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Tuning Co-Cu-Al catalysts and their reaction conditions on the CO₂ hydrogenation reaction to higher alcohols under mild conditions.

Vitor Duarte Lage^a, Anthony Le Valant^b, Nicolas Bion^b, Fabio Souza Toniolo^a

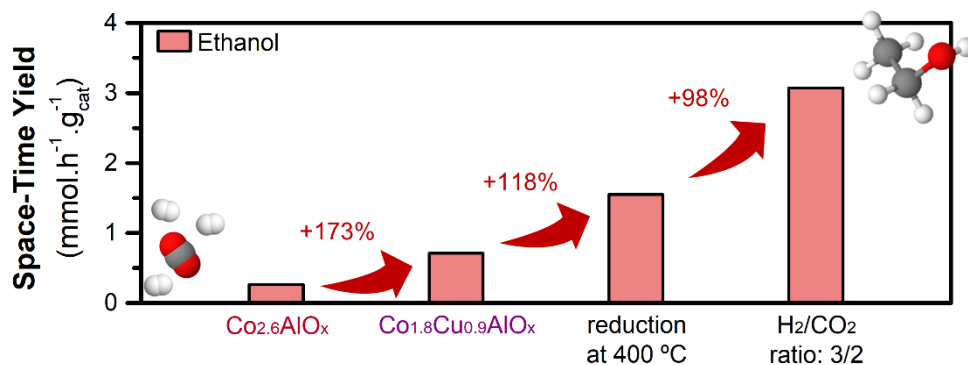
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Abstract

The catalytic conversion of CO₂ and H₂ into valuable chemicals is a promising alternative to the recent energy and environmental challenges. However, designing an earth-abundant catalyst capable of actively and selectively converting CO₂ into desirable products is yet a challenge. Herein, we report on a facile K-Co-Cu-Al catalyst prepared by a coprecipitation method for CO₂ hydrogenation to higher alcohols (HAs). We investigated different Co:Cu ratios, reduction temperatures, and reaction conditions (temperature, space velocity, and H₂/CO₂ ratio) to tune it, enhancing the selectivity and yield of higher alcohols. Co_{1.8}Cu_{0.9}AlO_x (1 wt% K), reduced at 400 °C, exhibits a high HAs selectivity of 44.8% (20.8% for ethanol) and space-time yield of 5.54 mmol·h⁻¹·g_{cat}⁻¹ (3.08 mmol·h⁻¹·g_{cat}⁻¹ of ethanol), under mild conditions (250 °C, 30 bar, H₂/CO₂ ratio of 1.5, and 14200 mL·g_{cat}⁻¹·h⁻¹), which represents one of the best performances among related studies, especially among Co-based catalysts.

Keywords: CO₂ hydrogenation; Ethanol production; CO₂ conversion; Co-based catalyst; Cu-based catalyst; Bimetallic catalyst.



28

29 **1. Introduction**

30 One of the most significant current scientific challenges is reducing the atmospheric
31 concentration of CO₂, an anthropogenic greenhouse gas responsible for global warming. To address
32 this challenge three main strategies can be employed: (i) reducing emissions; (ii) capturing and
33 storing; and (iii) utilizing or transforming CO₂. In that sense, the CO₂ hydrogenation reaction emerges
34 as a promising alternative to both capture and transform this anthropogenic gas, as CO₂, captured
35 from industrial effluents, can serve as a C1 building block to produce value-added products and
36 feedstock [1,2]. However, the CO₂ hydrogenation reaction can yield various possible products,
37 including CO, CH₄, C₂₊ hydrocarbons (HCs), methanol, and higher alcohols (HAs or C₂₊OH), each
38 with its advantages, disadvantages, and academic challenges [3–6].

39 Among these products, higher alcohols, particularly ethanol, have garnered significant
40 research and industrial attention due to their versatile applications as fuel, solvents, chemical
41 precursors, and cleaning agents. They also offer higher energy density, sustainability, and reduced
42 environmental impact compared to alternative substances [3,5–8]. Nonetheless, tailoring the
43 catalysts, and optimizing the process condition are key challenges in this field [4,5].

44 For the synthesis of HAs via CO₂ hydrogenation, various catalysts have been reported [9–
45 16], but certain trends have been identified, including Rh-based, Cu-based, Co-based [5,6,8], Pd-
46 based [5], and Mo-based [6,8] catalysts. Among these, Co- and Cu-based catalysts stand out as
47 non-noble metal catalysts [11], offering relative cost advantages. Co-based catalysts exhibit higher
48 CO₂ conversion [5,6,8], but methane is typically the predominant product formed [11], particularly in

49 their metallic form (Co^0). However, recent studies have demonstrated that modifying Co-based
50 catalysts through alloy formation or interaction with some oxide supports can reduce their ability to
51 break the C-O bond, favoring HAs formation [5,8]. These modified Co-based catalysts (CoAlO_x , Na-
52 Co/SiO_2 , $\text{Pt/Co}_3\text{O}_4$, LaCoGaO_3 , CoNiAlO_x) have been studied in both continuous and batch reactions
53 for HAs synthesis, exhibiting CO_2 conversion ranging from 5-67%, selectivity to HAs from 0.05-92%,
54 and space-time yield (STY) from $0.01\text{-}2.16\text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$ [8].

55 Cu has emerged as a promising metal for Co-based alloys [14,17], as it promotes CO-
56 insertion [18] and inhibits C-O bond cleavage [8,19]. Additionally, alkali metals have been
57 investigated as promoters to enhance basicity by donating electrons to Co sites. Amidst, Na, and K
58 have been extensively studied for HAs synthesis, as they have been reported to reduce CH_4
59 formation, increase CO_2 conversion, and tune HAs selectivity [5,6,11,20,21]. However, excess Na
60 (>5 wt%) can inhibit CO insertion, increasing CO selectivity [8]. For K, a wide range of weight content
61 (0.1-17.6 wt%) has been explored, with optimal composition falling between 0.5 to 4.6 wt%
62 [11,12,20–23].

63 Regarding the reaction conditions, determining the optimal temperature, H_2/CO_2 ratio, and
64 space velocity, among other parameters, is detrimental to improving the HAs synthesis. Temperature
65 plays a dual role, favoring CO_2 conversion with its increase but hindering HAs formation [5,24].
66 Similarly, increasing the H_2/CO_2 ratio also favors conversion, but excess H_2 can further hydrogenate
67 the reaction intermediate of ethanol, while decreasing it can favor methanol synthesis routes [5,25].
68 Adjusting the space velocity (SV) is also vital. Increasing SV results in lower conversion, whereas
69 lower velocities can favor some reaction pathways over others, leading to undesired products
70 [5,9,26]. In summary, optimizing these conditions is necessary to strike a balance between
71 conversion and product selectivity, thereby increasing the yield of the desired product [5]. Most Co-
72 based catalysts exhibit optimal performance in the temperature range of 140-250 °C with space
73 velocity between $3000\text{-}6000\text{ mL}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$ [6]. However, the effect of the H_2/CO_2 ratio has not been
74 widely explored.

75 To address the need for improving CO_2 conversion and inhibiting the formation of undesired
76 products, mainly methane, we propose investigating CoCu catalysts. In this study, we prepared a

77 series of $\text{Co}_{(2.8-n)}\text{Cu}_n\text{AlO}_x$ catalysts derived from layered-double hydroxides (LDH), carefully tailored
78 to retain 1 wt% of K. LDHs have garnered attention as promising precursors for heterogeneous
79 catalysts due to their thermal stability and the possibility of modifying the characteristics of the
80 resulting material such as surface area, particle size, electronic state and distribution of metal
81 species [14,27,28]. Moreover, LDH-derived catalysts can easily be synthesized on a large scale via
82 coprecipitation and have shown promising results in CO_2 hydrogenation to ethanol [11,14,24,29].

83 Herein, we aim to explore different Co:Cu ratios, reduction temperatures, and reaction
84 conditions (temperature, space velocity, and H_2/CO_2 ratio) to investigate their effects on CO_2
85 conversion, product selectivity, and yield. By fine-tuning the catalyst design and optimizing the
86 reaction conditions, we aspire to overcome the thermodynamic and kinetic limitations associated
87 with CO_2 hydrogenation and enhance the efficiency and viability of higher alcohol synthesis.

88 **2. Experimental**

89 2.1 Catalyst Preparation

90 The $\text{Co}_{(2.8-n)}\text{Cu}_n\text{AlO}_x$ samples were derived from the calcination of LDH clays, which were
91 prepared by a modified coprecipitation method [30,31]. The alkaline solution was formed by 2 M
92 NaOH (Sigma-Aldrich, $\geq 98\%$) and 0.5 M Na_2CO_3 (Sigma-Aldrich, $\geq 99.5\%$). The precursor solution
93 (1 M) was prepared by dissolving $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 98\%$), $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (Sigma-
94 Aldrich, $\geq 98\%$), and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 98\%$), in deionized water, with the desired
95 Co:Cu:Al molar ratio. The chosen M:Al ratio (M: active metals, i.e., Co and Cu) was 2.8, based on
96 other works reporting similar materials [30–34]. The selected molar ratios of Co and Cu, expressed
97 by the $\text{Co}/(\text{Co}+\text{Cu})$, were 0, 0.5, 0.66, and 1.

98 Both the precursor and alkaline solutions were added drop-wise to a recipient under agitation,
99 maintaining pH 10 by regulating the flow of the alkaline solution. After adding the precursor solution,
100 the resulting solution was aged overnight, filtered, and washed thoroughly in deionized water to
101 remove excess sodium [30,31]. The resulting filtered cake was suspended in a K_2CO_3 with
102 concentration adjusted to obtain approximately 1 wt% K in the catalyst [34,35]. Finally, the resulting
103 sludge was filtered and calcined in a muffle furnace in static air at 500 °C for 3 h [34,36].

104 2.2 Characterization

105 The metal content in each prepared sample was determined by ICP-OES (Inductively
106 Coupled Plasma Optical Emission Spectrometry) on a Perkin Elmer Optima 2000DV spectrometer.
107 Prior to analysis, the samples underwent acid digestion, i.e., dissolved in an HNO₃/HCl acidic mixture
108 (1:3 ratio) and heated by microwave. The solution was then injected into the plasma as an aerosol
109 generated by a nebulizer.

110 The identification of the crystalline phases and crystallographic properties of the prepared
111 samples were analyzed via X-ray diffraction (XRD) collected on a Rigaku Miniflex diffractometer
112 (30 kV, and 15 mA) with an X-ray tube Cu target (CuK α , $\lambda=1,5418 \text{ \AA}$). The diffractograms were
113 collected with Bragg angles ranging from 10^o to 80^o, using a continuous scan mode with a step size
114 of 0.05^o and a collection time of 1 s per step.

115 The textural properties such as surface area (A_{BET}), pore volume (V_{pore}), and pore diameter
116 (d_{pore}) of the calcined catalysts were determined by N₂ physisorption using a Micromeritics Tristar
117 instrument and calculated according to the method of Brunauer, Emmet and Teller (BET). The
118 samples were degassed at 200 °C overnight before the N₂ physisorption analysis.

119 The reduction profile of the catalysts was analyzed in temperature-programmed reduction
120 (TPR) experiments employing a Micromeritics Autochem II 2920 apparatus equipped with a thermal
121 conductivity detector (TCD). The samples were pretreated at 200 °C with an Ar flow (30 mL·min⁻¹)
122 for 1 h. Subsequently, the TPR experiments were carried out with approximately 125 mg of catalyst
123 in a 10% H₂/Ar flow (30 mL·min⁻¹) from 30 to 1000 °C (5 °C·min⁻¹) using a programmable temperature
124 controller. The reduction degree was then calculated by dividing the real H₂-intake by the theoretical
125 H₂-intake, which, was determined based on the ICP-OES results.

126 The basicity profile of the catalysts was analyzed in CO₂ temperature-programmed
127 desorption (CO₂-TPD) experiments in a multipurpose testing unit equipped with an online quadrupole
128 mass detector QUADSTAR 422 (QMS 200, BALZERS). For that, the sample (100 mg) was placed
129 into a quartz tube reactor, which was heated (10 °C·min⁻¹) to the desired temperatures (250, 400,
130 and 500 °C) under pure H₂ flow (60 mL·min⁻¹) for 30 min, and then cooled to room temperature in
131 ultra-high purity He flow (60 mL·min⁻¹). After pretreatment, the CO₂ adsorption stage was conducted

132 by passing pure CO₂ (30 mL·min⁻¹) for 30 min and then flushing the reaction with He (60 mL·min⁻¹)
133 for 60 min. The TPD was performed by heating (20 °C·min⁻¹) the sample to 800 °C. The effluent
134 gases were monitored by an online mass detector (m/z = 2, 4, 28, 30, 32, 44, and 46).

135 2.3 Catalytic Test

136 The CO₂ hydrogenation catalytic tests for the Co_(2.8-n)Cu_nAlO_x samples were executed in a
137 continuous fixed-bed stainless steel reactor. The sample (300 mg, 0.160-0.100 mm sieved fraction)
138 was placed between two layers of SiC (0.125 mm), enough to ensure an 8 cm height reaction bed
139 and to maintain the fluid dynamic conditions between different samples. Prior to the reaction, the
140 samples underwent *in situ* reduction at four different temperatures (250, 300, 400, and 500 °C) for
141 30 min (heating ramp: 5 °C·min⁻¹) under pure H₂ flow (30 ml·min⁻¹).

142 The initial tests were conducted at 250 °C and 30 bar in an H₂/CO₂/N₂ flow (ratio: 3/1/0.25)
143 with gas-hourly space velocity (GHSV) set to 14200 mL·g_{cat}⁻¹·h⁻¹ for 24 h. Subsequently, different
144 H₂/CO₂ ratio (H₂/CO₂/N₂ ratio: 3/2/0.25), GHSV (10625 mL·g_{cat}⁻¹·h⁻¹) and temperatures (200, 250 and
145 300 °C) were explored. The outlet products were analyzed online (each 36 min) in an Agilent 7890A
146 gas chromatograph (GC). The gas products (CO, CO₂, H₂, and N₂) were detected by a TCD detector.
147 Hydrocarbons and condensable liquid products were analyzed by an FID detector. The catalytic
148 performance was expressed by CO₂ conversion (X_{CO₂}), C-based product selectivity (S_i), and the
149 product space-time yield (STY_i), calculated by the equation as follows:

$$X_{CO_2} = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} \times 100\% \quad (1)$$

$$S_i = \frac{n_i \times C_i}{\sum(n_i \times C_i)} \times 100\% \quad (2)$$

$$STY_i = \frac{F_{CO_2,in} \times X_{CO_2} \times S_i}{m_{cat}} \quad (3)$$

150 where [CO₂]_{in} and [CO₂]_{out}, respectively, are the molar concentration of CO₂ in the inlet and outlet
151 flow; C_i refers the concentration of products (CO, CH₄, C_xH_n, CH₃OH, C₂H₅OH, C₃H₇OH, among
152 others) in the outlet flow; n_i represents the number of carbon atoms for product C_i; F_{CO₂,in} stands for
153 the flow rate of CO₂; and m_{cat} is the mass of catalyst.

154 3. Results and Discussion

155 3.1 Physical-Chemical Properties

156 The metallic weight content (wt%) obtained for the samples on the ICP-OES analysis, the
157 calculated molar ratio between Co:Cu:Al, and their textural properties, are summarized in **Table 1**.
158 Henceforth the catalysts are referred to as $\text{Cu}_{2.6}\text{AlO}_x$, $\text{Co}_{1.3}\text{Cu}_{1.3}\text{AlO}_x$, $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$, and $\text{Co}_{2.6}\text{AlO}_x$,
159 according to their Co:Cu:Al ratios. We verified that the $\text{Co}/(\text{Co}+\text{Cu})$ ratios agreed with expected
160 nominal values and that obtaining an M:Al ratio close to 2.8 was possible, as desired. The samples
161 did not present any detectable amounts of Na, confirming that the treatment with K_2CO_3 solution was
162 efficiently removed the excess Na. The K content for $\text{Cu}_{2.6}\text{AlO}_x$, $\text{Co}_{1.3}\text{Cu}_{1.3}\text{AlO}_x$, $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$, and
163 $\text{Co}_{2.6}\text{AlO}_x$ was 0.8, 0.7, 0.8 and 0.9 wt%, respectively, close to the expected 1 wt%.

164

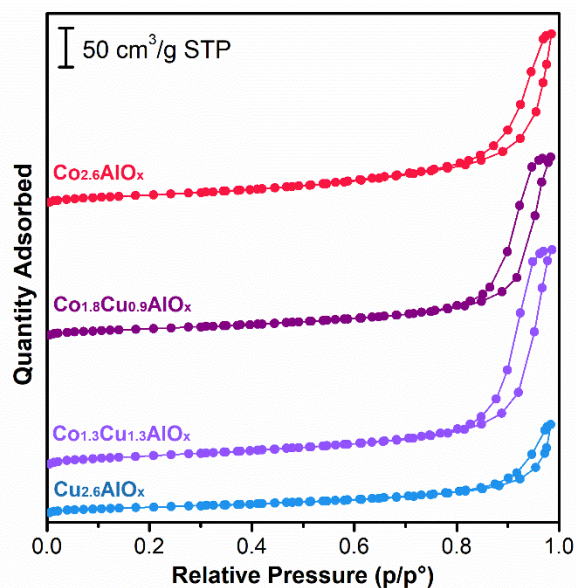
165 **Table 1.** Content of Co, Cu, Al, and K (determined by ICP-OES), Surface area (A_{BET}), pore volume
166 (V_{pore}), and pore diameter (d_{pore}) of the prepared catalysts after calcination at 500 °C.

Catalyst	Metallic content (wt%)				Co:Cu:Al Ratio	A_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	V_{pore} ($\text{cm}^3\cdot\text{g}^{-1}$)	d_{pore} (nm)
	Al	Co	Cu	K				
$\text{Cu}_{2.6}\text{AlO}_x$	9.3	0.0	57.5	0.8	0:2.6:1	56	0.18	9
$\text{Co}_{1.3}\text{Cu}_{1.3}\text{AlO}_x$	9.3	27.3	29.3	0.7	1.3:1.3:1	85	0.44	19
$\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$	9.0	34.9	18.7	0.8	1.8:0.9:1	69	0.37	18
$\text{Co}_{2.6}\text{AlO}_x$	9.1	52.2	0.0	0.9	2.6:0:1	78	0.35	13

167

168 Regarding the N_2 physisorption isotherms for $\text{Cu}_{2.6}\text{AlO}_x$ (blue), $\text{Co}_{1.3}\text{Cu}_{1.3}\text{AlO}_x$ (light purple),
169 $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ (dark purple), and $\text{Co}_{2.6}\text{AlO}_x$ (red) are shown in **Figure 1**. Based on the N_2
170 physisorption analysis, the calculated BET surface area for $\text{Cu}_{2.6}\text{AlO}_x$, $\text{Co}_{1.3}\text{Cu}_{1.3}\text{AlO}_x$, $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$,
171 and $\text{Co}_{2.6}\text{AlO}_x$ was 56, 85, 69, and 78 $\text{m}^2\cdot\text{g}^{-1}$, in that order. The values agree with the expected area
172 ($50\text{-}150\text{ m}^2\cdot\text{g}^{-1}$) for mixed oxides prepared by the modified coprecipitation method [30,36]. Moreover,
173 the hysteresis at high relative pressure (**Figure 1**) indicates the formation of a mesoporous material

174 [37], which is consistent with similar previously reported materials [27,32,37–39] and with the values
175 of pore diameter (**Table 1**).



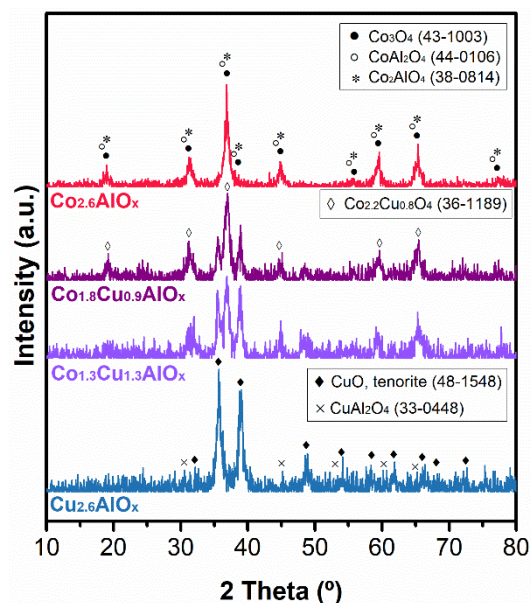
176

177 **Figure 1.** Nitrogen adsorption isotherms of for $\text{Cu}_{2.6}\text{AlO}_x$ (blue), $\text{Co}_{1.3}\text{Cu}_{1.3}\text{AlO}_x$ (light purple),
178 $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ (dark purple), and $\text{Co}_{2.6}\text{AlO}_x$ (red).

179

180 Powder XRD patterns for the samples calcined at 500 °C are presented in **Figure 2**. For
181 $\text{Cu}_{2.6}\text{AlO}_x$ (blue), a CuO (tenorite, PDF#48-1548) phase was identified. It is also possible to infer the
182 presence of small and poorly defined peaks that could be attributed to CuAl_2O_4 spinel (PDF#44-
183 0106). For $\text{Co}_{2.6}\text{AlO}_x$ (red), the Co_3O_4 (PDF#43-1003) and the Co_2AlO_4 inverse spinel (PDF#38-
184 0814) phases were compatible with the XRD pattern. It is also possible to infer the presence of
185 CoAl_2O_4 spinel (PDF#44-0106), as it presents the same position of diffraction lines only slightly
186 shifted to a lower angle. From the XRD patterns, it is difficult to distinguish Co_3O_4 from spinel-like
187 structures, as their lattice parameters are very similar [39]. As for $\text{Co}_{1.3}\text{Cu}_{1.3}\text{AlO}_x$ (light purple) and
188 $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ (dark purple), the presence of a mix of CuO, Co_3O_4 , and the Co-Al spinel-like
189 structures is the likely case. It is also reported on Co-Cu mixed oxides, such as $\text{Co}_{2.2}\text{Cu}_{0.8}\text{O}_4$
190 (PDF#36-1189), $\text{Co}_{2.05}\text{Cu}_{0.95}\text{O}_4$ (PDF#36-1189), and $\text{Co}_{2.84}\text{Cu}_{0.15}\text{O}_4$ (PDF#36-1189), to display the
191 same diffraction pattern as Co_3O_4 , with a slight shift in angle due to the small difference in Co and
192 Cu cationic radii, which implies that, through XRD, it is difficult to determine whether the pattern

193 corresponds to Co_3O_4 or a Co-Cu spinel [32,40]. Recent works reported similar materials containing
194 a mixture of different phases and spinel structures [31–33,37,39].



195

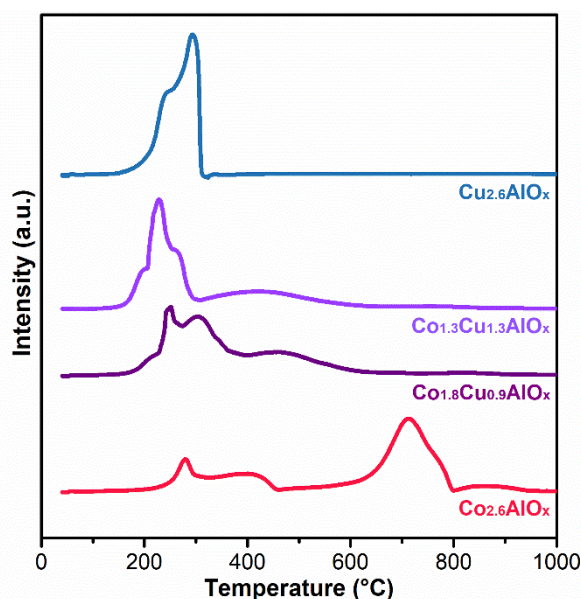
196 **Figure 2.** $\text{Cu}_{2.6}\text{AlO}_x$ (blue), $\text{Co}_{1.3}\text{Cu}_{1.3}\text{AlO}_x$ (light purple), $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ (dark purple), and $\text{Co}_{2.6}\text{AlO}_x$
197 (red) XRD patterns ($\text{CuK}\alpha$, $\lambda=1,5418 \text{ \AA}$).

198

199 The reduction profiles of the samples calcined at 500 °C were obtained using H_2 -TPR and
200 are presented in **Figure 3**. For $\text{Cu}_{2.6}\text{AlO}_x$ (blue), we observed a single reduction region around 200
201 and 300 °C, marking the reduction of Cu^{2+} to Cu^0 [41]. Similar reduction profiles for Cu-Al catalysts
202 derived from LDHs are reported in the literature [38,42–44]. For $\text{Co}_{2.6}\text{AlO}_x$ (red), we can ascribe at
203 least three distinct reduction regions: a peak at 250 °C, a broad region from 350 to 450 °C, and a
204 broad peak around 700 °C. The first peak and region are commonly attributed to the reduction of
205 Co^{3+} to Co^{2+} , and the reduction of Co^{2+} to Co^0 , whereas reduction peaks above 450 °C were
206 previously attributed to the reduction of spinel-like structures [27,35,45]. Furthermore, Co-Al
207 catalysts derived from LDHs have been reported with two distinct reduction regions, one around 250-
208 450 °C, attributed to the reduction of Co^{3+} to Co^{2+} , and other one around 550-700 °C, assigned to
209 the reduction of Co^{2+} to Co^0 [24,45–48]. For $\text{Co}_{1.3}\text{Cu}_{1.3}\text{AlO}_x$ (light purple) and $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ (dark
210 purple), we observed two distinct regions: one from 200 to 400 °C, which could be attributed to, first,
211 the reduction of Cu^{2+} to Cu^0 , along with the reduction of Co^{3+} to Co^{2+} [31,32,37].; and a second broad

212 region above 400 °C, ascribed to the two-step reduction of bulk Co^{3+} to Co^0 , the reduction of Co^{2+} to
213 Co^0 , and the reduction of spinel-like structures [31,37]. It is worth mentioning that adding Cu to the
214 Co-Al structure significantly reduced its reduction temperature. Moreover, when compared,
215 $\text{Co}_{1.3}\text{Cu}_{1.3}\text{AlO}_x$ and $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$, the reduction profile of $\text{Co}_{1.3}\text{Cu}_{1.3}\text{AlO}_x$ is slightly shifted to a lower
216 temperature. This shift to lower reduction temperatures of Co-containing catalysts can be explained
217 by hydrogen spillover from Cu metallic particles [31,32,37,49,50].

218



219

220 **Figure 3.** H_2 TPR profile of $\text{Cu}_{2.6}\text{AlO}_x$ (blue), $\text{Co}_{1.3}\text{Cu}_{1.3}\text{AlO}_x$ (dark purple), $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ (dark
221 purple), and $\text{Co}_{2.6}\text{AlO}_x$ (red) under 10% H_2 flow ($30 \text{ mL}\cdot\text{min}^{-1}$).

222

223 Based on the TPR analysis and elemental analysis of Co and Cu, we calculated the degree
224 of reduction of the samples. It is expressed as the experimental H_2 consumption (based on the peak
225 area of the TPR profiles) divided by the theoretical H_2 consumption (based on the nominal molar
226 content of Co and Cu in the samples, considering all Co as Co_3O_4 , and all Cu as CuO) in percentage.
227 That information is summarized in **Table 2**. The degree of reduction ranged from 88% to 99% with
228 the increase in Cu content in the samples. In other words, the measured H_2 consumption was lower
229 than the expected H_2 consumption, which could mean that not all Co is present as Co_3O_4 , mostly
230 likely due to spinel-like structures.

231

232

233 **Table 2.** Calculated experimental and theoretical H₂ consumption, and degree of reduction based
 234 on the 10% H₂-TPR profiles of the catalysts.

Catalyst	Experimental H ₂ consumption (mmol·g ⁻¹)	Theoretical H ₂ consumption (mmol·g ⁻¹)	Degree of Reduction (%)
Cu _{2.6} AlO _x	8.97	9.05	99
Co _{1.3} Cu _{1.3} AlO _x	9.62	10.79	89
Co _{1.8} Cu _{0.9} AlO _x	9.70	10.84	89
Co _{2.6} AlO _x	10.44	11.81	88

235

236 Information regarding surface basicity, an essential aspect of CO₂ hydrogenation catalysts,
 237 was assessed through CO₂-TPD experiments for the catalysts and is shown in **Figure 4**. All samples
 238 reduced at 250 °C (**Figure 4a**) displayed a sharp peak around 110 °C and a sinusoidal pattern from
 239 150 to 350 °C due to the re-adsorption of CO₂[51–54] Co_{1.3}Cu_{1.3}AlO_x and Co_{1.8}Cu_{0.9}AlO_x also
 240 displayed a broader peak around 250 and 300 °C. That broad peak at intermediate temperature
 241 became prominent when Co_{1.8}Cu_{0.9}AlO_x was reduced at 400 °C, but it disappeared when it was
 242 reduced at 500 °C (**Figure 4c**). Contrastingly, Co_{2.6}AlO_x, after reduction at 500 °C, displayed a sharp
 243 at 200 °C and a tail indicating CO₂ desorption up until 700 °C (**Figure 4b**). It is worth mentioning that
 244 CO₂-TPD experiments were carried out at different reduction temperatures for Co_{2.6}AlO_x and
 245 Co_{1.8}Cu_{0.9}AlO_x, as these samples were tested in such conditions in the CO₂ hydrogenation reaction
 246 (section 3.2.2).

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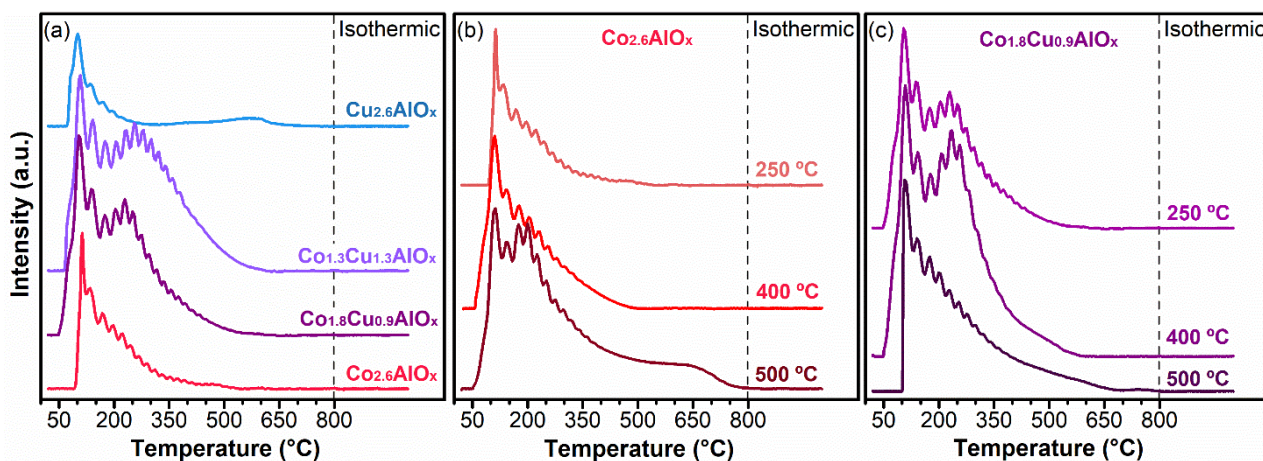


Figure 4. CO₂-TPD curves for the catalysts reduced at 250 °C (a), and for Co_{2.6}AlO_x (b), Co_{1.8}Cu_{0.9}AlO_x (c), after different reduction temperatures.

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According to the literature, it is possible to divide the CO₂-TPD profile into three regions according to the strength of the adsorption site. Below 200 °C, the desorption is ascribed to weakly adsorbed CO₂ [15–17,55–57]. This region can be assigned to Bronsted basicity sites, i.e., surface hydroxyl (-OH) [15,58–60]. The second desorption region, from 200 to 500 °C, is attributed to moderately adsorbed CO₂ [15,16,55,60] and associated with Lewis basicity, ergo oxygen sites [59], more specifically metal-oxygen pairs (M-O) [60]. It is reported that these moderate basic sites contribute to ethanol formation [25] and the activity of catalysts on the CO₂ hydrogenation reaction at that range of temperature [15]. The last region, above 500 °C, is attributed to strong basic sites [17,55], also associated with Lewis basicity [59], more specifically to low coordination oxygen atoms [60]. Strong CO₂ adsorption sites are reported to favor CO₂ methanation [61] and, in the case of Co-based catalysts, are associated with Co⁰ species [17].

Therefore, it is possible to infer that combining Co and Cu led to an increase in CO₂ adsorption, which becomes evident when comparing the calculated CO₂ uptake from the monometallic catalysts, Cu_{2.6}AlO_x and Co_{2.6}AlO_x, to the bimetallic catalysts, Co_{1.3}Cu_{1.3}AlO_x and Co_{1.8}Cu_{0.9}AlO_x, which is summarized in **Table 3**. Co_{1.3}Cu_{1.3}AlO_x and Co_{1.8}Cu_{0.9}AlO_x (**Figure 4a**) also displayed a desorption peak at the moderate basicity region (250 °C), attributed to CO₂ hydrogenation activity. Furthermore, the moderate basicity peak on the TPD profile of Co_{1.8}Cu_{0.9}AlO_x increased when the sample was reduced at 400 °C (**Figure 4c**), leading to nearly double CO₂ uptake. Upon reducing Co_{1.8}Cu_{0.9}AlO_x at 500 °C, the CO₂ uptake was cut to half, and the peak at

270 250 °C disappeared. The CO₂ uptake of Co_{2.6}AlO_x increased with the increase in the reduction
 271 temperature. At 500 °C, all three desorption regions were identified: two sharp peaks for weakly and
 272 moderately adsorbed CO₂; and a broad region from 500 to 700 °C, attributed to strongly adsorbed
 273 CO₂. The effect of reduction temperature on Co_{2.6}AlO_x and Co_{1.8}Cu_{0.9}AlO_x activity was further
 274 discussed along with the catalytic tests (section 3.2.2).

275

276 **Table 3.** Calculated CO₂ uptake based on the CO₂-TPD results for the samples.

Catalyst	Reduction Temperature (°C)	CO ₂ uptake (μmol·g ⁻¹)
Cu _{2.6} AlO _x	250	10.1
Co _{1.3} Cu _{1.3} AlO _x	250	57.2
Co _{1.8} Cu _{0.9} AlO _x	250	43.4
	400	84.5
	500	42.9
Co _{2.6} AlO _x	250	17.8
	400	31.1
	500	55.5

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278 3.2 Tuning Catalytic Performance

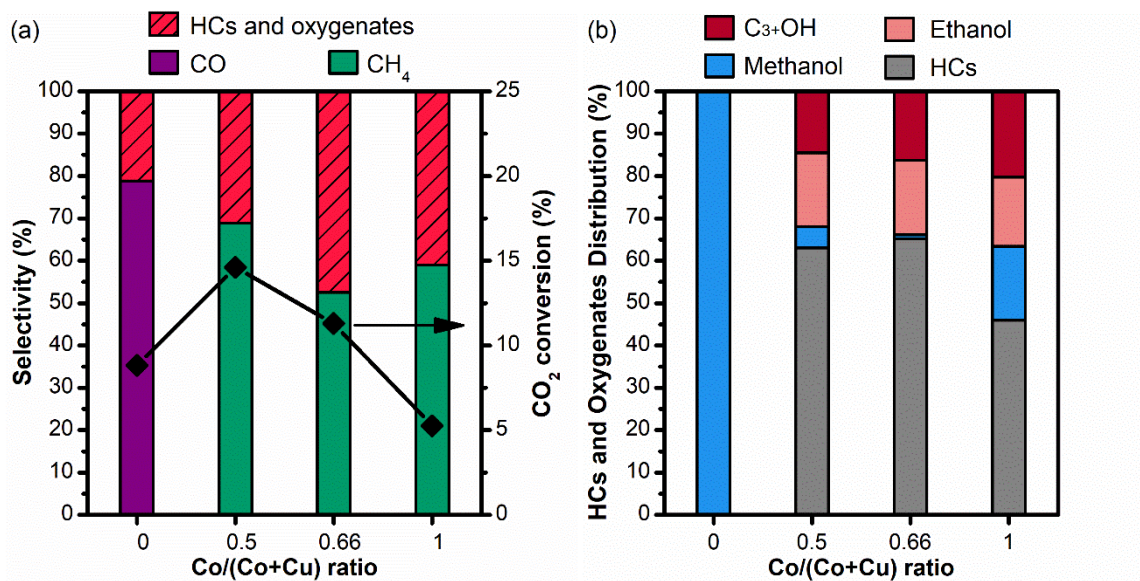
279 We initially tested the catalysts, namely Cu_{2.6}AlO_x, Cu_{1.3}Co_{1.3}AlO_x, Cu_{1.8}Co_{0.9}AlO_x, and
 280 Co_{2.6}AlO_x, in the CO₂ hydrogenation reaction at 30 bar, 250 °C, H₂/CO₂ ratio of 3, gas-hourly space
 281 velocity (GHSV) of 14200 mL·g_{cat}⁻¹·h⁻¹. Henceforth, the products are coded as CH₄ (methane), CO
 282 (carbon monoxide), C₂₋₅ alkanes and alkenes (HCs), methanol, ethanol, and C₃₊OH (propanol,
 283 isopropanol, and other C₃₊ oxygenates).

284 We evaluated their CO₂ conversion, product selectivity (HCs and oxygenates, CO, and CH₄),
 285 HCs and oxygenates (methanol, ethanol, and C₃₊OH) distribution, and space-time yield (STY). For
 286 the first test, each sample was reduced at the reaction temperature (250 °C) in pure hydrogen. Later,
 287 we evaluated the effect of changing this temperature of reduction and some reaction parameters. All
 288 the results expressed below are summarized in **Table S1** and **Table S2**.

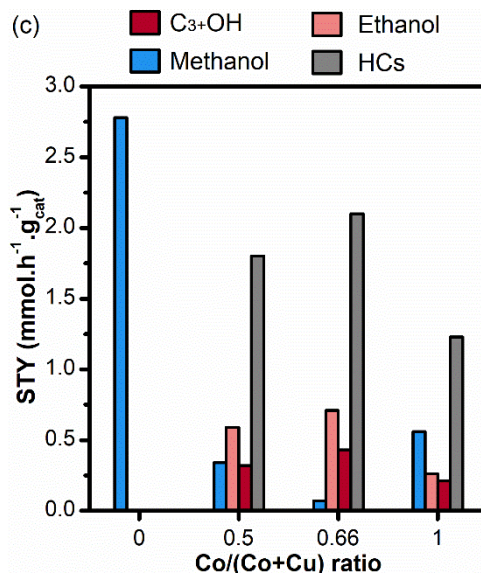
289 3.2.1 Effect of Co-Cu Ratio

290 The effect of combining Co and Cu was evidenced by the increase in CO₂ conversion and
 291 selectivity towards products of interest. For that, the molar ratios between cobalt and copper in the
 292 catalysts can be expressed by the Co/(Co+Cu) ratio. The Co/(Co+Cu) ratios for the samples
 293 Cu_{2.6}AlO_x, Cu_{1.3}Co_{1.3}AlO_x, Co_{1.8}Cu_{0.9}AlO_x, and Co_{2.6}AlO_x are, respectively, 0, 0.5, 0.66, and 1. The
 294 changes in CO₂ conversion and selectivity towards the different products are expressed in **Figure 5**.

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299 **Figure 5.** Effect of Co/(Co+Cu) ratio on the selectivity and CO₂ conversion (a), HCs and
 300 oxygenates distribution (b), and the STY of products of interest (c) (250 °C, 30 bar, H₂/CO₂ = 3,
 301 GHSV = 14200 mL·g_{cat}⁻¹·h⁻¹).

302

303 It is possible to observe an increase in CO₂ conversion and selectivity towards products of
304 interest, i.e., hydrocarbons and oxygenates (red), when combining cobalt and copper (**Figure 5a**).
305 Both mixed Co-Cu catalysts, Cu_{1.3}Co_{1.3}AlO_x and Cu_{1.8}Co_{0.9}AlO_x, displayed CO₂ conversion above
306 10%, whereas the values of conversion for the single metal catalysts, Cu_{2.6}AlO_x and Cu_{2.6}AlO_x, were
307 below 10%. When comparing the HCs and oxygenates distribution (**Figure 5b**), Cu_{2.6}AlO_x displayed
308 100% selectivity towards methanol, whereas Cu_{1.3}Co_{1.3}AlO_x, Cu_{1.8}Co_{0.9}AlO_x, and Cu_{2.6}AlO_x produced
309 HCs (gray), ethanol (light red), C₃₊OH (dark red) and methanol (blue). One can infer that combining
310 Co and Cu increases the yield of higher alcohols and hydrocarbons, implying that the Co-Cu
311 combination favors chain growth. Moreover, Cu_{1.8}Co_{0.9}AlO_x, with the Co/(Co+Cu) ratio of 0.66, led to
312 the lowest selectivity towards undesired products, i.e., CH₄ (green) and CO (purple), and the higher
313 yield of both ethanol and C₃₊OH, namely 0.71 and 0.43 mmol.h⁻¹.g⁻¹ (**Figure 5c**). This synergic effect
314 between Co and Cu has been previously reported for improving HAs selectivity from syngas
315 [18,31,62,63] and CO₂ hydrogenation [14,19,55]. Subramanian et al. [62], for instance, observed that
316 mixed CoCu particles were more selective towards HAs than CoCu core-shell particles, inferring that
317 both Co and Cu sites must be present on the surface. Sun et al. [18] concluded that each metal
318 played a role in the synthesis of HAs (Cu, activation of surface CO*; and Co, hydrogenation, and
319 chain growth). Moreover, through DFT data and experimental results, Liu et al. [20] observed that
320 there is an ideal Co/(Co+Cu) ratio to maintain optimum CO* surface coverage to produce ethanol.
321 Both Liu et al. [19] and Wang et al. [55] observed the best ethanol selectivity and STY at Co/(Co+Cu)
322 ratios of 0.5 and 0.66.

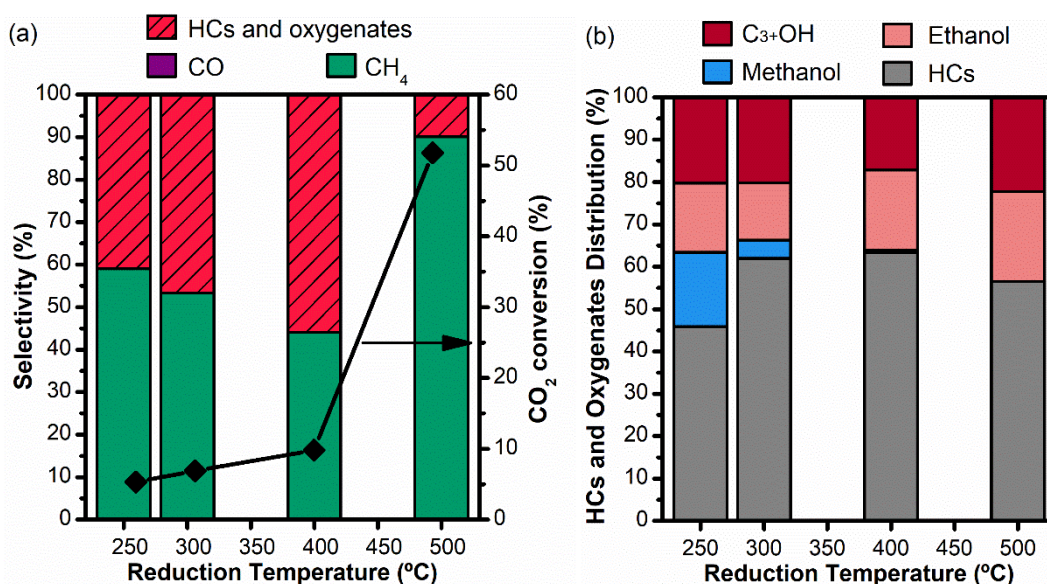
323 Considering these results, Cu_{1.8}Co_{0.9}AlO_x displayed the highest STY of HAs and the second-
324 highest CO₂ conversion of all four catalysts; hence we decided to investigate the effect of reduction
325 temperature on this sample. Additionally, we decided to compare the results of Cu_{2.6}AlO_x and
326 Cu_{2.6}AlO_x to highlight the Co-Cu catalyst.

327 3.2.2 Effect of Reduction Temperature

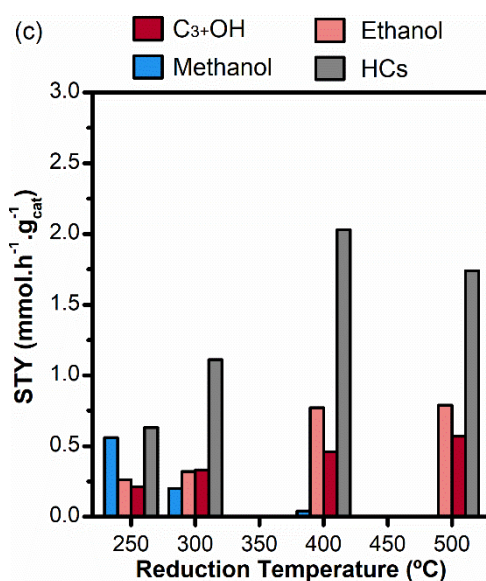
328 First, we evaluated the influence of the reduction temperature (pure H₂, 30 ml.min⁻¹) on the
329 activity of the catalysts. Based on the TPR results and the literature [38,42–44], Cu_{2.6}AlO_x was not

330 tested with different reduction temperatures, since 250 °C is sufficient for the reduction and activation
 331 of copper. Moreover, the effect of reduction temperatures on $\text{Co}_{2.6}\text{AlO}_x$ catalytic performance on the
 332 CO_2 hydrogenation to higher alcohols is displayed in **Figure 6**. The increase in the reduction
 333 temperature led to an increase in CO_2 conversion for $\text{Co}_{2.6}\text{AlO}_x$, with a decrease in CH_4 selectivity
 334 until 400 °C (**Figure 6a**). Reducing $\text{Co}_{2.6}\text{AlO}_x$ at 500 °C led to a noticeable increase in CO_2
 335 conversion with the consequent increase in CH_4 selectivity. The HCs and oxygenates distribution did
 336 not change from 400 to 500 °C (**Figure 6b**). The yield of HAs and HCs was hindered by the reduction
 337 at 500 °C (**Figure 6c**).

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342 **Figure 6.** Effect of the reduction temperature on the selectivity and CO₂ conversion (a), HCs and
343 oxygenates distribution (b), and the STY of products of interest (c) of Co_{2.6}AlO_x (250 °C, 30 bar,
344 H₂/CO₂ = 3, GHSV = 14200 mL·g_{cat}⁻¹·h⁻¹).

345

346 As previously discussed in the TPR analysis, at temperatures above 400 °C, the reduction
347 procedure likely leads to the reduction of bulk Co and spinel-like structures [27,31,35]. Excess Co⁰
348 and larger metallic particles can favor methanation reaction [1,2], justifying the increase in CO₂
349 conversion and CH₄ selectivity. Furthermore, in the CO₂-TPD analyses, the profile of Co_{2.6}AlO_x
350 reduced at 500 °C displayed remarkable desorption up until 700 °C, marking strong basicity sites,
351 which promotes methanation [61].

352 Furthermore, the same reduction temperatures were tested on Co_{1.8}Cu_{0.9}AlO_x, and its
353 catalytic performance is presented in **Figure 7**.

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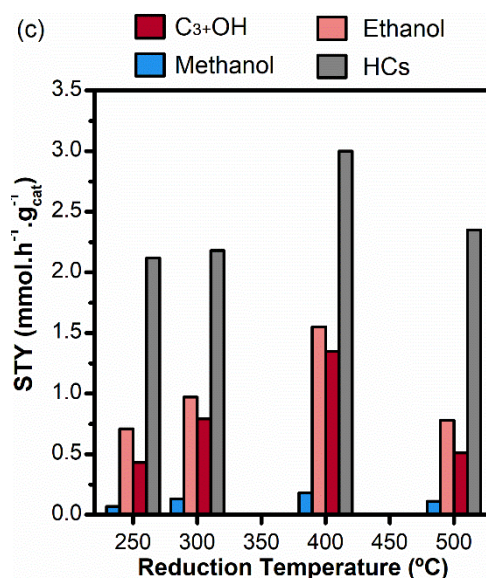
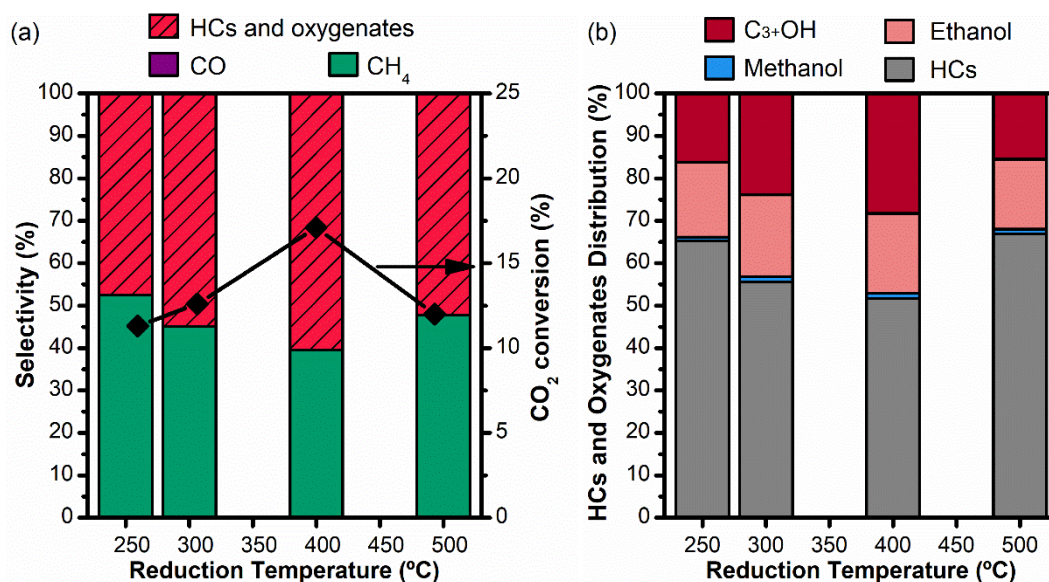
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362 **Figure 7.** Effect of the reduction temperature on the selectivity and CO₂ conversion (a), HCs and
 363 oxygenates distribution (b), and the STY of products of interest (c) of Co_{1.8}Cu_{0.9}AlO_x (250 °C,
 364 30 bar, H₂/CO₂ = 3, GHSV = 14200 mL·g_{cat}⁻¹·h⁻¹).

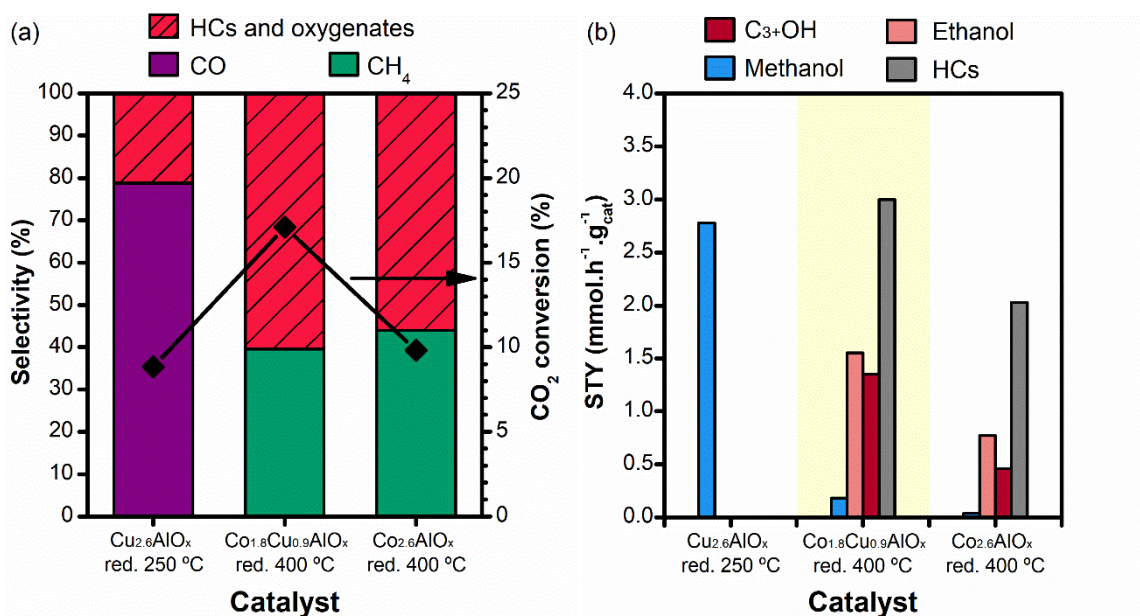
365

366 Similar to Co_{2.6}AlO_x, increasing the reduction temperature led to a decrease in CH₄ selectivity
 367 for Co_{1.8}Cu_{0.9}AlO_x and an increase in CO₂ conversion up to 400 °C. Contrastingly, reducing
 368 Co_{1.8}Cu_{0.9}AlO_x at 500 °C led to a decrease in CO₂ conversion (**Figure 7a**) without a significant
 369 change in the distribution of HCs and oxygenates (**Figure 7b**). The highest STY of HAs was for the
 370 sample reduced at 400 °C, namely 1.55 and 1.35 mmol.h⁻¹.g⁻¹, in that order, for ethanol and C₃+OH,
 371 which represents an increase of approximately 2 and 3 times, respectively, in yield of both HAs

372 (**Figure 7c**). It is likely that above 400 °C, the reduction increases the $\text{Co}^0/\text{Co}^{\delta+}$ ratio on the surface;
373 as a result, hindering the catalyst activity [24,64,65]. As reported, an optimum $\text{Co}^0/\text{Co}^{\delta+}$ ratio is
374 necessary to tune a cobalt-based catalyst activity and selectivity in the CO_2 hydrogenation reaction
375 [8,24,55,66]. Furthermore, these catalytic test results reflect the CO_2 -TPD profile for the different
376 reduction temperatures of $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ (**Figure 4**). Reducing at 500 °C reduced by half the
377 calculated CO_2 uptake and led to the disappearance of the peak attributed to moderate basicity and
378 associated with ethanol selectivity [25] and CO_2 hydrogenation activity [15].

379 A comparison between $\text{Cu}_{2.6}\text{AlO}_x$, $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$, and $\text{Co}_{2.6}\text{AlO}_x$ catalytic tests results is
380 shown in **Figure 8**, each catalyst after its best-tested pretreatment, i.e., $\text{Co}_{2.6}\text{AlO}_x$ and $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$
381 reduced at 400 °C, and $\text{Cu}_{2.6}\text{AlO}_x$ reduced at 250 °C. Comparatively, the CO_2 conversions for
382 $\text{Cu}_{2.6}\text{AlO}_x$, $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$, and $\text{Co}_{2.6}\text{AlO}_x$ at the optimal reduction temperature were 8.8%, 17.2%,
383 and 9.8%, in that order (**Figure 8a**). $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ reduced at 400 °C converted nearly twice as
384 much CO_2 as the other two compared catalysts. Moreover, mixing Co-Cu increased the HAs
385 selectivity (28.5%) and hydrocarbons (31.3%). Regarding the yield of products of interest
386 (**Figure 8b**), $\text{Cu}_{2.6}\text{AlO}_x$ reduced at 250 °C produced only methanol, circa $2.78 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$, while
387 the Co-containing catalysts also yielded HAs (C_{2-3}), HCs (C_{2-5}). The yield of HAs and HCs, for
388 $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ reduced at 400 °C, were approximately 2.90 and 3.00 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$, respectively. In
389 that sense, $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ yielded as much HAs as $\text{Cu}_{2.6}\text{AlO}_x$ yielded methanol. Henceforth, we
390 evaluated the effect of reaction conditions of $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ reduced at 400 °C.

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392

393 **Figure 8.** Comparison of the selectivity and CO₂ conversion (a), and the STY of products of

394 interest (b) of the catalysts after the best reduction pretreatment: Cu_{2.6}AlO_x (250 °C),

395 Co_{1.8}Cu_{0.9}AlO_x (400 °C), and Co_{2.6}AlO_x (400 °C), on the CO₂ hydrogenation reaction (250 °C,

396 30 bar, H₂/CO₂ = 3, GHSV = 14200 mL·g_{cat}⁻¹·h⁻¹).

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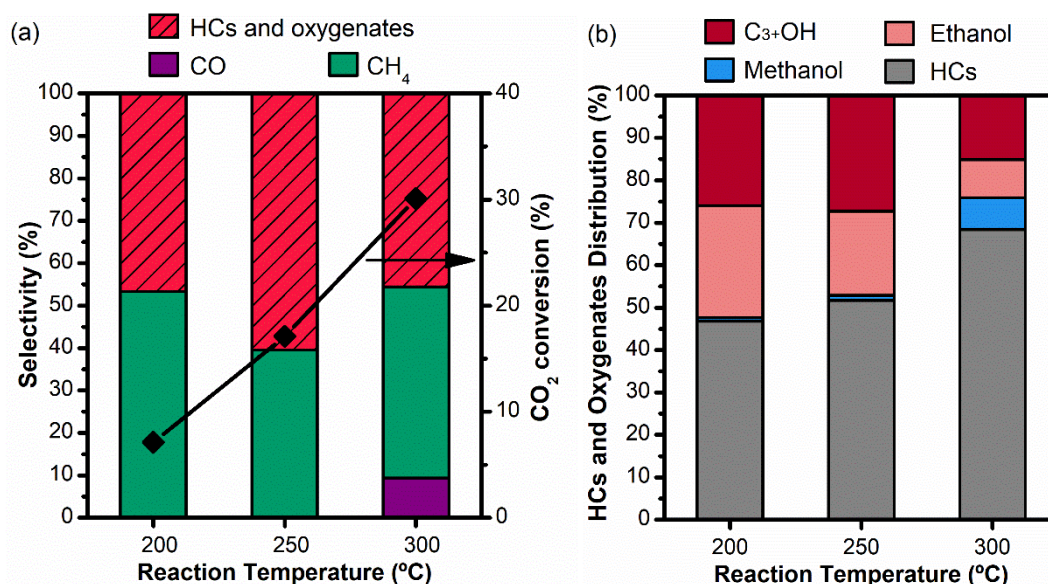
398 3.2.3 Effect of the Reaction Temperature

399 We evaluated the influence of the reaction temperature, 50 °C above and below the

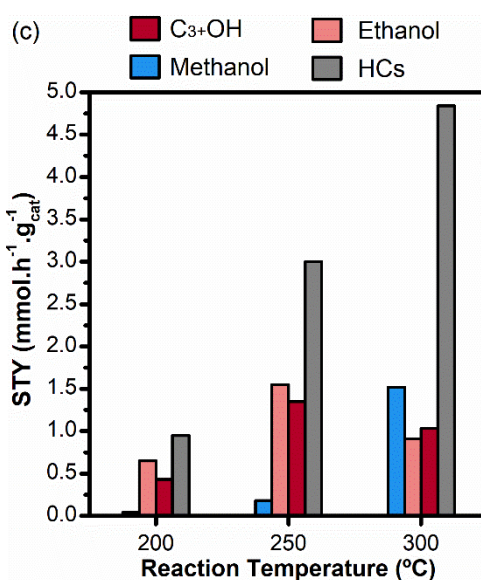
400 previously used temperature (250 °C), on the activity of Co_{1.8}Cu_{0.9}AlO_x catalytic performance on the

401 CO₂ hydrogenation to HAs, which is displayed in **Figure 9**.

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405 **Figure 9.** Effect of the reaction temperature on the selectivity and CO₂ conversion (a), HCs and
 406 oxygenates distribution (b), and the yield of products of interest (c) of Co_{1.8}Cu_{0.9}AlO_x reduced at
 407 400 °C (30 bar, H₂/CO₂ = 3, GHSV = 14200 mL·g_{cat}⁻¹·h⁻¹).

408

409 Increasing the reaction temperature from 200 to 300 °C increased CO₂ conversion, from
 410 7.1% at 200 °C to 30.1% at 300 °C (**Figure 9a**). However, the highest STY for the products of interest
 411 (HCs and oxygenates) was at 250 °C. The increase in reaction temperature to 300 °C led to CO
 412 formation. Moreover, the increase in reaction temperature from 250 to 300 °C promoted the
 413 production of hydrocarbons (**Figure 9b**). Decreasing it from 250 to 200 °C caused an increase in
 414 ethanol selectivity and a decrease in HCs selectivity. In short, even though the increase in reaction

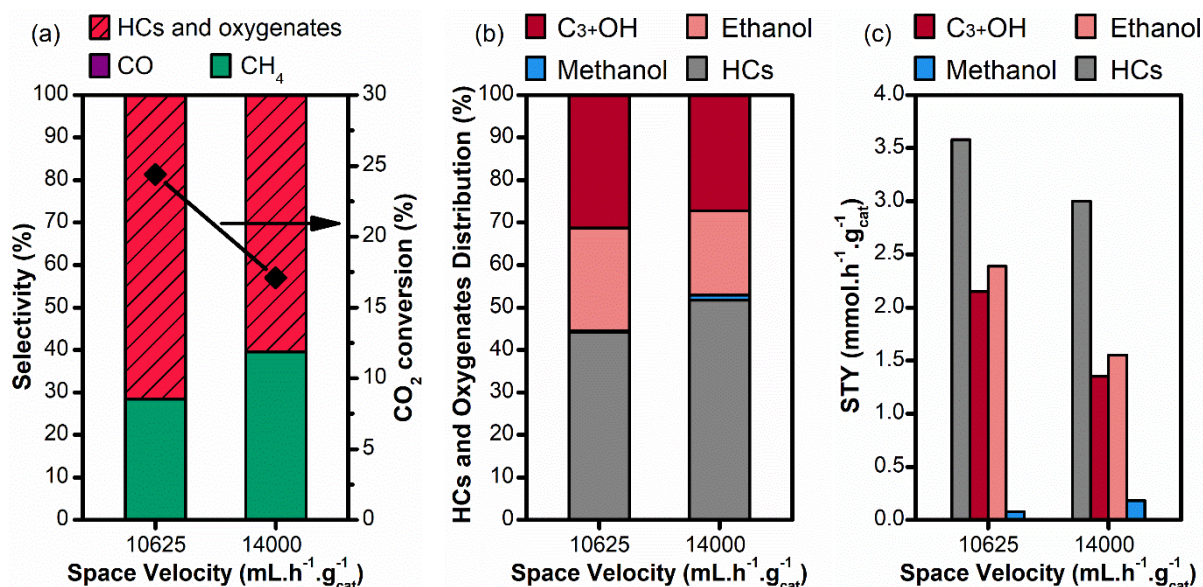
415 temperature promoted the CO₂ conversion, the yield of higher alcohols was hindered at 300 °C
416 (**Figure 9b**). Overall, the yield of ethanol and C₃₊OH was higher at 250 °C.

417 The increase in reaction temperature leads to an increase in CO₂ conversion, which can be
418 accompanied by an increase in the yield of higher alcohols [64,67] even when HAs selectivity is
419 hindered by the increase in temperature [24], here evidenced when reaction temperature increased
420 from 200 to 250 °C. However, the increase in the reaction temperature can also favor the production
421 of side products, such as CO [20], hydrocarbons [68], and methanol [65,69]. As reviewed by Zeng
422 et al. [6], most of the recently reported Co-based catalysts operate well from 140 to 250 °C, whereas
423 the temperature for Mo-based, Rh-based, and Cu-based catalysts ranges from 200-340 °C, 240-
424 270 °C, and 300-350 °C, respectively.

425 3.2.4 Effect of the Space Velocity

426 We tested the effect of space velocity on Co_{1.8}Cu_{0.9}AlO_x catalytic performance, by decreasing
427 the gas-hourly space velocity (GHSV) of the reaction system from 14200 to 10625 mL.h⁻¹.g_{cat}⁻¹, and
428 the results are shown in **Figure 10**.

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431 **Figure 10.** Effect of the space velocity on the selectivity and CO₂ conversion (a), HCs and
432 oxygenates distribution (b), and the yield of products of interest (c) of Co_{1.8}Cu_{0.9}AlO_x reduced at
433 400 °C (250 °C, 30 bar, H₂/CO₂ = 3).

434 As explained by Si et al. [9], higher space velocity hinders CO insertion, which has slow
435 reaction rate than the C-C coupling and hydrogenation reactions; hence lowering the space velocity
436 could benefit the HAs selectivity. On the other hand, lowering too much the space velocity could lead
437 to a decrease in STY. Overall, this decrease in space velocity was beneficial to the yield of HAs and
438 led to an increase in CO₂ conversion from 17.1% to 24.4%, an increase of roughly 40% (**Figure 10a**).
439 This change also inhibited the production of methane. Moreover, aside from reduced methanol
440 selectivity, the HCs and oxygenates distribution remained roughly the same (**Figure 10b**). This
441 decrease in space velocity promoted the formation of HAs, namely, the yield of ethanol and C₃₊OH
442 increased approximately 1.5 times each (**Figure 10c**). Xu et al. [10] also observed an increase in
443 CO₂ conversion and a decrease in CO selectivity with the decrease in space velocity, implying that
444 increasing the contact time promotes CO conversion to HAs and HCs. Noteworthy, Co_{1.8}Cu_{0.9}AlO_x
445 did not yield any CO at the space velocity tests.

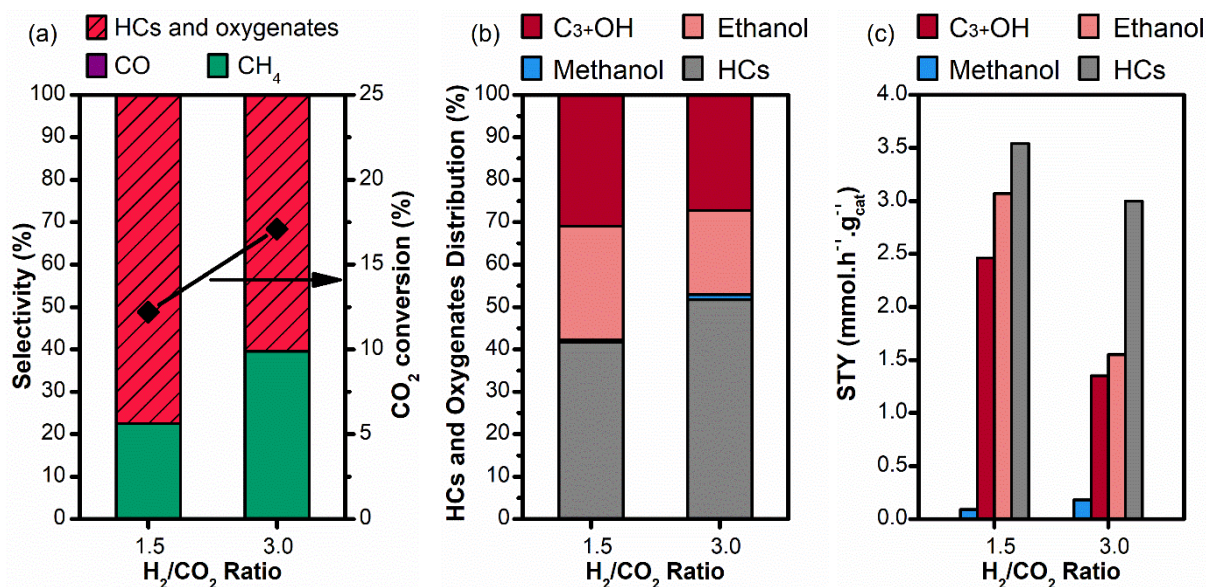
446 *3.2.5 Effect of the H₂/CO₂ ratio*

447 Next, we also evaluated the effect of changing the H₂/CO₂ ratio from 3 (3:1), as commonly
448 used in most of the recently reported literature [6,9–16], to 1.5 (3:2) on the activity of Co_{1.8}Cu_{0.9}AlO_x
449 catalytic performance on the CO₂ hydrogenation to HAs, which can be seen on **Figure 11**.

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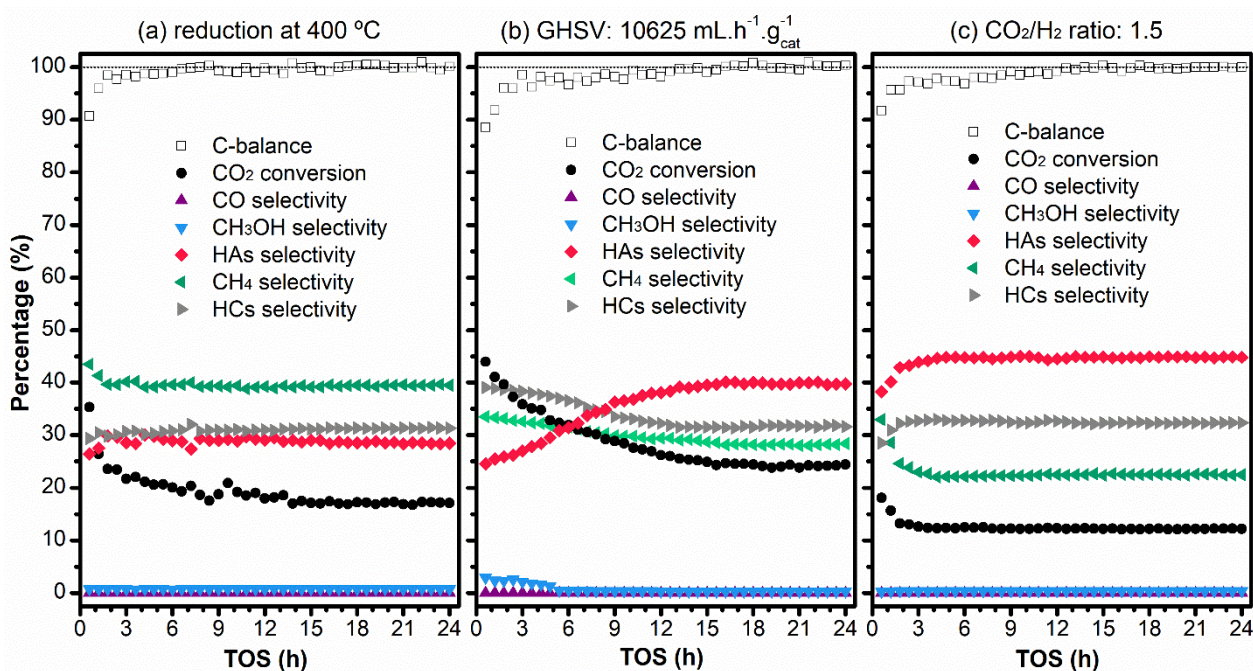
Figure 11. Effect of the H₂/CO₂ ratio on the selectivity and CO₂ conversion (a), HCs and oxygenates distribution (b), and the yield of products of interest (c) of Co_{1.8}Cu_{0.9}AlO_x reduced at 400 °C (250 °C, 30 bar, GHSV: 14200 mL·g_{cat}⁻¹·h⁻¹).

Reducing the H₂/CO₂ ratio from 3 (3:1) to 1.5 (3:2), we observed a reduction in the nominal value of CO₂ conversion from 17.1% to 12.2%, respectively (**Figure 11a**). However, decreasing the H₂/CO₂ ratio implies reducing the amount of H₂ and increasing the amount of CO₂; therefore, at an H₂/CO₂ ratio of 3:2, more CO₂ was fed to the reactor, namely 60%, more than at H₂/CO₂ ratio of 3:1. Hence, reducing the H₂/CO₂ ratio from 3 (3:1) to 1.5 (3:2) led to an increase in the amount of CO₂ converted, in terms of moles of CO₂ converted per hour at the same space velocity, here evaluated for both tests with different H₂/CO₂ ratio. Methane production is also inhibited, decreasing CH₄ selectivity from 39.5% to 22.5%. This reduction in the H₂/CO₂ ratio also promoted the selectivity towards HAs, namely ethanol, and C₃+OH composed approximately 58% of the HCs and oxygenates distribution at H₂/CO₂ ratio of 3:2, compared to 47.1% at H₂/CO₂ ratio of 3:1 (**Figure 11b**). Furthermore, this represents an increase of about 2 and 1.8 times, respectively, to the STY of ethanol and C₃+OH, whereas the yield of HCs increased by roughly 1.2 times. It is reported that the increase in H₂/CO₂ ratio leads to a decrease in HAs selectivity [25].

3.2.6 Stability of Co_{1.8}Cu_{0.9}AlO_x under different conditions

472 The 24 h stability profiles of $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ reduced at 400 °C are displayed in **Figure 12**, at
 473 the initial conditions (250 °C, 30 bar, $\text{H}_2/\text{CO}_2 = 3$, $\text{GHSV} = 14200 \text{ mL}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$), after reducing in
 474 space velocity ($\text{GHSV} = 10625 \text{ mL}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$) (**Figure 12b**), and after changing H_2/CO_2 ratio to 1.5
 475 (**Figure 12c**). In all conditions, the carbon balance (C-balance) reaches 95-102% after the first 3 h
 476 of reaction, probably due to reactor wash-out after opening. $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$, at the initial conditions
 477 (**Figure 12a**), achieves stability after 12 h of reaction. Meanwhile, at GHSV of $10625 \text{ mL}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$
 478 (**Figure 12b**), this period was stretched in 3 h. On the other hand, reducing the H_2/CO_2 ratio from 3
 479 to 1.5 (**Figure 12c**) leads to the reactional system reaching stability right after the reactor wash-out.
 480 Moreover, after reaching stability, the CO_2 conversion and HAs selectivity did not change during the
 481 24 h test at that condition, i.e., $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ did not deactivate. Considering the stability test and
 482 yield of products of interest, the H_2/CO_2 ratio change rendered the best catalytic performance for
 483 $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$.

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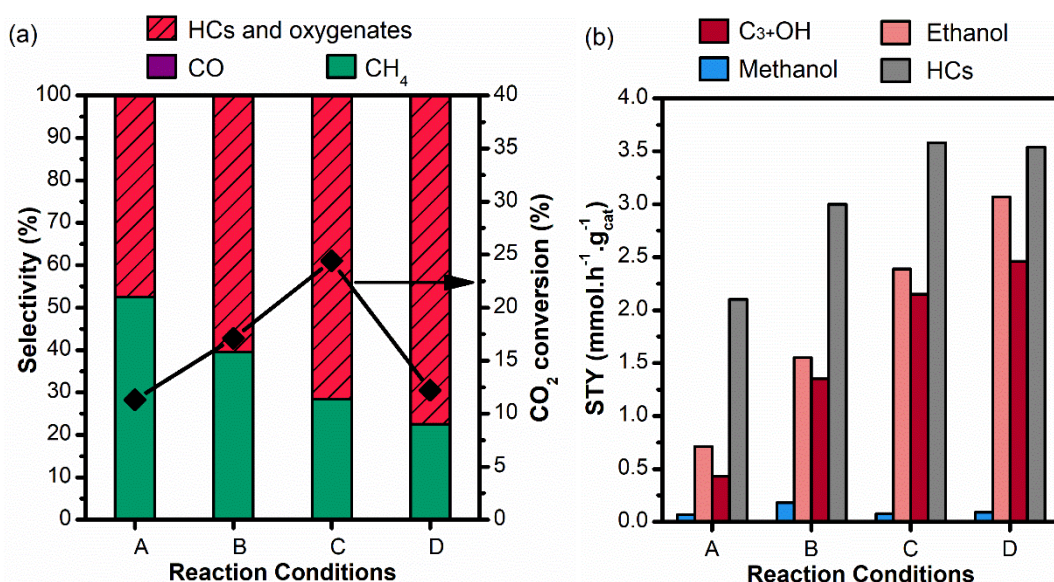
486 **Figure 12.** 24 h-TOS of $\text{Co}_{1.8}\text{Cu}_{0.9}\text{AlO}_x$ reduced at 400 °C at 250 °C and 30 bar after (a) initial
 487 conditions ($\text{H}_2/\text{CO}_2 = 3$, $\text{GHSV} = 14200 \text{ mL}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$); (b) decreasing GSHV to $10625 \text{ mL}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$
 488 ($\text{H}_2/\text{CO}_2 = 3$); and (c) changing H_2/CO_2 ratio to 1.5 ($\text{GHSV} = 14200 \text{ mL}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$).

489

490 3.2.7 Final Remarks and Comparisons

491 Finally, the changes in CO₂ conversion, product selectivity, and STY of each of the tuning
 492 steps towards improving Co_{1.8}Cu_{0.9}AlO_x catalytic performance are presented in **Figure 13**. We also
 493 compared our best results with the current CO₂ hydrogenation literature, summarized in **Table 4**. In
 494 short, there is a progressive decrease in the selectivity of undesired products with each step
 495 (**Figure 13a**). Co_{1.8}Cu_{0.9}AlO_x reduced at 250 °C (reaction condition A) displays HCs and oxygenates
 496 selectivity of 47.5%, later increased to 60.5% by tuning the reduction temperature to 400 °C
 497 (reaction condition B). The decrease in space velocity from 14200 to 10625 mL·h⁻¹·g_{cat}⁻¹ (reaction
 498 condition C) leads to HCs and oxygenates selectivity of 71.6%, whereas changing the H₂/CO₂ ratio
 499 from 3 to 1.5 (reaction condition D) increases it to 77.5%. It is worth mentioning that very few of the
 500 reviewed works have worked with a space velocity above 6000 mL·h⁻¹·g_{cat}⁻¹ [9,13], which is usually
 501 done to minimize the selectivity of undesired products, such as CH₄ and CO, yet we still managed
 502 to achieve HCs and oxygenates selectivity above 70% working above 10000 mL·h⁻¹·g_{cat}⁻¹. The
 503 selectivity of Co_{1.8}Cu_{0.9}AlO_x towards undesired products was one of the lowest in the current literature
 504 (**Table 4**).

505



506

507 **Figure 13.** Comparison of Co_{1.8}Cu_{0.9}AlO_x production selectivity and CO₂ conversion (a) and STY
 508 (b), at 250 °C and 30 bar, after each change in reaction conditions: (A) reductive pretreatment at
 509 250 °C (H₂/CO₂ = 3, GHSV = 14200 mL·h⁻¹·g_{cat}⁻¹); (B) reductive pretreatment at 400 °C (H₂/CO₂ = 3,
 510 GHSV = 14200 mL·h⁻¹·g_{cat}⁻¹); (C) decreasing GSHV to 10625 mL·h⁻¹·g_{cat}⁻¹ (H₂/CO₂ = 3); and (D)

511 changing H₂/CO₂ ratio to 1.5 (GHSV: 14200 mL·h⁻¹·g_{cat}⁻¹).

512

513 **Table 4.** Comparison of the catalytic performance in the current CO₂ hydrogenation literature.

Catalyst	T (°C)	P (bar)	GHSV (*)	X _{CO₂} (%)	STY (**)	Selectivity (%)					Ref.
						CO	CH ₄	HCS (C ₂₊)	ROH		
									C ₁	C ₂	
sp-CuNaFe	310	30	28800	32.3	3.32 ^f	--	--	55.0	--	10	[9]
CZA/K-CMZF	320	50	6000	42.3	2.24 ^d	13.8	--	67.6	1.3	17.4 ^d	[10]
4.6K-CMZF	320	50	6000	30.4	1.47 ^d	30.6	--	52.4	1.3	15.9 ^d	[11]
2.5K5Co-In ₂ O ₃	380	40	2250 ^b	36.6	0.73 ^d	80.8	--	6.5 ^c	1.6 ^c	11.1 ^{c, d}	[12]
2K20Fe5Rh-SiO ₂	250	75	7000	18.4	0.79 ^a	--	46	--	13.8	15.9	[13]
Cu-CoGa-0.4	220	30	6000	17.8	1.35	2.3	43.5	1.9	27.5	23.8	[14]
CoGa _{1.0} Al _{1.0} O ₄ /SiO ₂	270	30	3000	4.4	0.3	27.3	--	39.3	13.3	20.1	[15]
25Na-Co/SiO ₂	310	50	6000	53.2	1.1	3	61.8	24.3	12.9 ^e		[16]
Co _{1.8} Cu _{0.9} AlO _x	250	30	10625	24.4	2.39	0	28.4	31.6	0.3	17.3	This Work
Co _{1.8} Cu _{0.9} AlO _x ^g	250	30	14200	12.2	3.08	0	22.5	32.3	0.4	20.8	This Work

514 * GHSV expressed in mL·g_{cat}⁻¹·h⁻¹ and H₂/CO₂: 3.

515 ** STY of ethanol expressed in mmol·g_{cat}⁻¹·h⁻¹.

516 ^a calculated based on 18.8 mL·g⁻¹·h⁻¹ of ethanol, STY after 6h

517 ^b calculated based on provided flow (37.5 mL·min⁻¹) and catalyst mass (1 g)

518 ^c calculated based on HCs and oxygenates selectivity and distribution

519 ^d HAs (C₂₊+OH) selectivity or STY

520 ^e Alcohol (ROH) selectivity

521 ^f calculated based on 153 mg·g_{cat}⁻¹·h⁻¹

522 ^g H₂/CO₂: 3:2 (1.5).

523

524 Regarding the space-time yield of Co_{1.8}Cu_{0.9}AlO_x, after reduction at 400 °C, reaction condition
 525 B (250 °C, 30 bar, H₂/CO₂: 3, GHSV: 14200 mL·h⁻¹·g_{cat}⁻¹), the yield of ethanol was 1.55 mmol·h⁻¹·g_{cat}⁻¹
 526 (STY_{HCS}: 3.00; STY_{C₃+OH}: 1.35). at these reaction conditions, the ethanol STY of Co_{1.8}Cu_{0.9}AlO_x is
 527 higher or comparable to most of the current literature (**Table 4**). After tuning the space velocity,
 528 reaction condition C (250 °C, 30 bar, H₂/CO₂: 3, GHSV: 10625 mL·h⁻¹·g_{cat}⁻¹), the ethanol STY
 529 reached 2.39 mmol·h⁻¹·g_{cat}⁻¹ (STY_{HCS}: 3.24; STY_{C₃+OH}: 2.15). Meanwhile, tuning the H₂/CO₂ ratio,
 530 reaction condition D (250 °C, 30 bar, H₂/CO₂: 1.5, GHSV: 14000 mL·h⁻¹·g_{cat}⁻¹), led to an ethanol STY
 531 of 3.08 mmol·h⁻¹·g_{cat}⁻¹ (STY_{HCS}: 3.54; STY_{C₃+OH}: 2.46).

532 Comparatively, Xu et al. [10] reported a tandem catalyst composed of a CuZnAl catalyst to
 533 favor CO formation, and a K-CuMgZnFe catalyst to favor HAs formation reaching STY of 2.24

534 mmol·h⁻¹·g_{cat}⁻¹ (310 °C, 50 bar, H₂/CO₂: 3, GHSV: 6000 mL·h⁻¹·g_{cat}⁻¹) for higher alcohols (ethanol and
535 C₃₊ oxygenates). Even though the tandem catalyst displayed elevated CO₂ conversion (42.3%), the
536 higher alcohol selectivity (17.4%) was lower than the one displayed by of Co_{1.8}Cu_{0.9}AlO_x (39.7% for
537 reaction condition C and 44.8% for reaction condition D). In the end, Co_{1.8}Cu_{0.9}AlO_x ethanol STY in
538 both reaction conditions was similar or higher than the higher alcohol (ethanol and C₃₊ oxygenates)
539 STY displayed by the tandem catalysts working at a much higher pressure (50 bar). Furthermore, Si
540 et al. [9] reported a sputtering CuNaFe catalyst with high STY of alkene of 680 mg·h⁻¹·g_{cat}⁻¹ and
541 ethanol of 153 mg·h⁻¹·g_{cat}⁻¹ (310 °C, 30 bar, H₂/CO₂: 3, GHSV: 28800 mL·h⁻¹·g_{cat}⁻¹), which converts
542 to 3.32 mmol·h⁻¹·g_{cat}⁻¹ (MM_{ethanol}: 46.07 g·mol⁻¹). The ethanol STY of sp-CuNaFe was similar to the
543 displayed by Co_{1.8}Cu_{0.9}AlO_x at reaction condition D (H₂/CO₂: 1.5). The sp-CuNaFe catalyst operates
544 at double the GHSV of our experiments. It is also important to mention that, at reaction condition D,
545 we reduced the amount of H₂ used in the process, ergo diminishing its cost. Noteworthy,
546 Co_{1.8}Cu_{0.9}AlO_x, under certain conditions, displays one of the highest ethanol STY of the literature, to
547 the best of our knowledge.

548 Lastly, it is essential to acknowledge that the CO₂ hydrogenation reaction to ethanol and
549 other higher alcohols (HAs) is currently rated at Technology Readiness Level (TRL) 1-2, indicating
550 that it is transitioning from pure to applied research [70]. Therefore, one should expect few reports
551 on catalysts, especially non-noble-based ones, with high selectivity to ethanol or other HAs, due to
552 the existing challenges in the CO₂ hydrogenation process. Achieving high yields of products is
553 challenging due to the thermodynamic stability of CO₂, which often requires high temperatures,
554 pressures, excess overpotentials, or the use of catalysts with low availability and high costs [3,71].
555 However, progress is being made over time as new active materials demonstrate the potential to
556 increase yield and selectivity to alcohols, making this process more feasible.

557 In this context, our work presents a non-noble-based catalyst that, under mild conditions,
558 displayed conversion rates comparable to current results while showing superior selectivity and yield
559 towards higher alcohols, particularly ethanol. This achievement represents a significant
560 advancement in the field and offers promising potential for the synthesis of higher alcohols from CO₂.

561 As we advance toward higher TRLs, it becomes crucial to consider implementation aspects,

562 including addressing separation and recycling steps, and their impact on the process's cost and
563 emission reduction efficiency. These factors play a significant role in ensuring the practical viability
564 and sustainability of the CO₂ hydrogenation to higher alcohols, making it essential to explore efficient
565 and cost-effective approaches for separation, recycling, and overall process optimization.

566 **4. Conclusion**

567 Overall, Co.Cu.Al proves to be a performant catalyst to produce ethanol (and potential other
568 oxygenates) via the CO₂ hydrogenation reaction at mild reaction conditions. Co_{1.8}Cu_{0.9}AlO_x, at the
569 best-tested reaction conditions (250 °C, 30 bar, H₂/CO₂: 1.5, GHSV = 14000 mL·h⁻¹·g_{cat}⁻¹), displays
570 very low CH₄ selectivity (22.5%) and very high selectivity towards products of interest (77.5), i.e.,
571 HCs and oxygenate. The space-time yields in these conditions are 3.54, 3.08, and
572 2.46 mmol·h⁻¹·g_{cat}⁻¹ for hydrocarbons (C₂₋₅), ethanol, and C₃₊OH, respectively. The ethanol STY is
573 one the highest among related studies, that is, for continuous reactors. The yield of hydrocarbons
574 and C₃₊OH also represents potential pathways for other utilizations of such catalysts. Finally, tuning
575 the catalyst proves to be a viable alternative to improve the catalytic activity, as the CO₂
576 hydrogenation reaction is shown to be sensitive to space velocity and H₂/CO₂ ratio, among other
577 reaction conditions. The overall gain in ethanol space-time yield from the reaction condition A
578 (Co_{1.8}Cu_{0.9}AlO_x reduced at 250°C – 250 °C, 30 bar, H₂/CO₂: 3, GHSV: 14000 mL·h⁻¹·g_{cat}⁻¹) to reaction
579 condition D (Co_{1.8}Cu_{0.9}AlO_x reduced at 400°C – 250 °C, 30 bar, H₂/CO₂ = 1.5,
580 GHSV = 14000 mL·h⁻¹·g_{cat}⁻¹) was of 4.3-fold. In short, this work shed light on designing and tuning
581 high-efficiency Co-Cu bimetallic catalysts for converting CO₂ into chemicals of industrial interest.

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809 **7. Appendix A (Supplementary Material)**810 **Table S1.** Reaction data for all presented catalysts and reaction conditions. All catalytic tests were
811 conducted at 30 bar.

Catalyst	T _R ^a (°C)	T ^a (°C)	R _b	GHSV (^c)	X _{CO2} (%)	Selectivity (%)						Yield (mmol.g _{cat} ⁻¹ .h ⁻¹)			
						CO	CH ₄	HCs (C ₂₋₅)	ROH			HCs (C ₂₋₅)	ROH		
									C ₁	C ₂	C ₃₊		C ₁	C ₂	C ₃₊
Cu _{2.6} AlO _x	250	250	3:1	14200	8.8	78.8	0	0	21	0	0	0	2.78	0	0
Co _{1.3} Cu _{1.3} AlO _x	250	250	3:1	14200	14.6	0	68.9	19.6	1.6	5.4	4.5	1.77	0.34	0.59	0.32
Co _{1.8} Cu _{0.9} AlO _x	250	250	3:1	14200	11.3	0	52.5	31.0	0.4	8.4	7.7	2.12	0.07	0.71	0.43
Co _{2.6} AlO _x	250	250	3:1	14200	5.3	0	59	18.8	7.2	6.7	8.3	0.63	0.56	0.26	0.21
Co _{2.6} AlO _x	300	250	3:1	14200	6.9	0	53.4	28.9	2.0	6.3	9.4	1.11	0.2	0.32	0.33
Co _{2.6} AlO _x	400	250	3:1	14200	9.8	0	44.1	35.4	0.3	10.6	9.6	2.03	0.04	0.77	0.46
Co _{2.6} AlO _x	500	250	3:1	14200	51.8	0	90.1	5.6	0.0	2.1	2.2	1.74	0	0.79	0.57
Co _{1.8} Cu _{0.9} AlO _x	300	250	3:1	14200	12.6	0	45.1	30.5	0.7	10.6	13.1	2.18	0.13	0.97	0.79
Co _{1.8} Cu _{0.9} AlO _x	400	250	3:1	14200	17.1	0	39.5	31.3	0.7	12.0	16.5	3	0.18	1.55	1.35
Co _{1.8} Cu _{0.9} AlO _x	500	250	3:1	14200	12.0	0	47.8	34.9	0.6	8.6	8.1	2.35	0.11	0.78	0.51
Co _{1.8} Cu _{0.9} AlO _x	400	200	3:1	14200	7.1	0	53.4	21.8	0.4	12.3	12.1	0.95	0.04	0.65	0.43
Co _{1.8} Cu _{0.9} AlO _x	400	300	3:1	14200	30.1	9.4	45	31.2	3.4	4.1	6.9	4.84	1.52	0.91	1.03
Co _{2.6} AlO _x	400	200	3:1	14200	3.0	0	49	19.3	2.3	16.5	12.9	0.34	0.1	0.37	0.19
Co _{2.6} AlO _x	400	300	3:1	14200	19.5	14.2	40.6	28.7	5.1	5.5	5.9	3.25	1.49	0.81	0.6
Co _{1.8} Cu _{0.9} AlO _x	400	250	3:1	10625	24.4	0	28.4	31.6	0.3	17.3	22.4	3.24	0.08	2.39	2.15
Co _{1.8} Cu _{0.9} AlO _x	400	250	3:2	14200	12.2	0	22.5	32.3	0.4	20.8	24.0	3.54	0.12	3.08	2.46

812 ^a T_R: reduction temperature; and T: reaction temperature.813 ^b R: H₂/CO₂ ratio.814 ^c GHSV expressed in mL.g_{cat}⁻¹.h⁻¹.

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816 **Table S2.** Hydrocarbons yield distribution for all presented catalysts and reaction conditions. All
817 catalytic tests were conducted at 30 bar.

Catalyst	T _R ^a (°C)	T ^a (°C)	R _b	GHSV (^c)	X _{CO2} (%)	HCs Yield (mmol.g _{cat} ⁻¹ .h ⁻¹) ^d								
						C2=	C2	C3=	C3	C4=	C4	C5=	C5	
Cu _{2.6} AlO _x	250	250	3:1	14200	8.8	0	0	0	0	0	0	0	0	0
Co _{1.3} Cu _{1.3} AlO _x	250	250	3:1	14200	14.6	0.00	1.06	0.01	0.70	0	0	0	0	0
Co _{1.8} Cu _{0.9} AlO _x	250	250	3:1	14200	11.3	0.02	1.14	0.21	0.76	0	0	0	0	0
Co _{2.6} AlO _x	250	250	3:1	14200	5.3	0	0.42	0	0.21	0	0	0	0	0
Co _{2.6} AlO _x	300	250	3:1	14200	6.9	0.1	0.43	0.27	0.18	0.07	0.02	0.01	0.03	0.03
Co _{2.6} AlO _x	400	250	3:1	14200	9.8	0	1.02	0.21	0.72	0.04	0.04	0	0	0
Co _{2.6} AlO _x	500	250	3:1	14200	51.8	0.03	1.06	0.15	0.37	0.06	0.02	0.02	0.03	0.03
Co _{1.8} Cu _{0.9} AlO _x	300	250	3:1	14200	12.6	0.03	1.09	0.31	0.64	0.07	0.04	0	0	0
Co _{1.8} Cu _{0.9} AlO _x	400	250	3:1	14200	17.1	0.13	1.3	0.56	0.73	0.19	0.07	0.01	0.01	0.01
Co _{1.8} Cu _{0.9} AlO _x	500	250	3:1	14200	12.0	0.12	1	0.36	0.63	0.09	0.1	0.02	0.03	0.03
Co _{1.8} Cu _{0.9} AlO _x	400	200	3:1	14200	7.1	0.03	0.51	0.04	0.33	0.01	0.03	0	0	0
Co _{1.8} Cu _{0.9} AlO _x	400	300	3:1	14200	30.1	0.45	1.68	0.95	0.91	0.33	0.28	0.06	0.18	0.18
Co _{2.6} AlO _x	400	200	3:1	14200	3.0	0	0.17	0	0.15	0	0.02	0	0	0
Co _{2.6} AlO _x	400	300	3:1	14200	19.5	0.52	1.19	0.36	0.89	0.15	0.12	0.01	0.01	0.01
Co _{1.8} Cu _{0.9} AlO _x	400	250	3:1	10625	24.4	0.17	1.16	0.83	0.59	0.25	0.17	0.03	0.04	0.04
Co _{1.8} Cu _{0.9} AlO _x	400	250	3:2	14200	12.2	0.29	1.29	0.85	0.63	0.29	0.09	0.04	0.06	0.06

818 ^a T_R: reduction temperature; and T: reaction temperature.819 ^b R: H₂/CO₂ ratio.820 ^c GHSV expressed in mL.g_{cat}⁻¹.h⁻¹.821 ^d HCs are separated by the number of carbons and whether they are paraffins (C2, C3) or olefins (C2=, C3=).