sub>, and  
27  
28 in line with the data from Figure 4 for ZrO<sub>2</sub> materials, it can be observed that the  
29  
30 material with the highest Cu load presented an oxidation conversion curve with a very  
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32 slow reaction rate from the initial cycles, and as the number of reaction cycles  
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34 proceeded only the material with Cu contents below 50 %wt. maintained the reactivity.  
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38 Figure 5b shows the reduction conversion curves of the different materials grouped by  
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40 material support. During the first minute of these curves, a pure N<sub>2</sub> stream was feed to  
41  
42 the TGA. A practically negligible loss in the weight of the samples is observed in this  
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44 period which means that the CLOU effect is avoided under the operating conditions.  
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46 After the first minute, a stream with 20 vol% of H<sub>2</sub> in N<sub>2</sub> was passed through the sample  
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48 and very similar reduction conversion curves were obtained for all materials despite of  
49  
50 its support or synthesis method, achieving total conversion in less than one minute.  
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52 However, in the case of the materials onto Al<sub>2</sub>O<sub>3</sub> prepared by SD, in agreement with the  
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3 results obtained on the oxidation reaction curves, the reduction reaction rate was a bit  
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5 slower than for the materials onto  $\text{Al}_2\text{O}_3$  prepared by other synthesis routes.  
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7 On view of the characterization results and the experimental data from Figure 4 and the  
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9 experimental curves presented in Figure 5, it seems that the materials onto  $\text{Al}_2\text{O}_3$  and  
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11  $\text{MgAl}_2\text{O}_4$  with Cu contents between 60 to 65 %wt. could be suitable for the Ca/Cu  
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13 process in terms of chemical stability. At this point the materials supported onto  $\text{ZrO}_2$   
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15 were discarded from further study as the development of suitable CuO-based materials  
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17 onto this support should be investigated at lower calcination temperatures during  
18  
19 synthesis in order to obtain the structure t-  $\text{ZrO}_2$ . However the Ca/Cu looping process  
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21 takes place at high temperatures and therefore the formation of m-  $\text{ZrO}_2$  during  
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23 operation would be also possible so the use of this support in this kind of processes  
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25 should be avoided. Moreover, the Cu load that would allow for a stable material on  
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27  $\text{ZrO}_2$  with the current m- $\text{ZrO}_2$  structure in the material would introduce an excessive  
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29 inert fraction in the reactors which would affect negatively the process energy  
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31 balances<sup>9</sup>.  
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**Figure 5:** a) Oxidation reaction curves of CuO-based materials depending on the material support ( $T=870^{\circ}\text{C}$ , 20vol%  $\text{O}_2$ , cycle number=20 and 100): (left)  $\text{Al}_2\text{O}_3$ , (center)  $\text{MgAl}_2\text{O}_4$ , (right)  $\text{ZrO}_2$ . b) Reduction reaction curves of CuO-based materials depending on the material support ( $T=870^{\circ}\text{C}$ , 20vol%  $\text{H}_2$ , cycle number=100): (left)  $\text{Al}_2\text{O}_3$ , (center)  $\text{MgAl}_2\text{O}_4$ , (right)  $\text{ZrO}_2$ .

All the materials were examined after testing in the TGA to observe any sign of agglomeration caused by the redox cycles. In this way, the samples onto  $\text{Al}_2\text{O}_3$  and

MgAl<sub>2</sub>O<sub>4</sub> prepared by COP were not affected in any case by agglomeration phenomena. On the other hand, the samples synthesized by MM tended to form an external hard layer that was breakable but in contrast, high agglomeration was observed in SD and DP samples after the reduction/oxidation cycles.

In view of the experimental results obtained at this point, COP has been selected as a suitable route to produce materials with the best long term performance. Thereby, the materials with Cu loads around 65%wt. either onto Al<sub>2</sub>O<sub>3</sub> or MgAl<sub>2</sub>O<sub>4</sub> were the COP materials with the highest Cu content that also presented high chemical stability.

In Figure 6a the SEM images of fresh samples of the selected CuO-based materials in powder form are shown in a scale of 10 μm. The SEM analysis carried out to the selected samples with Cu loads around 65 %wt. in oxidized form showed that there is a homogeneous dispersion of CuO on to the inert support in both solids. The light areas of SEM images are related with the presence of Cu, and the dark grey zones indicate the presence of Al and/or Mg. It can be appreciated in the Figure that copper particles were a bit smaller than the particles of the material used as support. Regardless the support used, the MgAl<sub>2</sub>O<sub>4</sub> material showed substantially smaller particles than the Al<sub>2</sub>O<sub>3</sub>. Finally, both materials presented a homogeneous dispersion of the compounds throughout all the sample.

### 3.2.2. Materials in pellet form

The materials selected in powder form as optimal candidates for the Ca/Cu looping process were pelletized in order to analyze their mechanical stability. In addition the Cu material with the highest Cu load (70 %wt.) onto MgAl<sub>2</sub>O<sub>4</sub> was also pelletized to determine the limit of Cu load that can reach this type of materials. In this way three types of pellets (P\_Cu65Al\_COPa, P\_Cu65Al\_COPb, P\_Cu65Al\_COPc) were prepared

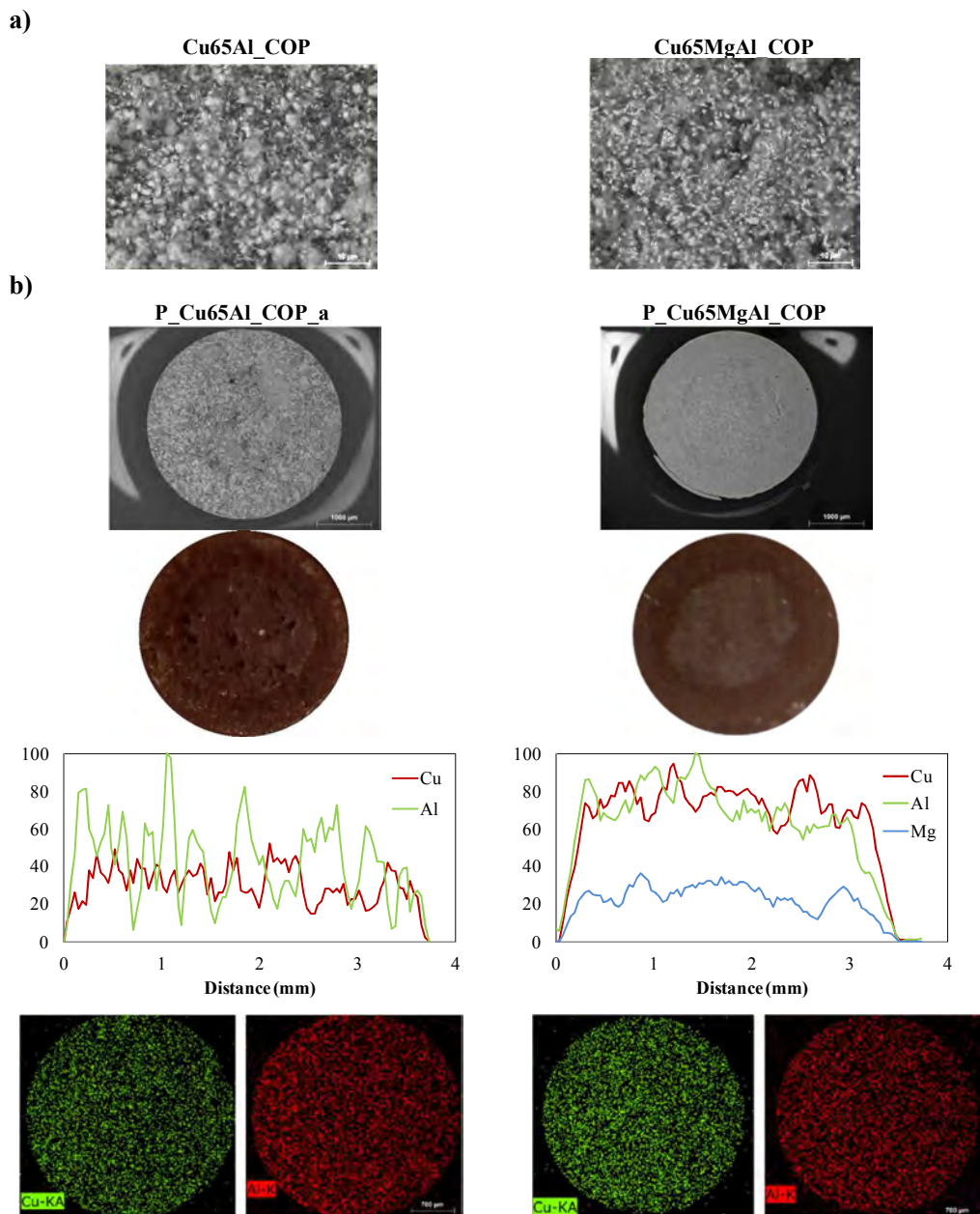
from the Cu65Al\_COP powder, whose main difference was the pellet density. Small quantities of a material used as a binder was incorporated during the preparation of the pellets onto Al<sub>2</sub>O<sub>3</sub>, and therefore the Cu content in these pellets decreased a bit (Cu load around 60%wt.) with respect to the pellets supported on to MgAl<sub>2</sub>O<sub>4</sub> (without binder material). In addition, pellets from the Cu65MgAl\_COP and Cu70MgAl\_COP materials were also prepared (P\_Cu65MgAl\_COP, P\_Cu70MgAl\_COP). Table 2 details the main characteristics of the pellets.

**Table 2:** Characteristics of pellets supported on Al<sub>2</sub>O<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub> made from the selected powdered materials. *The dimensions of the pellets are: diameter = height = 3.3·10<sup>-3</sup> m for the pellets onto Al<sub>2</sub>O<sub>3</sub> and diameter = height = 3.0·10<sup>-3</sup> m for the pellets onto MgAl<sub>2</sub>O<sub>4</sub>.*

Reference	Origin material	$\rho$ (kg m <sup>-3</sup> )	%wt. Cu	$\varepsilon$ (%)	OTC (mgO mg solid <sup>-1</sup> )
P_Cu65Al_COP_a	Cu65Al_COP	2300	59.4	48	0.149
P_Cu65Al_COP_b	Cu65Al_COP	2900	57.5		0.143
P_Cu65Al_COP_c	Cu65Al_COP	2540	58.8	43	0.148
P_Cu70MgAl_COP	Cu70MgAl_COP	2160	69.0		0.174
P_Cu65MgAl_COP	Cu65MgAl_COP	2260	65.0		0.160

The materials were cut and the cross-section was analyzed by SEM-EDX to determine their homogeneity. Figure 6(b) shows an example of the SEM images, photographs and EDX figures obtained for the two different pellets produced with the different supports (P\_Cu65Al\_COP and P\_Cu65MgAl\_COP). The EDX applied to the pellets diameter showed an homogeneous dispersion of the Cu<sup>2+</sup>, Al<sup>3+</sup> and Mg<sup>2+</sup> ions when present. In

the mapping obtained by EDX to the Cu and Al elements individually, can be appreciated a uniform distribution of the elements throughout both pellets.



**Figure 6:** a) SEM images for fresh selected materials in powder form; b) SEM and EDX analysis for fresh pellets: SEM images (first row), photographs (second row) and EDX figures (third row).

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3 Following a similar procedure as done for the materials in powder form the evolution of  
4 pellets oxygen transport capacity with the number of reaction cycles was assessed in the  
5 TGA apparatus described in the experimental section. Figure 7a (left) shows the  
6 evolution of OTC (mg O/mg oxidized material) during more than 150 reaction cycles of  
7 the COP materials with 65 %wt. of Cu load on to  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$ . According to the  
8 Figure, both materials presented highly stable oxygen transport capacity with maximum  
9 losses of 1% of OTC in the last cycles.  
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18 It must be highlighted that the materials in pellet form showed similar OTC values to  
19 the powders which means that all the Cu remains active during the oxidation and  
20 reduction reactions and there is no formation of inaccessible sites of copper inside the  
21 pellet along the cycles. In the case of the OTC of the pellet onto  $\text{Al}_2\text{O}_3$ , the value has  
22 been slightly reduced with respect to the pellet onto  $\text{MgAl}_2\text{O}_4$  due to the addition of  
23 small quantities of binder as it has been mentioned in the previous paragraphs.  
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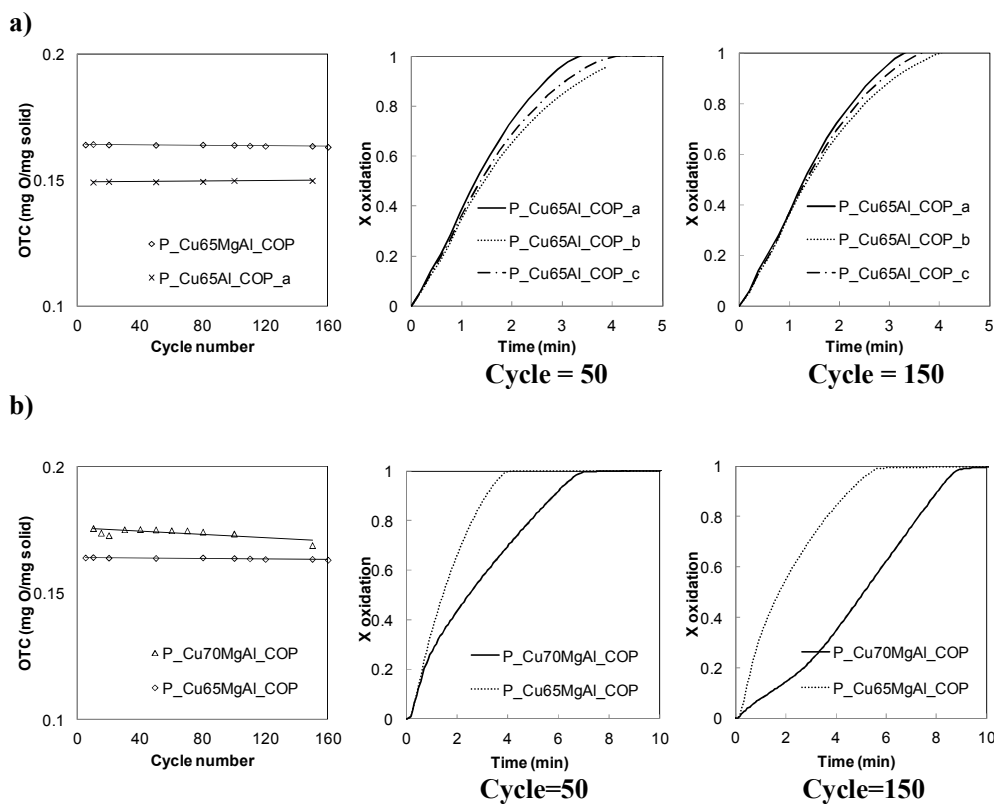
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31 Regarding to the oxidation conversion curves of the pellets supported on  $\text{Al}_2\text{O}_3$   
32 synthesized by Johnson Matthey for cycles 50 and 100 (Figure 7 (a, right)), it can be  
33 observed that all the pellets reach complete conversion in less than 4 minutes but slight  
34 differences on the slope of the curves among the materials can be appreciated. These  
35 differences are more relevant during the 50<sup>th</sup> cycle being the P\_Cu65Al\_COP\_b which  
36 presents the smaller slope followed by P\_Cu65Al\_COP\_c. In addition, these pellets that  
37 have the greatest values of density presented slightly slower reaction rates at the initial  
38 cycles which could be due to the decrease in porosity of these materials and therefore  
39 the slightly greater difficulty to the  $\text{O}_2$  to access to the Cu active sites.  
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51 However it can be observed that the slope of the oxidation conversion of the three  
52 pellets is practically the same in the 100<sup>th</sup> cycle which means that the oxygen is able to  
53 easily access inside the pellet as long as the cycles proceed. As well as the reduction  
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3 conversion curves of the materials in powder form, no remarkable differences were  
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5 detected among materials in the reduction curves of the pellets as these curves were  
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7 highly repetitive in terms of the number of cycles and the reduction occurred very fast.

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9 In view of the results obtained for the chemical stability of the pellets with 65 %wt. onto  
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11  $\text{Al}_2\text{O}_3$ , a similar study was carried out for the pellet with 65 %wt. onto  $\text{MgAl}_2\text{O}_4$ .  
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13 Besides, the mechanical stability of the material with 70 %wt. onto  $\text{MgAl}_2\text{O}_4$  was  
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15 tested. Figure 7 (b, left) shows the evolution of OTC (mg O/mg oxidized material)  
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17 during more than 150 reaction cycles of the COP materials with 65 and 70 %wt. of Cu  
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19 load onto  $\text{MgAl}_2\text{O}_4$ . According to this Figure, the OTC of the pellet with 65 %wt. of Cu  
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21 load remained highly stable along 150 cycles. However, the loss in the OTC in the  
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23 pellet with 70%wt. of Cu can be clearly appreciated and it descends slowly and  
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25 progressively from cycle 1 to cycle 150. Then, there seems to be a limit in Cu content to  
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27 obtain highly stable materials and this limit has been found around 70%wt of Cu load  
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29 for the  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  supports. It seems that an increase up to 70%wt. of Cu load  
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31 in the material results in a non-homogeneous mixture between the different phases  
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33 present in the material. This aspect together with the decrease in hardness of the pellet  
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35 due to the reduction of spinel content <sup>87</sup>, which is required in a certain proportion since  
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37 it allows the improvement of the mechanical properties of the pellet, makes that there is  
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39 a maximum Cu load in the materials that should not be exceeded to develop highly  
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41 stable materials.  
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**Figure 7: a) Left:** OTC for pellets with Cu load around 65%wt. on to  $Al_2O_3$  and  $MgAl_2O_4$  during approximately 150 oxidation-reduction cycles. **Right:** Oxidation curves for pellets with different characteristics made from the powdered material  $Cu65Al\_COP$  with 20vol%  $O_2$  at 870°C (cycles = 50 and 100); **b) Left:** OTC for pellets on to  $MgAl_2O_4$  with 65%wt. and 70%wt. during approximately 150 oxidation-reduction cycles. **Right:** Oxidation curves for  $CuO-Al_2O_3$  and  $CuO-MgAl_2O_4$  pellets with 20vol%  $O_2$  at 870°C: (left) cycle = 50, (right) cycle = 150.

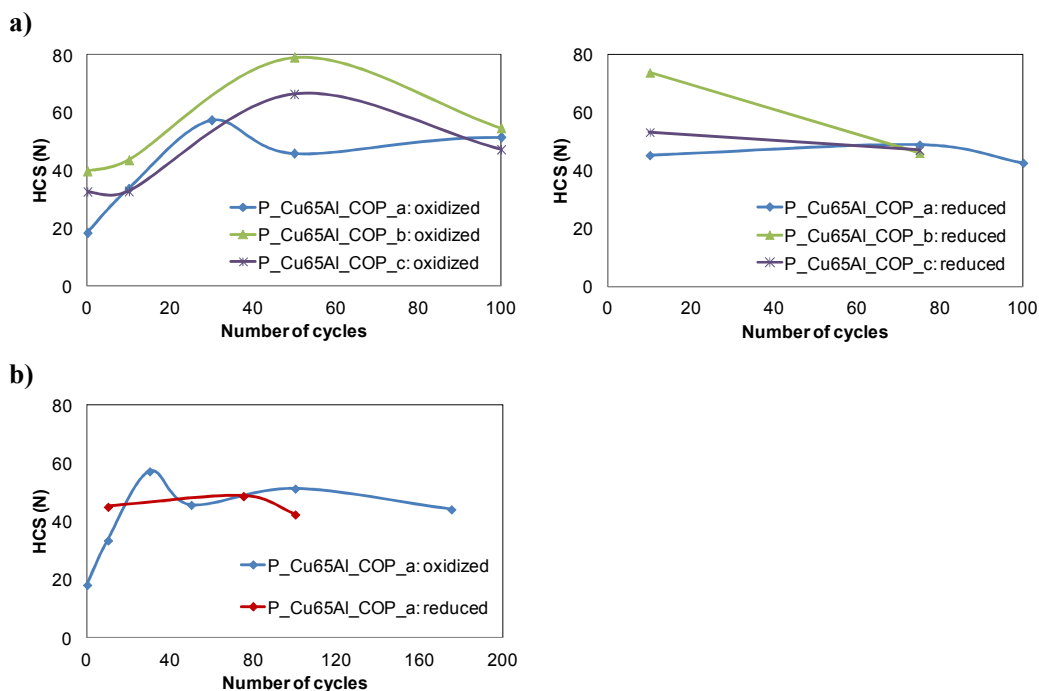
Finally, an additional study was carried out in order to analyze the mechanical strength of several pellets after cycles in oxidized and reduced conditions. Three pellets made from the powdered material synthesized by COP and supported on  $Al_2O_3$  with 65wt% of Cu load, but with different physical properties ( $P_{Cu65Al\_COP\_a}$ ,  $P_{Cu65Al\_COP\_b}$  and  $P_{Cu65Al\_COP\_c}$ ), were tested in a Shimpo Dynamometer to determine the horizontal crushing strength after several number of cycles (10, 50, 75,

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3 100, 200), both in oxidized and reduced forms. In Figure 8a the values of horizontal  
4 crushing strength (HCS) of oxidized and reduced pellets tested for different redox  
5 cycles are plotted.  
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9 The oxidized pellets followed a progressive trend of increase in strength during the first  
10 35 - 45 cycles, achieving values of HCS up to 55 N in all cases. After this period, during  
11 the cycles 60 - 100 two pellets (P\_CuAl\_COP\_b and P\_CuAl\_COP\_c) lose strength  
12 until values around 60 N and other keep similar values during these cycles  
13 (P\_CuAl\_COP\_a). In this way, the pellet P\_Cu65Al\_b, that is the material with the  
14 highest density, showed the highest increase on strength (until 80 N approximately)  
15 however the prompt drop in HCS was also produced in oxidized and reduced forms.  
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19 On the other hand, the reduced pellets were initially hardest than the oxidized and  
20 although the pellet with the greater density showed a rapid drop, the other pellets  
21 keeping similar values of HCS for 80 cycles.  
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25 Therefore the pellet with the lowest density (P\_Cu65Al\_COP\_a) presented the best  
26 mechanical behavior in multiple cycles. The HCS values for both oxidized and reduced  
27 pellet of P\_Cu65Al\_COP\_a after 175 cycles are reported in Figure 8b. As it can be  
28 concluded by this study, the pellet with the lowest density is associated also with the  
29 highest porosity value which would decrease the thermal shock resistance produced  
30 during cycles. It is also interesting to highlight that the HCS values of this pellet during  
31 the course of the cycles in oxidized and reduced forms were very similar which is a very  
32 important aspect in order to develop materials with high mechanical resistance to  
33 oxidizing and reducing conditions at high temperature.  
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**Figure 8:** **a)** Horizontal crushing strength in 100 cycles of oxidized pellets (left) and reduced pellets (right); **b)** Horizontal crushing strength in oxidized and reduced pellets of S0397-1047-2 along 175 cycles.

#### 4. CONCLUSIONS

Materials with Cu contents between 48 %wt. to 75 %wt. supported onto  $\text{Al}_2\text{O}_3$ ,  $\text{MgAl}_2\text{O}_4$  and  $\text{ZrO}_2$  were synthesized by SP, COP, DEP and MM. Highly stable materials with Cu loads around 65%wt. onto  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  has been obtained by COP. The results confirmed a good dispersion between the active phase and the support in both, materials in powder and pellet form. It is essential not to exceed the amount of boundary copper that the material is capable of containing in order to obtain a good dispersion of the different phases inside the material as an increase until 70%wt. of Cu in pellets meant a marked decrease in oxidation reaction rate after cycles. On the other

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3 hand, materials onto ZrO<sub>2</sub> with similar Cu content by COP showed a progressive lost in  
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5 oxygen transport capacities from the first cycles which it has been associated to the  
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7 formation of monoclinic ZrO<sub>2</sub>. On the other hand, SD and DP were not a suitable routes  
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9 for this kind of materials as materials by SD presented low specific surface areas and  
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11 the DP method resulted in materials with very large CuO crystals.

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13 The evolution of the OTC of the selected materials in powder form was fairly stable  
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15 along 100 reduction/oxidation cycles. In the same way, the mechanical stability of the  
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17 pellets during 150 cycles has been successfully confirmed and the oxygen transport  
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19 capacity was evaluated finding a maximum loss of 1% in the last cycles. Similar HCS  
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21 values and no agglomeration signs along multiple cycles were found for the pellets  
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23 which is a very important result since the point of view of the mechanical stability and  
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25 therefore these pellets are suitable candidates for the Ca/Cu process. Moreover, the  
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27 scaling up of the co-precipitation procedure would not present too many difficulties  
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29 because of the simplicity of the equipment and the good homogeneity obtained by this  
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31 method.  
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45 MINECO).  
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Highly loaded CuO-Al<sub>2</sub>O<sub>3</sub> pellet with long-term chemical and mechanical stability

