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1 **Insight into the mechanism of glycerol**
2 **hydrogenolysis to 1,2-propanediol: benefits of**
3 **Cu promotion by La**

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15 **Abstract**

16 The effect of La promotion on a Cu/ γ -Al₂O₃ catalyst for glycerol hydrogenolysis towards
17 1,2-propanediol, as alternative for its petroleum based production route, was investigated under
18 continuous flow operation in a trickle bed reactor. The La-Cu interaction led to co-existence of
19 Cu⁺ and Cu⁰ species. The activity rather decreased with La/Cu ratio, owing to a tradeoff between
20 stability and activity. Sintering of the Cu particles occurred, but was less pronounced in the presence
21 of La. Characterization showed that with increasing La/Cu ratio, the number of weak and moderate
22 acid sites increased while that of the strong acid sites decreased. Our results indicate that Cu⁺, rather
23 than the support, plays a key role in the acetol formation and consequently in the selectivity towards
24 1,2-propanediol. Compared to a Cu catalyst, the La-Cu one exhibited a better glycerol conversion
25 stability over time (relative decrease of 12.5% vs. 25%) and 1,2-propanediol selectivity (94% vs.
26 82%).

27 **1 Introduction**

28 Glycerol has emerged as a biomass-based feedstock in the chemical, solvent and fuel industry.[1-
29 3] The majority (60-70 %) of the natural glycerol is co-produced with biodiesel by transesterification,
30 the resulting mixture containing approximately 10 vol.% of glycerol.[3, 4] It is one of the key platform
31 chemicals in these industries thanks to its unique chemical versatility originating from the three
32 hydroxyl groups on its C3-backbone. In a hydrogenolysis reaction, the cleavage of a C-O or C-C bond
33 occurs simultaneously with hydrogen addition.[5] The cleavage of a primary C-O bond in glycerol
34 results in 1,2-propanediol (*i.e.* propylene glycol), while that of the secondary C-O yields 1,3-
35 propanediol. 1,2-propanediol has a wide range of applications depending on its purity, including

36 food, pharmaceuticals, cosmetics, as a monomer for resins, aircraft deicing fluids, automotive
37 coolants, paints and coatings, liquid detergents, inks, varnishes, tobacco humectants, etc.[6]
38 Currently, it is produced from the petroleum derived and explosive propylene oxide, in the presence
39 of an acid catalyst.[6] Thus, the valorization of glycerol contributes to the development of safer and
40 sustainable production route for currently petroleum-based 1,2-propanediol.

41 Cu-based catalysts are often applied in industry due to their lower price compared to noble metals
42 and their enhanced selectivity to C-O bond cleavage, which is higher compared to Co- or Ni-
43 catalysts.[7, 8] Initially, many industrially used commercial Cu catalysts have been investigated for
44 glycerol hydrogenolysis.[9-14] Later, other Cu-based supported over MgO[15-17], SiO₂[18-22] or
45 Al₂O₃[23-33] were also reported by various researchers.

46 Significant efforts have been made in preparing effective and stable Cu-based catalysts in the last
47 two decades. Typically, promoters are required to limit the tendency of Cu to sinter.[34-37]
48 Undoubtedly, the Cu dispersion and/or interaction between Cu species, the support, and a
49 promotor are the main factors in determining the catalytic activity, selectivity and stability. In our
50 previous work[38], Ba, Ce, Cs and La were investigated as dopants, *c.g.* promoters, for the
51 hydrogenolysis of glycerol into 1,2-propanediol over a Cu/ γ -Al₂O₃ catalyst. The addition of Ba or Ce
52 increased the initial activity, while La allowed to establish the most stable activity in terms of glycerol
53 conversion over time (relative decrease of ca. 25 % over 68 h time on stream).

54 Two alternative mechanisms are mainly reported in the literature for the production of
55 1,2-propanediol from glycerol: the dehydration-hydrogenation mechanism (involving acidic sites)
56 [39, 40] and the dehydrogenation-dehydration-hydrogenation mechanism (involving basic
57 sites)[41]. It is commonly accepted that γ -Al₂O₃ has intrinsic acidity[42], automatically leading to the
58 assumption that the hydrogenolysis of glycerol proceeds according to the dehydration-

59 hydrogenation mechanism on Cu based catalysts. In this case, the dehydration step would occur on
60 an acid site, available on the support, while the hydrogenation step is then catalyzed by a Cu⁰
61 particle. However, various researchers are convinced that Cu⁰ is the active site for both steps in the
62 dehydration-hydrogenation mechanism.[43-46] Other researchers believe in the synergetic effect
63 between Cu⁺ and Cu⁰, or in the role of Cu⁺ as active site, i.e., assuming that Cu is not entirely present
64 in the pure metallic state.[11, 19, 21, 33, 47-49] Vila *et al.*[27] pointed out that Cu⁺ species in a Cu/ γ -
65 Al₂O₃ catalyst improved the glycerol conversion, while the differences in 1,2-propanediol selectivity
66 could be related to the different Cu⁰/Cu⁺ in the catalysts. Generally, Cu catalysts show a high
67 selectivity towards 1,2-propanediol, however, some C-C cleavage to 1,2-ethanediol can be
68 observed. The retro-aldol condensation reaction that leads to the C-C cleavage, requires hydrogen.
69 Hence, it is commonly accepted that it is catalyzed by a metallic site, in this case Cu⁰. [50-52]
70 However, the effect of strong acidic sites cannot be ruled out in a C-C cleavage. [51, 53] To elucidate
71 the role of the different Cu species, a well-controlled preparation of catalysts with various Cu⁺ or
72 Cu⁰ amounts is necessary. La was found to impact on the presence of Cu⁺ and Cu⁰ sites in Cu/SiO₂
73 catalysts. [54, 55] Insights in this respect on γ -Al₂O₃ supported Cu catalysts for glycerol
74 hydrogenolysis are, however, still lacking.

75 In this work, we aim to investigate the effect of La promotion on γ -Al₂O₃ supported Cu species to
76 gain insight into their catalytic mechanism for glycerol hydrogenolysis. To this end, a series of
77 La-Cu catalysts was prepared by sequential impregnation. By varying the La and Cu loading, twelve
78 different promotion ratios were obtained with various distribution of the Cu⁺ and Cu⁰ species. The
79 catalysts were comprehensively characterized in terms of textural and physicochemical properties,
80 crystallographic and morphological structure, reduction behavior and surface species to better
81 understand the effect of the promotion ratio. We selected five La-Cu catalysts, with specific

82 characteristics, to perform liquid phase glycerol hydrogenolysis in a fixed bed reactor operated in
83 trickle flow regime and compared them to a bare Cu catalyst. The effect of the La/Cu mass ratio was
84 investigated by comparing the surface species, catalysts activity and 1,2-propanediol selectivity for
85 these six catalysts. The catalysts stability was investigated by comparing the Cu⁰ particle size *prior*
86 and *post* reaction.

87 **2 Experimental**

88 **2.1 Catalyst synthesis**

89 All the catalysts in this work, indicated as xLa-yCu/γ-Al₂O₃, in which x and y are the corresponding
90 weight percentage (wt.%), were synthesized using a sequential wet impregnation method. The La
91 and Cu loading varied between 0 and 2.5 wt.%, and 10 and 25 wt.%, respectively. In this method,
92 the support, γ-Al₂O₃ (Sasol, Puralox SCCa-150/200), was suspended in 10 ml demineralized water
93 per gram of support. At the same time, the promoter precursor, La(NO₃)₃.6H₂O (Sigma-Aldrich, ≥ 99
94 %), was dissolved in 6.6 ml distilled water per wt.% of La. The suspensions were mixed and stirred
95 at 500 rpm at room temperature for 2 h. Subsequently, the water was evaporated at 363 K, after
96 which the sample was further dried in air at 393 K for 1.5 h and calcined at 673 K, using a ramp of 2
97 K min⁻¹ in static air for 2 h. In the second step, the x wt.% La/γ-Al₂O₃ powder was suspended in 150
98 mL demineralized water, mixed and stirred at 500 rpm for 2 h with the desired amount of metal
99 precursor, Cu(NO₃)₂.5/2H₂O (Sigma-Aldrich, ≥ 99 %), which was dissolved in 75 mL demineralized
100 water. The catalyst was obtained after the same thermal treatment as in the La-loading step. For
101 comparison, a bare Cu/γ-Al₂O₃ catalyst was also prepared.

102 2.2 Catalyst characterization

103 The elemental analysis was performed by inductively coupled plasma-optic emission
104 spectroscopy over a 720-ES ICP-OES equipment (Agilent) with axial viewing and simultaneous
105 Charge Coupled Device detection. Before the elemental analysis, the sample was prepared by
106 dissolving 10 mg of dried and grounded sample in concentrated aqua regia solution (HNO₃:HCl, 1:3,
107 v:v). The solution was heated to 383 K during 2 h in the autodigestor Vulcan 42 (Questron) and
108 diluted up to 20 ml with ultrapure water before analysis.

109 The specific surface area and pore volume of the catalyst were measured through N₂-sorption
110 experiments at 77 K using a Tristar II 3020 Micrometrics apparatus. The specific surface area, S_{BET} ,
111 was determined using the five-point Brunauer-Emmett-Teller method. The total pore volume, V_p ,
112 was estimated from the adsorbed nitrogen amount at relative pressure of 0.98. The pore size
113 distribution and average pore size, D_p , were calculated according the Barrett-Joyner-Halenda
114 formula applied to the desorption isotherm.

115 Powder X-ray diffraction (XRD) patterns were obtained using a Bruker D8-AXS Discover device
116 and a linear Vantec detector, using with a CuK_α X-ray source ($\lambda = 1.54 \text{ \AA}$) under continuous scan
117 mode over a 2θ range of 15° to 75°, with a step size of 0.02°.[56] The reduction was performed *in-*
118 *situ* with 5 vol.% H₂-He at 1.1 NmL s⁻¹ with a temperature increase up to 723 K (ramp: 8 K min⁻¹). For
119 the presentation of the results, the observed intensity was normalized based on the intensity of the
120 highest peak. The Scherrer equation, was used to determine the size of the crystals in the calcined,
121 reduced or spent catalysts.

122 The dispersion, D_{Cu^0} , the mean Cu surface area, MSA_{Cu^0} , and the average diameter of the Cu
123 aggregates, ϕ_{Cu^0} , were determined by dissociative N₂O adsorption according to the method of

124 Gervasini *et al.*[57] on the Micrometrics Autochem II 2920 equipped with a TCD-detector. This
125 method determines the D_{Cu^0} , and MSA_{Cu^0} with qualitative and quantitative information by a
126 successive analysis of H₂-TPR, a surface oxidation by N₂O and the H₂-TPR of the freshly oxidized Cu
127 surface (defined as s-TPR). s-TPR allows to distinguish between surface Cu species and bulk Cu.[57]
128 To desorb any potentially adsorbed species, the temperature was first increased to 473 K (ramp: 90
129 K min⁻¹), held constant for 5 min, and cooled to 323 K. In the next step, the reducibility of the
130 catalysts was evaluated by H₂-TPR, pursuing complete reduction of CuO to Cu⁰. A gaseous 10%H₂-Ar
131 mixture with a flow rate of 1 NmL s⁻¹ was sent over the catalyst while heating to 723 K at a ramp of
132 8 K min⁻¹. Once at 723 K, the temperature was held constant for 30 min during which the Cu^x species
133 were reduced to Cu⁰. Next, the temperature was reduced to 323 K. In the second step, a constant
134 flow of 1 vol.% N₂O-Ar gas with a flow rate of 0.25 NmL s⁻¹ (Air Liquide) was sent over the catalyst at
135 323 K for 1 h, during which surface Cu⁰ species reacted with N₂O and formed Cu⁺. In the third step
136 again a 10 vol.% H₂-Ar gas at a flow rate of 1 NmL s⁻¹ was sent over the catalyst, while heating this
137 time to 1073 K (ramp: 20 K min⁻¹) thereby reducing the surface Cu⁺ species to Cu⁰. The amount of
138 consumed H₂ was measured by a thermal conductivity detector (TCD). The Cu dispersion, D_{Cu^0} ,
139 defined as the ratio of the Cu exposed at the surface to the total amount Cu, was calculated from
140 the amount of H₂ consumed in the s-TPR analysis. The mean Cu surface area, MSA_{Cu^0} [m² g⁻¹_{cat}], is
141 a measure for the number of active sites on the catalyst and calculated with equation (1), in which
142 n_{H_2} stands for the experimentally consumed number of moles of H₂ [μmol_{H2} g⁻¹_{cat}], SF is the
143 assumed O/Cu ratio (2 mol_{Cu} mol⁻¹_{H2}), N_A is the Avogadro's number and C_M is the average number
144 of Cu atoms per area, assuming equally exposed (100), (110) and (111) planes, i.e.
145 $1.47 \cdot 10^{19}$ atoms_{Cu} m⁻²_{Cu}.

$$MSA_{Cu^0} = \frac{n_{H_2} \cdot SF \cdot N_A}{10^6 \cdot C_M} \quad (1)$$

146 The average diameter of the Cu aggregates, ϕ_{Cu^0} [nm], is determined from MSA_{Cu^0} via Eq. (2),
 147 where SK is a constant representing the available surface area of a particle ($SK = 5$) and ρ_{Cu} the
 148 density of Cu (8.92 g cm⁻³).

$$\phi_{Cu^0} = \frac{10^3 \cdot SK \cdot wt.\%_{Cu}}{MSA_{Cu^0} \cdot \rho_{Cu}} \quad (2)$$

149 For the determination of acid sites, ammonia (NH₃) was used as a probe molecule during TPD. For
 150 the measurement of the total number of acid sites, ca. 0.2 g of catalyst (or pure support) was diluted
 151 with 0.8 g of inert material. First, this diluted sample was heated in an inert atmosphere (Ar, 0.42
 152 NmL s⁻¹) up to 473 K (ramp: 90 K min⁻¹). After 5 min, the temperature was decreased to 383 K and
 153 kept at that temperature for 20 min. Next, the catalyst was reduced using 10 vol.%H₂-Ar (1 NmL s⁻¹)
 154 while heating to 473 K (ramp: 8 K min⁻¹) after which the temperature was kept for 15 min. After the
 155 reduction, the temperature was decreased to 423 K and the gas flow was switched to 4 vol.% NH₃-
 156 He with a flow rate of 0.25 NmL s⁻¹. After 30 min, the gas was switched to Ar (0.42 NmL s⁻¹) to remove
 157 the physisorbed NH₃. Finally, the temperature was increased to 873 K at a heating rate of 10 K
 158 min⁻¹. The amount of desorbed NH₃ was detected by a TCD.

159 The composition and oxidation state of the elements present on the catalysts surface were
 160 determined using X-ray photoelectron spectroscopy (XPS). The XPS spectra were recorded at a
 161 residual pressure of 10⁻⁹ mbar on a Kratos Axis UltraDLD electron energy spectrometer operating
 162 with a monochromatic Al-K α (1486.6 eV). The pass energy of the hemispherical analyzer was set at
 163 160 eV for the wide scan and 40 eV for narrow scans. In the latter conditions, the full width at half
 164 maximum (FWHM) of the Ag 3d_{5/2} peak of a standard silver sample was about 0.9 eV. Charge

165 stabilization was achieved by using the Kratos Axis device. Peak decomposition was performed using
166 curves with a 70% Gaussian type and a 30% Lorentzian type and a Shirley nonlinear sigmoid-type
167 baseline. The following peaks were used for the quantitative analysis: O 1s, C 1s, La 3d, Cu 2p, and
168 Cu LMM Auger peak. Molar fractions were calculated using peak areas normalized on the basis of
169 acquisition parameters after a Shirley background subtraction and corrected with experimental
170 sensitivity factors and transmission factors provided by the manufacturer. The binding energy (BE)
171 scale was calibrated by measuring C 1s peak (BE = 284.8 eV) from the surface contamination and
172 the accuracy of the measurement was ± 0.1 eV. Differential surface charging of the samples was
173 ruled out by checking the reproducibility of XPS measurements in repeated scans under different X-
174 ray exposures. Software CasaXPS was used for the analysis of XPS spectra, separating elemental
175 species in different oxidation states, and calculating relative concentrations of chemical elements.

176 Scanning (Transmission) Electron Microscopy was performed with a Cs corrected JEOL JEM-2200FS
177 instrument[58] equipped with a Schottky-type field-emission gun and JEOL JED-2300D energy-
178 dispersive X-ray (EDX) detector, at 200 kV. Specimen preparation consisted of immersing a lacey
179 carbon film supported on a Ni grid into the sample powder. Dark-field STEM images give the best
180 contrast to the identification of particles. For the spent 1.5La-10Cu, 1.5La-20Cu, 2.0La-10Cu and
181 2.0La-20Cu catalysts, the particle size distribution of the large particle population (> 10 nm) was
182 determined based on almost 500 particles. For the 1.0La-10Cu catalyst, the particle size distribution
183 was established on 117 particles, due to a limited amount of STEM images. For the 10Cu catalyst,
184 only 30 particles were measured as sintering was clear on every image.

185 **2.3 Catalyst performance testing**

186 The performance of the catalysts was assessed for liquid phase glycerol (99.5%, Sigma-Aldrich)
187 hydrogenolysis in a high-throughput kinetics mechanistic investigation set-up.[59] The reaction was

188 performed within the intrinsic kinetic regime, which was assessed by typical correlations[60, 61] and
189 experimentally proven in previous work[46], under steady state conditions in a fixed bed reactor
190 operating in a trickle-bed regime.

191 The reactor effluent was analyzed using a gas chromatograph equipped with a flame ionization
192 detector and an Agilent CP-Was 57 CB glycols column using 1,4-butanediol as an external standard.
193 The calibration factors are listed in Table SI.1.

194 Conversion was defined according to equation (3), where F_G^0 and F_G represent respectively the
195 molar in- and outlet flow rates of glycerol (mol s^{-1}).

$$X_G = \frac{F_G^0 - F_G}{F_G^0} \quad (3)$$

196 The selectivity towards a component i was calculated on a molar carbon basis according to
197 equation (4), with $a_{c,G}$ the number of carbon atoms in glycerol, F_i^0 and F_i the molar in- and outlet
198 flow rates of a component i (mol s^{-1}) respectively.

$$S_{i,G} = \frac{a_{c,i} \cdot (F_i - F_i^0)}{a_{c,G} \cdot (F_G - F_G^0)} \quad (4)$$

199 The activity is defined as the ratio of the mass flow rate in which glycerol is converted,
200 $\dot{m}_{G,converted}$ ($\text{kg}_G \text{s}^{-1}$), to the total amount of catalyst used, W_{cat} (kg_{cat}).

$$activity = \frac{\dot{m}_{G,converted}}{W_{cat}} \quad (5)$$

201 3 Results and discussion

202 Industrially, a high density of active sites on the catalysts, which is mostly achieved at high metal
203 loadings, is desirable to maximize the volumetric activity. However, to prove relationships between
204 catalyst structure and catalytic performance, more moderate metal loadings (< 20 wt.%) are
205 advisable [62, 63]. In our previous work[38], it was clear that a small amount of 1.0 wt.% of La
206 sufficed to increase the stability of a 10 wt.% of Cu/Al₂O₃ catalyst. In this work, the La/Cu mass ratio
207 was varied around that central point, aiming at changing the distribution of the Cu⁺ and Cu⁰ species.
208 Therefore, a series of La-Cu/γ-Al₂O₃ catalysts with nominal La and Cu values: x wt.% La – 10 wt.% Cu
209 (x = 0, 1.0, 1.5, 2.0), x wt.% La – y wt.% Cu (x = 1.5, 2.0, 2.5 and y = 15, 20, 25) were prepared.

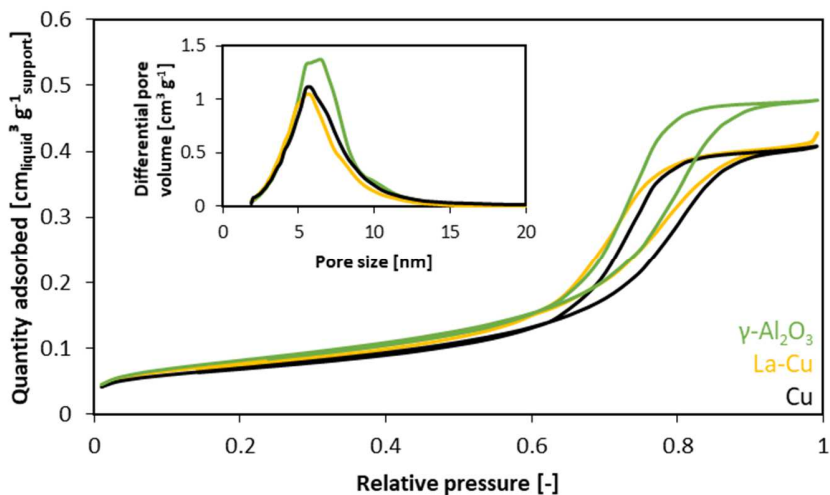
210 No lanthanum was leached during the synthesis as the La loading in the intermediate La/γ-Al₂O₃
211 materials was similar as for the La-Cu/γ-Al₂O₃ catalyst (Table SI.2). The actual La and Cu loadings in
212 the calcined catalysts were systematically lower than the nominal ones, Table SI.3. This was
213 attributed to the hygroscopic nature of the precursors, leading to an overestimation of the actually
214 introduced amounts during the synthesis.

215 To understand the nature of the Cu species present on the catalyst's surface and their evolution,
216 the catalysts were characterized in three states: after calcination, after reduction and *post*-reaction
217 (*i.e.* spent catalyst). On that ground, the role of Cu species in the catalytic performance for glycerol
218 hydrogenolysis was investigated.

219 **3.1 Catalyst characterization**

220 **3.1.1 Textural properties**

221 The support and the catalysts were characterized by N₂ sorption. A type-IV N₂-adsorption isotherm
222 is observed for all catalysts, see Figure 1 and Figure SI.1, which is expected since the support
223 (PURALOX® γ -Al₂O₃) is mesoporous.[64] The presence of mesopores (2 – 50 nm) is confirmed by the
224 pore size distribution (Table SI.3). The hysteresis loops are classified as type H1, which is typical for
225 materials with cylindrical pore channels.[65] The BET surface area exhibits a small decrease upon
226 the La and Cu impregnation without a clear trend as a function of metal loading or promotor ratio.
227 A similar observation was made for the mesoporous volume and the mean pore volume or size. The
228 BET surface area ranged between 164 and 192 m² g⁻¹_{support} (Table SI.3) while the mesoporous volume
229 and mean pore size varied between 0.38 – 0.47 cm³ g⁻¹_{support} and 6.4 – 8.6 nm, respectively (Table
230 SI.3). Therefore, it is concluded that the promotion has no significant impact on the textural
231 properties of the support.



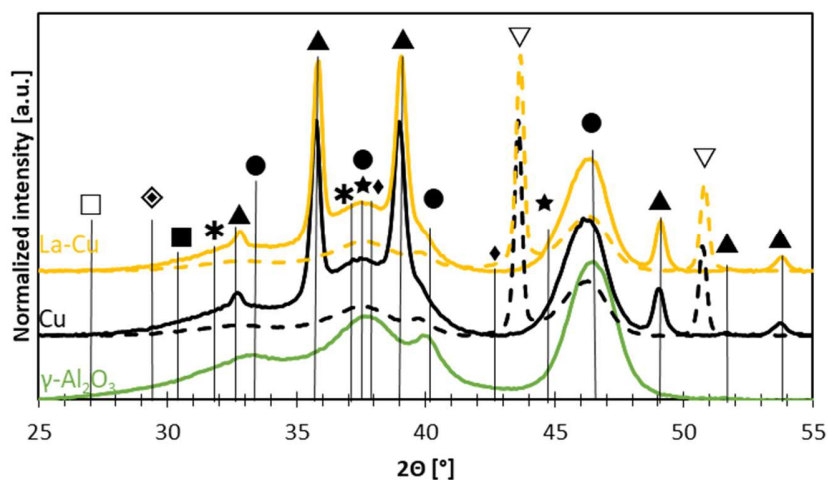
232

233 **Figure 1. N₂-sorption isotherms and differential pore size distribution of the support (green), 10Cu**
234 **catalyst (black) and 1.0La-10Cu (yellow) catalysts, as representative for the La-Cu catalysts.**

235 3.1.2 Crystallographic and morphological structure

236 The crystalline phases of the support and the calcined and reduced catalysts were determined by
237 XRD, as shown in Figure 2 and Figure SI.2. Broad diffraction peaks for γ - Al_2O_3 at 31.8° , 37.5° , 39.2° ,
238 and 45.7° , respectively corresponding to the $\text{Al}_2\text{O}_3(220)$, $\text{Al}_2\text{O}_3(311)$, $\text{Al}_2\text{O}_3(222)$, $\text{Al}_2\text{O}_3(400)$ facets are
239 detected for all catalysts, see Figure 2. This indicates a limited crystallinity of the support. The
240 calcined La-Cu catalysts exhibited main characteristic diffraction peaks of $\text{CuO}_{(002)}$ at 35.4° and
241 $\text{CuO}_{(111)}$ at 38.6° , and minor diffraction peaks at 32.5° ($\text{CuO}_{(-110)}$), 48.7° ($\text{CuO}_{(-202)}$), 51.4° ($\text{CuO}_{(112)}$) and
242 53.5° ($\text{CuO}_{(020)}$). For none of the catalysts, the most characteristic peak of $\text{Cu}_2\text{O}_{(111)}$ at 36.4° could be
243 detected. Therefore, it can be deduced that, if present, Cu_2O was either highly dispersed or
244 amorphous, or in a very little amount. As the La-loading was below $8.5 \mu\text{mol}_{\text{La}} \text{m}^{-2}$ [66], the
245 characteristic peaks of lanthanum oxides (La_2O_3 and LaO) were not observed. The main diffraction
246 peaks of the mixed Cu-Al phase, $\text{CuAl}_2\text{O}_4(400)$ at 36.8° and $\text{CuAlO}_2(012)$ at 37.1° , overlap with the broad
247 diffraction peak for $\text{Al}_2\text{O}_3(311)$. Most likely, those phases were not present, as they only form above
248 773 K , according to the $\text{CuO}-\text{Al}_2\text{O}_3$ phase diagram.[67, 68]

249 After reduction at 723 K , the representative Cu^0 XRD peaks appeared at 43.3° for $\text{Cu}^0_{(111)}$ and at
250 50.5° for $\text{Cu}^0_{(200)}$. No characteristic peaks of CuO remained and, again, no characteristic peak of Cu_2O
251 at 36.4° was identified, impeding any conclusion on Cu_2O . Based on the Scherrer equation, the Cu^0
252 crystallite sizes were in the range from 40 nm to 80 nm (Table SI.4), while on the calcined, *i.e.* prior
253 to the reduction, catalysts the CuO crystallite sizes were calculated in the range of 20 to 40 nm
254 (Table SI.2).e. This indicates that during the reduction, the Cu crystallites doubled in size compared
255 to the initial CuO .

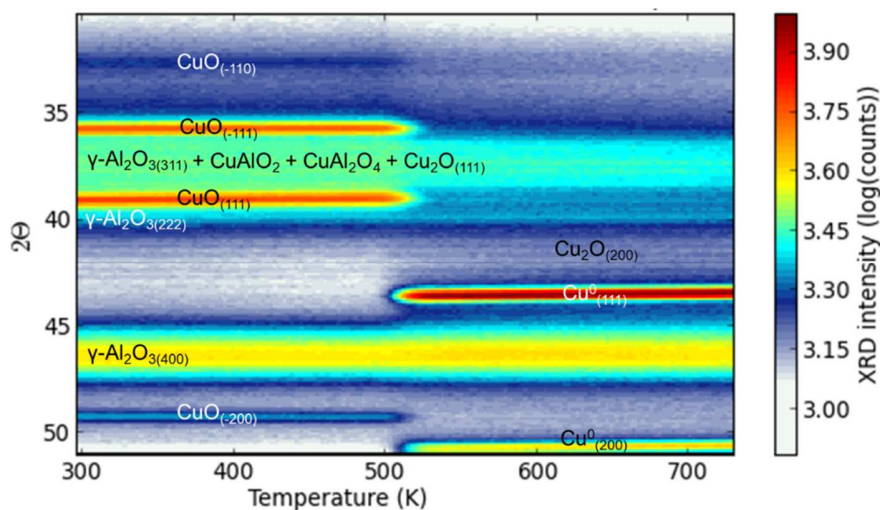


256

257 **Figure 2.** XRD pattern of the support (green) and the calcined (full line) and reduced (dashed lines) 10Cu
 258 catalyst (black) and 1.0La-10Cu (yellow) catalysts, as representative for the La-Cu catalysts. Phases
 259 patterns from JCPDS: with LaO (■, 00-033-0716), La₂O₃ (□, 03-065-3185), CuLaO₂ (◇, 00-35-1403), CuO
 260 (▲, 00-045-0937), Cu₂O (◆, 00-005-0667), Cu⁰ (▽, 00-004-0836), γ-Al₂O₃ (●, 00-050-0741), CuAl₂O₄ (★, 00-
 261 33-0448) and CuAlO₂ (*, 01-075-1792)

262 To study the evolution of the Cu oxidation state during the reduction, the 1.0La-10Cu catalyst was
 263 investigated by means of *in situ* XRD, see Figure 3. The characteristic peaks of CuO at 32.5°, 35.4°,
 264 38.6° and 48.7° decrease between 500 and 520 K in favor of the Cu⁰ main peaks at 43.3° and 50.5°.
 265 The broad diffraction peaks for γ-Al₂O₃ at 39.2 and 45.7° kept their intensity during the reduction
 266 process. However, it is clear that the intensity between 34.5° and 38.6° changes during the reduction
 267 process. This area does not only correspond to the pattern of γ-Al₂O_{3,(311)} but also to Cu₂O₍₁₁₁₎ and
 268 the mixed Cu-Al phases, CuAlO₂ and CuAl₂O₄, most likely indicating (some) reduction of the Cu
 269 species. On the other hand, an increase in intensity at around 42.3°, corresponding to Cu₂O₍₂₀₀₎,
 270 could also be observed in Figure 3. The low intensity of the Cu₂O species is most likely due to the
 271 low amount (and crystallinity) of Cu₂O and, hence, its presence was further investigated by XPS, see
 272 section 3.1.4. Whereas Cu₂O could not be observed in the regular XRD measurements of the calcined
 273 and reduced catalysts, thanks to the *in situ* XRD it appears that in the calcined catalyst Cu₂O mainly

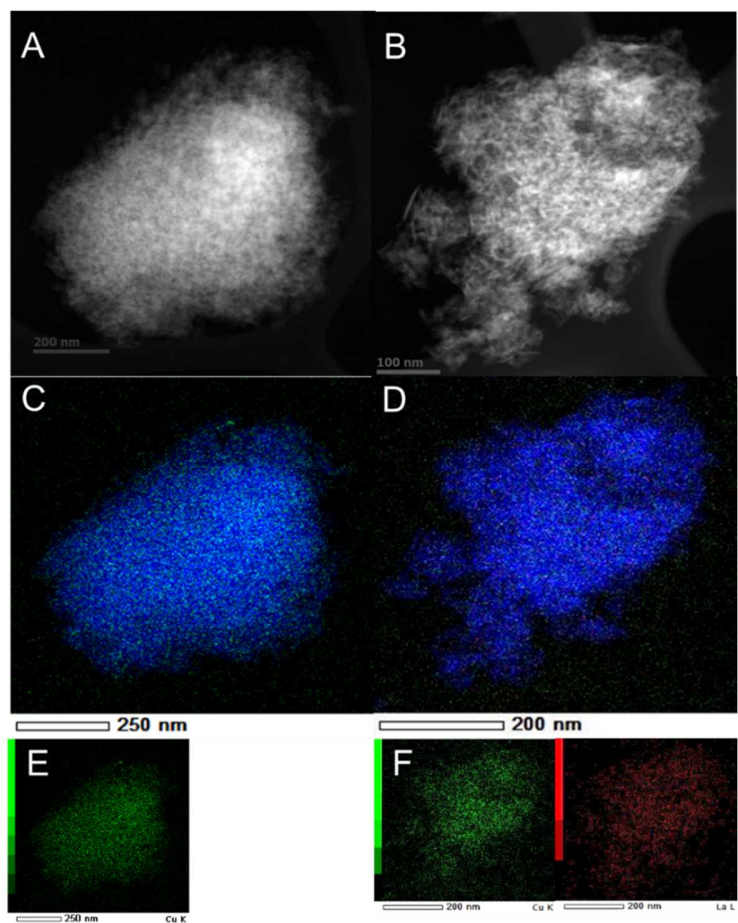
274 consists of $\text{Cu}_2\text{O}_{[111]}$, with a minor amount of $\text{Cu}_2\text{O}_{[200]}$. The reduced catalysts have a higher fraction
275 of $\text{Cu}_2\text{O}_{[200]}$.



276

277 **Figure 3. Contour plots of the diffraction peaks as function of temperature between 32° and 52° during**
278 **reduction with 1.1 NmL s⁻¹ 5 vol.% H₂-He of Cu oxides present in the 1.0La-10Cu catalyst.**

279 The material's morphology was further investigated *via* STEM. In calcined (Figure SI.3) and reduced
280 (Figure 4) samples of the 10Cu and 1.0La-10Cu catalysts, the porous structure was visible[69, 70],
281 while for the 1.0La-10Cu even the presence of cylindrical channels, as evidenced by N₂-sorption, was
282 observed. For both catalysts, it is clear that La and Cu remain highly dispersed over the $\gamma\text{-Al}_2\text{O}_3$
283 support. (Figure 4E and F) after reduction. For the 2.0La-10Cu catalyst (Figure SI.4), a catalyst grain
284 with larger Cu particles was found, however, the number was too small to obtain a particle size
285 distribution. In most images, no well-defined Cu-particles were identified, leading to the hypothesis
286 that most Cu particles are highly dispersed nanoparticles. The presence of a few larger Cu particles
287 is in agreement with the Cu^0 crystallites detected by XRD (Table SI.4).



288

289 **Figure 4.** Dark-field STEM image of 10Cu (A) and 1.0La-10Cu (B) ex-situ reduced at 723 K using 10 vol.%
 290 H₂-Ar. The corresponding EDX elemental map with the distribution of Al (blue), Cu (green) and La (red) is
 291 shown in C and D. The individual EDX maps of Cu and La are shown in E, corresponding to the dark-field
 292 image A, and in F, corresponding to the dark-field image B.

293 3.1.3 Active sites related properties

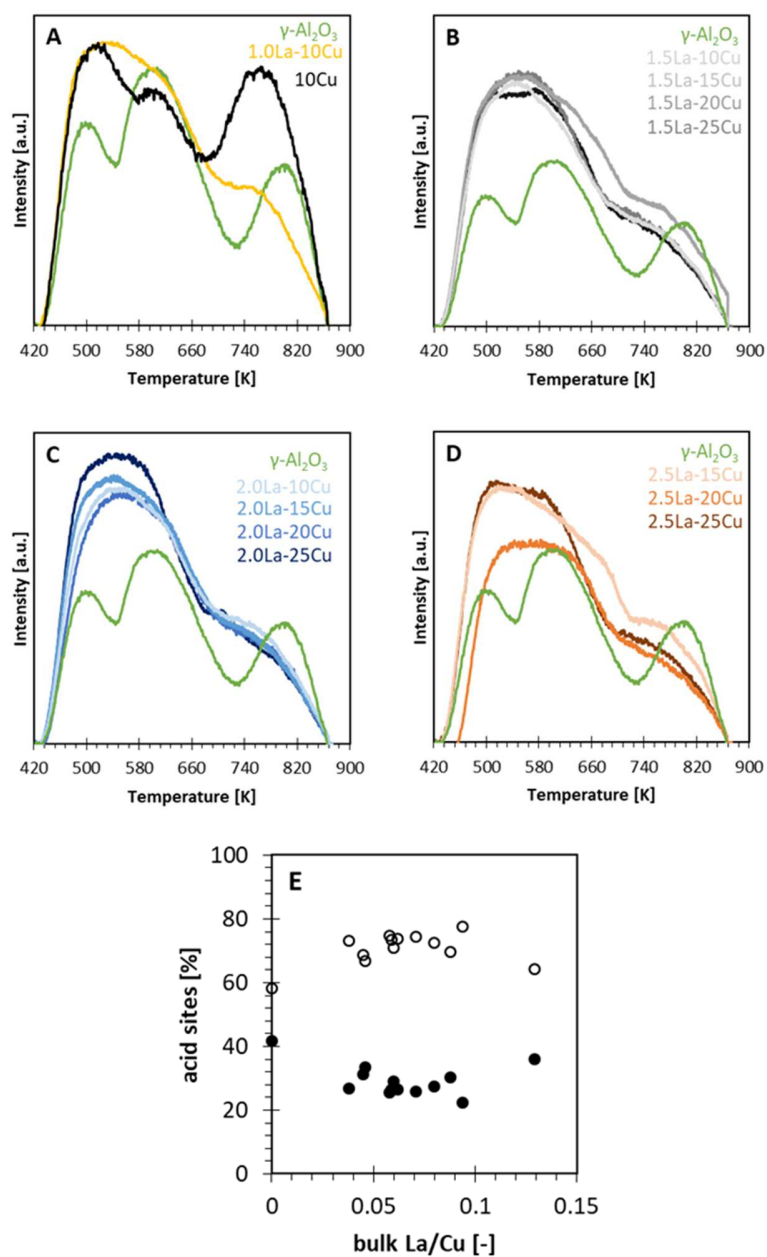
294 As Cu⁰ is needed for the hydrogenation reaction to achieve 1,2-propanediol, the catalysts have to
 295 be reduced prior to reaction. Hence, a more elaborate characterization of the reduced catalysts is
 296 needed to gain insights into the catalyst's surface and the role of Cu⁰.

297 The mean surface area of the Cu aggregates, MSA_{Cu^0} , and the average diameter of the aggregates,
 298 ϕ_{Cu^0} in the reduced catalysts were determined *via* N₂O adsorption. The MSA_{Cu^0} was found to be
 299 between 17 and 34 m² g⁻¹_{cat}, which is on the higher side of the range reported for typical supported

300 Cu-based catalysts in literature with similar Cu loading ($10\text{-}30\text{ m}^2\text{ g}^{-1}_{\text{cat}}$).[71-73] The average
301 diameter, ϕ_{Cu^0} , increases with the Cu loading (Figures SI.5A). This is expected, since a higher Cu
302 loading enhances the probability of agglomeration and/or growth of the Cu particles during
303 synthesis.[74] The catalysts exhibited a dispersion, D_{Cu^0} , between 4 % and 20 %. The dispersion
304 decreases with increasing Cu loading (Figure SI.6B), as it is inversely related to ϕ_{Cu^0} , see Table SI.4.

305 The acidity of the reduced catalysts was compared with that of the bare support, see Figure 5. The
306 addition of Cu resulted in a slight increase of the total acidity (Table SI.5). Compared to the calcined
307 support, the addition of Cu resulted to the formation of weak and strong acid sites (Figure 5A).
308 Moreover, it is clear that the interaction between La and Cu resulted in a different NH_3 -TPD profile
309 compared to that obtained for the Cu-only catalyst. All La-promoted catalysts exhibited a significant
310 increase in the signal in the weak-moderate acid site region, compared to the support, and a lower
311 signal in the region of the strong acid sites.

312 The effect of the promotor ratio on the distribution of acid site types in the catalyst is depicted in
313 Figure 5E. Promotion slightly increased the fraction of weak-moderate acid sites and decreased the
314 number of strong acid sites. Lee *et al.*[75] reported that a higher La content decreased the strong
315 acidity in zeolites, due to the preferential interaction between La and strong acid hydroxyl groups
316 on the surface. XPS (*vide infra*) showed an increased amount of surface Cu^+ , which correspond to
317 Lewis acidity species because of the electron affinity [19, 21, 28, 76-79], upon La-promotion (Figure
318 SI.10B). It was possible to estimate the distribution of the acid sites induced by the Cu^+ (Table SI.5).



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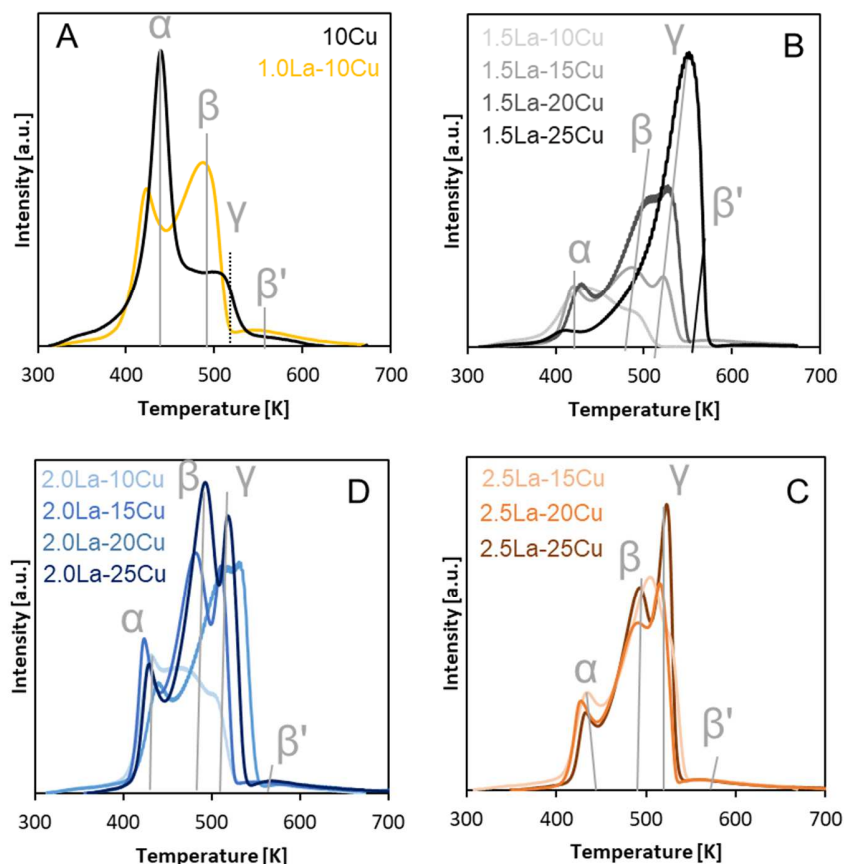
323

324

Figure 5. NH₃-TPD profiles of the calcined support (green) and (A): 10Cu (black), 1.0La-10Cu (yellow); (B): 1.5La-yCu; (C): 2.0La-yCu and (D): 2.5La-yCu catalysts. Intensities were normalized per support mass, such that additional acidity generated by metal deposition can be visually identified. (E) Effect of the bulk La/Cu mass ratio on the fraction of amount of weak-moderate (○) and strong (●) acid sites, as determined by NH₃-TPD.

325 3.1.4 Overall reduction behavior

326 The effect of promotion on the Cu species of the calcined catalysts and their reduction behavior
327 was investigated by H₂-TPR, of which the reduction profiles are shown in Figure 6. This analysis
328 provides insight into the overall surface species and catalyst reducibility, while an XRD measurement
329 (section 3.1.2) provides only information about the reduction of crystalline phases. It can be clearly
330 seen that the addition of La to the 10Cu catalyst (Figure 6A) decreased the intensity of the α peak,
331 while that of the β peak increased. The first reduction peak, α , might be ascribed to highly dispersed
332 CuO species[80] and/or (Cu-O-Cu)²⁺ species[47], the second reduction peak, β , to the reduction of
333 CuO particles with weak support interactions[81, 82]. The 1.0La-10Cu catalyst did not show any bulk
334 CuO, corresponding to the γ -peak[80-82], but had a higher number of CuO particles with strong
335 support interactions[81, 82], corresponding to β' . This species could correspond to the CuAl₂O₄
336 crystallites which were not clearly detectable with XRD in section 3.1.2. For the other catalysts
337 (Figure 6B to D), three main reduction peaks were distinguished. At higher Cu-loadings, the
338 reduction peaks shifted to higher temperature. The reduction peak γ increased with higher Cu-
339 loading, as a result of larger Cu particles, see Table SI.4. For all catalysts, the hydrogen consumption
340 during H₂-TPR was somewhat lower than the stoichiometric value for complete reduction from CuO
341 to Cu⁰, resulting in a degree of reduction between 76 % and 98 % (Table SI.4). Most likely, the
342 remaining amount of non-reduced Cu ^{δ +} species have a stronger interaction with the support, such
343 as CuAlO₂ or Cu₂O. This value related to the amount of Cu²⁺ in the calcined sample is in agreement
344 with the determined amount of Cu²⁺ on the calcined catalysts by XPS (Table SI.6). In short, it is
345 plausible that in addition to Cu⁰ species, a lower amount of Cu ^{δ +} species remains present after
346 reduction, as also indicated by the *in situ* XRD in Figure 3.



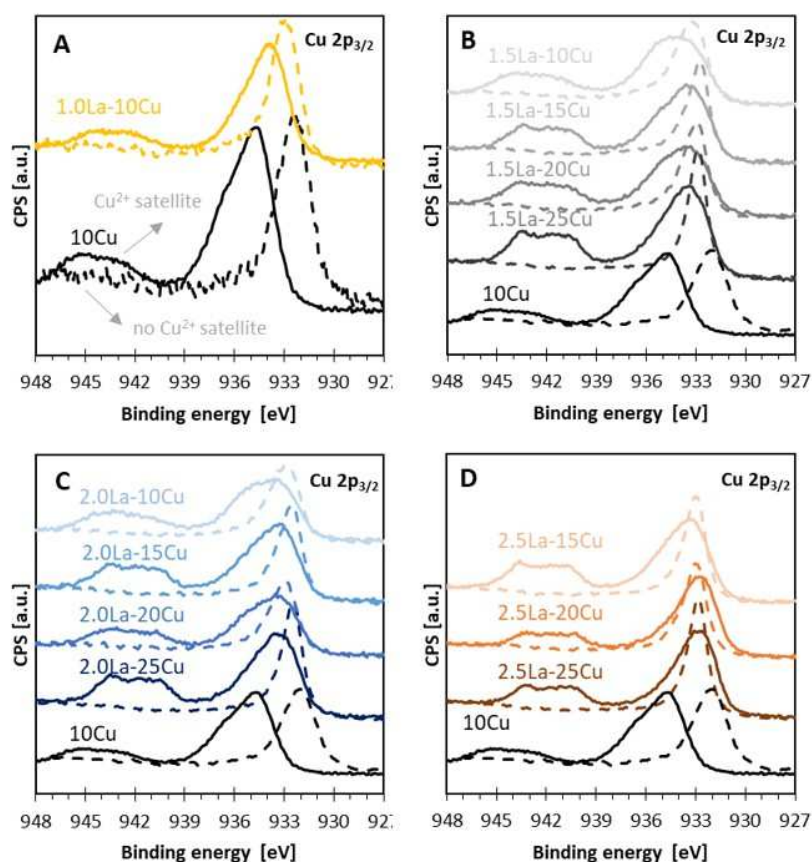
347

348 **Figure 6.** TPR profiles of the calcined catalysts with (A): 10Cu (black), 1.0La-10Cu (yellow); (B): 1.5La-yCu;
 349 (C): 2.0La-yCu and (D): 2.5La-yCu.

350 3.1.5 Identification of the surface species

351 The effect of the promotion on the chemical surface composition and oxidation states in the
 352 calcined and reduced La-Cu catalysts was analyzed *via* XPS. Being a surface technique, the
 353 representativeness of the results to the whole catalyst should be verified by comparing the La/Al
 354 and Cu/Al mass ratios, in the calcined catalysts, determined by XPS (surface composition) to those
 355 determined by ICP (bulk composition), see Table SI.3. Note that the La surface composition almost
 356 corresponds to that of the bulk, even though Cu is deposited after La (Figure SI.8A). For all calcined
 357 catalysts, the low Cu/Al ratios in XPS clearly indicate that quite some Cu is present as bulk Cu, rather

358 than being exposed at the surface (Figure SI.8B). The photoelectron peaks at 932.6 eV were assigned
359 to the binding energy (BE) of Cu 2p_{3/2}, as illustrated in Figure 7. The presence of a pronounced
360 satellite peak between 942 eV and 948 eV was ascribed to a contribution by Cu²⁺. Due to the
361 asymmetry of the Cu 2p_{3/2} peak, the Cu²⁺ species in the calcined catalysts are ascribed to CuO (933.5
362 eV) and CuAl₂O₄ (935 eV).[83] The latter is apparently in contrast with the XRD diffraction pattern
363 (section 3.1.2). However, XPS being a surface analysis technique, this can be interpreted as a
364 difference between the surface and bulk composition. When comparing the Cu 2p_{3/2} BE of the
365 Cu-only calcined catalysts to the La-Cu catalysts, a shift to lower BE was observed (Figure SI.9A, Table
366 SI.6). This may indicate that as La is added first, the Cu particles are preferentially located next to
367 the La particles rather than covering them, as the bulk La/Al corresponded well with the surface
368 La/Al ratio (Figure SI.8A). The shift to lower BE for Cu 2p_{3/2} points to the overlap of the d-orbitals of
369 La and Cu, indicating a strong La-Cu interaction.[84] The latter can lead to the formation of Cu
370 species with a lower oxidation state, such as Cu⁺, which is in agreement with the observations by in
371 situ XRD (Figure 3). As such, the relative amount of Cu²⁺ in the calcined catalysts decreases with the
372 percentage of surface La and varies between 100 % and 80 % (Figure SI.9B, Table SI.6).



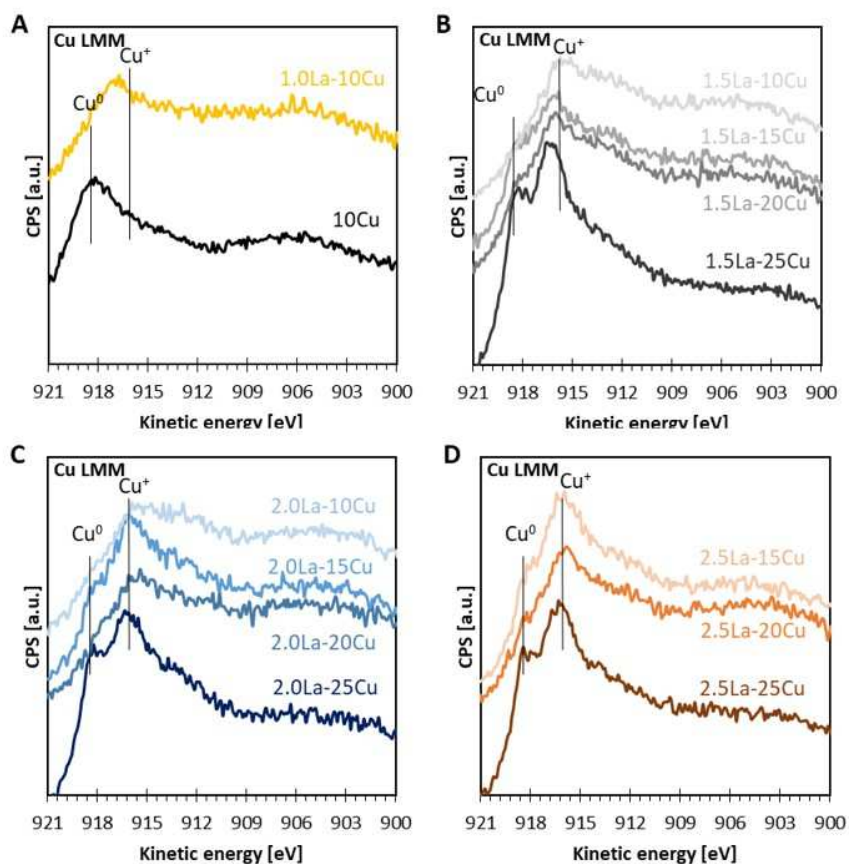
373

374 **Figure 7. Cu 2p_{3/2} spectra of calcined (full line) and reduced (dashed line) 10Cu catalyst (black) and**
 375 **(A): 1.0La-10Cu (yellow); (B): 1.5La-yCu; (C): 2.0La-yCu and (D): 2.5La-yCu.**

376 For the reduced catalysts, the Cu/Al ratio decreased approximately 50 % compared to the calcined
 377 samples (Table SI.7, *cf.* Table SI.6). As the reduction temperature is not sufficiently high to allow the
 378 diffusion of Cu into the Al₂O₃ structure[27, 85], this indicates a lower dispersion (and, hence,
 379 sintering) of the Cu particles. This is in agreement with the change in Cu crystallite size observed by
 380 XRD (Table SI.4, *cf.* Table SI.3). There was no satellite peak between 942 and 944 eV ascribed to Cu²⁺,
 381 implying reduction of Cu²⁺ to Cu⁺ and/or Cu⁰ (Figure 7). Comparing the calcined to the reduced
 382 catalysts (Table SI.6, *cf.* Table SI.7), a shift to lower BE was observed for all catalysts. The largest
 383 shift, from 934.6 eV (Cu²⁺) to 932.3 eV (Cu⁰), was observed for the unpromoted Cu catalyst, while
 384 the La-Cu catalysts showed a smaller shifts, due to the strong interaction between La and Cu. One

385 can presume that the larger shift for the unpromoted Cu catalysts is either to the larger particle size
386 or less Cu⁺.

387 Due to the similar BE between Cu⁺ (932.2 ± 0.1 eV) and Cu⁰ (932.6 ± 0.3 eV), it is hard to
388 discriminate between those Cu species.[86] To clearly distinguish between Cu⁺ and Cu⁰ in the
389 reduced catalysts, a deep analysis of the Auger Cu LMM region was performed. The Cu LMM
390 spectrum shows larger differences (1.8 eV) between the kinetic energy (KE) of the Cu species
391 compared to the BE. As shown in Figure 8, the Cu LMM spectra of the reduced La-Cu catalysts
392 present an asymmetrical broad peak, suggesting the coexistence of Cu⁺ and Cu⁰ on the catalysts
393 surface.[86] The higher the Cu loading, the more pronounced the Cu⁰ and Cu⁺ peaks are. Even if the
394 intensity of the Auger peaks is low, the concentration of the individual species could be determined
395 by the use of Cu standards. Notwithstanding that, caution is needed when interpreting the results
396 as small shifts in KE could result in different fractions of Cu⁰ and Cu⁺. When looking carefully at the
397 individual Cu⁰ and Cu⁺ species present on the surface of the reduced catalysts, the strong La-Cu
398 interaction is again noticeable. The higher the La/Cu surface mass ratio, the higher the percentage
399 of Cu⁺ species remained present after the reduction (*vide supra*, Figure SI.10). The values are
400 summarized in Table SI.7. It was also evidenced by the Wagner plot[86] that the surface of the
401 reduced La-Cu catalysts is covered with Cu⁺ rather than with Cu⁰ (Figure SI.11). Only the bare Cu
402 catalyst showed more Cu⁰ than Cu⁺ on the reduced catalyst surface.



403

404 **Figure 8. Cu LMM spectra of the catalysts after reduction at 623 K using 100 %H₂ at 0.33 NmL s⁻¹.**

405 **(A): 10Cu (black), 1.0La-10Cu (yellow); (B): 1.5La-yCu; (C): 2.0La-1yCu and (D): 2.5La-yCu.**

406 In summary, the La promotion has no pronounced effect on the textural properties of the calcined
 407 catalysts. The calcined catalysts exhibit a homogenous distribution of dispersed La and Cu particles.
 408 The La-Cu interaction resulted in Cu species with lower oxidation states, but the major part of the
 409 species remained in the Cu²⁺ oxidation state on the calcined catalysts. After reduction, the Cu
 410 agglomerates remain well dispersed and the dispersion of Cu⁰ on the reduced catalysts decreases
 411 with increasing Cu loading. Most of the Cu⁰ particles sizes are between 1-10 nm while some larger
 412 bulk Cu⁰ crystallites are also present. Due to the important La-Cu interaction, a significant amount
 413 of non-reduced Cu⁺ species remains present after the reduction – most probably at the surface of

414 the Cu⁰ particles – whereby, the acidity of the catalysts also slightly increases, as Cu⁺ species are
415 considered as moderate (Lewis) acids.

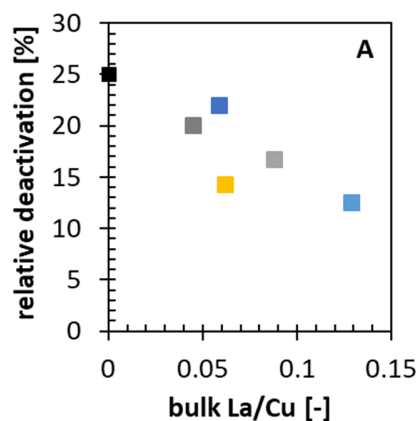
416 **3.2 Glycerol hydrogenolysis**

417 To investigate the effect of La/Cu mass ratio on the catalytic performance, *i.e.* the catalyst's
418 stability, activity and selectivity, five La-Cu catalysts were selected and compared to the 10Cu
419 catalyst. A La-Cu catalyst with the similar MSA_{Cu^0} as the 10Cu catalyst but different Cu particle sizes,
420 *i.e.* 1.5La-20Cu was selected. The 1.0La-10Cu and 2.0La-20Cu catalysts were also selected as those
421 exhibited the same promoter ratio, however, with different Cu particles. Finally, the La-Cu catalysts
422 with respectively the highest and lowest MSA_{Cu^0} , *i.e.* 1.5La-10Cu and 2.0La-10Cu, were also
423 selected.

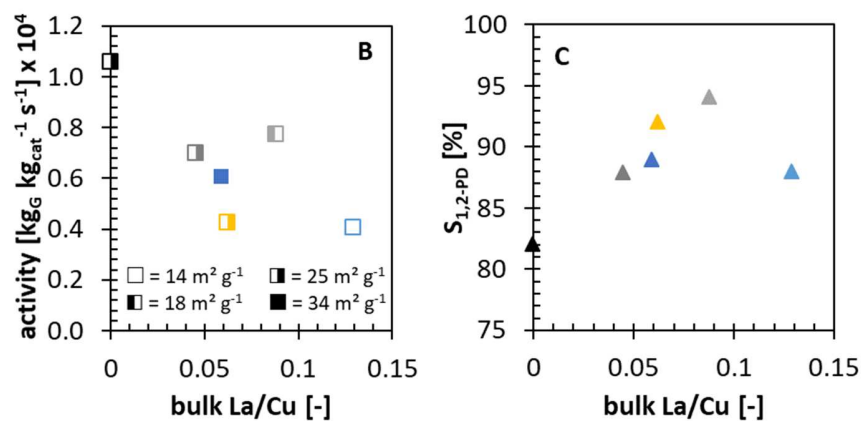
424 **3.2.1 Catalytic performance**

425 Figure 9A shows the effect of the La/Cu mass ratio on the catalyst stability, expressed as the
426 relative decrease in glycerol conversion over 68 h TOS (Table SI.8 till Table SI.13). It is clear that La-
427 Cu catalyst exhibited a better catalyst stability compared to the pure Cu catalyst. The increased
428 stability was attributed to a lower amount of sintering (*vide supra*, section 3.2.2).

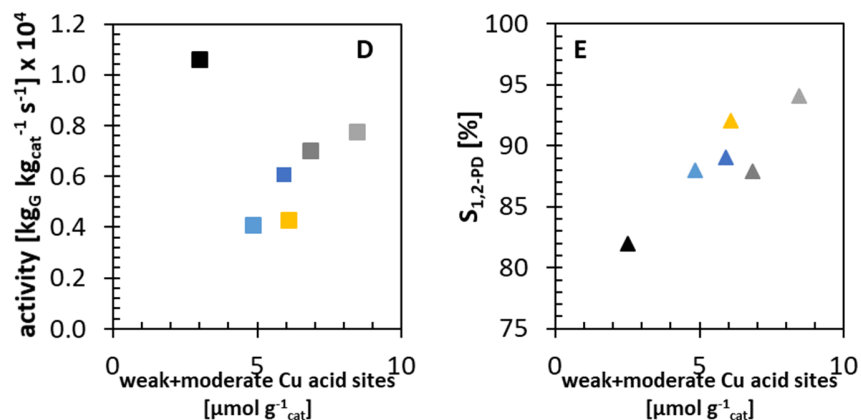
429 The effect of the promotion on the catalyst activity is shown in Figure 9B. La-promotion did not
430 increase the activity, in agreement with our previous work[38]. For a constant MSA_{Cu^0} , the activity
431 even rather decreases upon La 'promotion'. This indicates that a tradeoff will be needed between
432 stability and activity. The pure Cu catalyst has a higher activity even though no acidic Cu⁺ is present
433 on the surface (Table SI.7). However, a small acid contribution of Cu was estimated (Figure 9D),
434 which could be the result of some Cu-Al₂O₃ interactions. Therefore, it seems that the active sites on
435 the pure Cu and the La-Cu catalysts are different.



436



437



438

439 Figure 9. Effect of bulk La/Cu mass ratio on (A) the stability, (B) activity and (C) 1,2-propanediol
 440 selectivity. Effect of the weak and moderate Cu acid sites on (D) the activity and (E) 1,2-propanediol
 441 selectivity. Activity and selectivity are determined after 12 h time on stream at 125 kg_{cat} s mol⁻¹_{glycerol}, 473
 442 K, a total H₂ pressure of 7.5 MPa and a molar H₂ to glycerol ratio of 7 for the 10Cu (black), 1.5La-20Cu
 443 (dark grey), 2.0La-20Cu (dark blue), 1.0La-10Cu (yellow), 1.5La-10Cu (light grey) and 2.0La-10Cu (light
 444 blue).

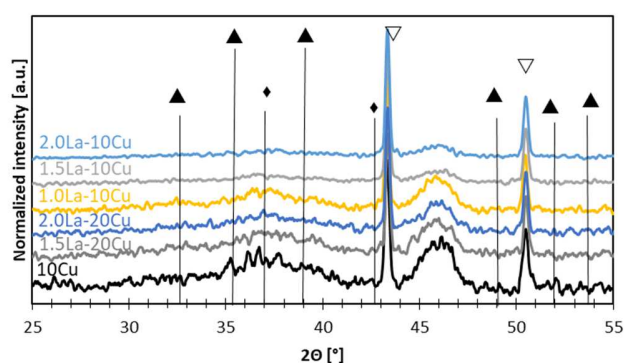
445 The 1,2-propanediol selectivity seemed to increase up to a La/Cu mass ratio of 0.088 (*i.e.* the 1.5La-
446 10Cu catalyst), see Figure 9C. The 2.0La-10Cu catalyst, which has the largest La/Cu mass ratio,
447 showed a lower 1,2-propanediol selectivity. The latter has almost the same total acidity compared
448 to the 1.5La-10Cu catalyst (Table SI.5) but exhibited different acid site distribution (Figure 5E). To
449 better understand this effect, Figure 9E depicts selectivity as a function acid sites introduced by the
450 Cu loading, *i.e.* the concentration of weak and moderate sites that exceed the ones of the bare
451 support (Table SI.5). It is clear that the increasing number of weak-moderate Cu acid sites
452 contributes to the increase in selectivity, where that is not the case for the support acid sites (Figure
453 SI.11A). It seems that the main difference between a pure Cu/Al₂O₃ and the La-Cu/Al₂O₃ catalysts is
454 attributed to the Lewis acidity of Cu⁺, as results of the La-Cu interactions. The weak-moderate Cu⁺
455 acid sites in La-Cu catalysts, enhanced glycerol conversion to acetol (Figure SI.11B), which is the rate
456 determining step[46], and consequently resulted in higher 1,2-propanediol selectivity.

457 A minor amount of 1,3-propanediol or degradation products, such as 1-propanol and 2-propanol,
458 were also observed over some catalysts (Table SI.8 till Table SI.13). For all catalysts, the undesired
459 C-C cleavage, forming 1,2-ethanediol was observed. The selectivity of 1,2-ethanediol was not
460 directly related to the number of strong acid sites (Figure SI.11C), which are generally assumed to
461 promote C-C cleavage. This could be related to the low selectivity towards the product and a higher
462 experimental error. However, the La-Cu catalysts exhibited an increase in 1,2-ethanediol selectivity
463 with increasing total number of acid sites per Cu⁰ site (Figure SI.11D). This indicates that for the
464 direct hydrogenolysis of glycerol to 1,2-ethanediol and methanol both an acid and a metal site are
465 required, rather than only a metal site.

466

467 3.2.2 Spent catalyst characterization

468 During reaction, the catalyst can undergo changes in particle size, oxidation state and morphology.
469 Therefore, the six investigated catalysts were also thoroughly characterized *post* reaction (68 h TOS).
470 The La-Cu catalysts are not subject to leaching (Table SI.14 *cf.* Table SI.2). From the XRD patterns of
471 the spent catalysts, shown in Figure 10, one can see that the CuO signal reappeared, especially in
472 the case of the 10Cu catalyst. This indicates that some amount of the Cu species reoxidized or some
473 CuO sintered during the reaction. Further, it can be observed that the diffraction peaks of Cu⁰ are
474 very sharp, indicating larger crystallite sizes.

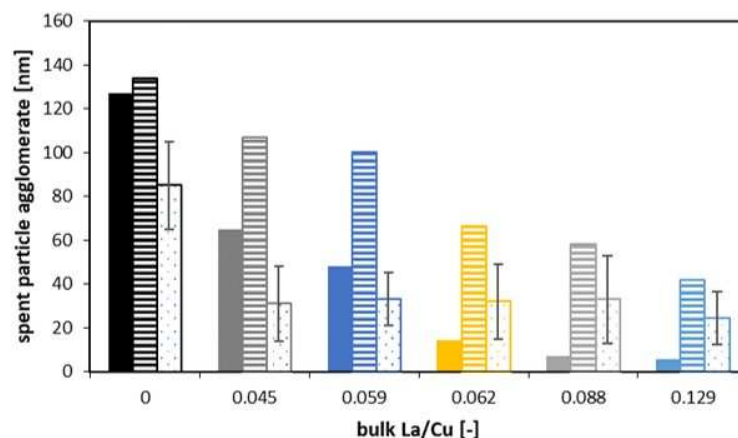


475

476 **Figure 10.** XRD pattern of the spent 10Cu (black), 1.5La-20Cu (dark grey), 2.0La-20Cu (dark blue), 1.0La-
477 10Cu (yellow), 1.5La-10Cu (light grey) and 2.0La-10Cu (light blue) catalyst with CuO (▲), Cu₂O (◆) and
478 Cu⁰ (▽).

479 Based on the Scherrer equation, Cu⁰ crystallites in the range of 50 to 150 nm were observed on
480 the spent catalyst, see Figure 11, but this size decreased with increasing La/Cu mass ratio. This trend
481 was also confirmed by dissociative N₂O adsorption on the spent catalysts. To investigate the
482 morphology of the spent catalysts, STEM images of the spent catalysts, without any pretreatment,
483 were made and a particle size distribution was determined (Figure SI.12). Based on dark-field STEM,
484 the stabilizing effect of La was evident. The effect of the promotor ratio was less straightforward to
485 interpret (Figure 11) as compared to other characterization method. Thus, La-promotion inhibited

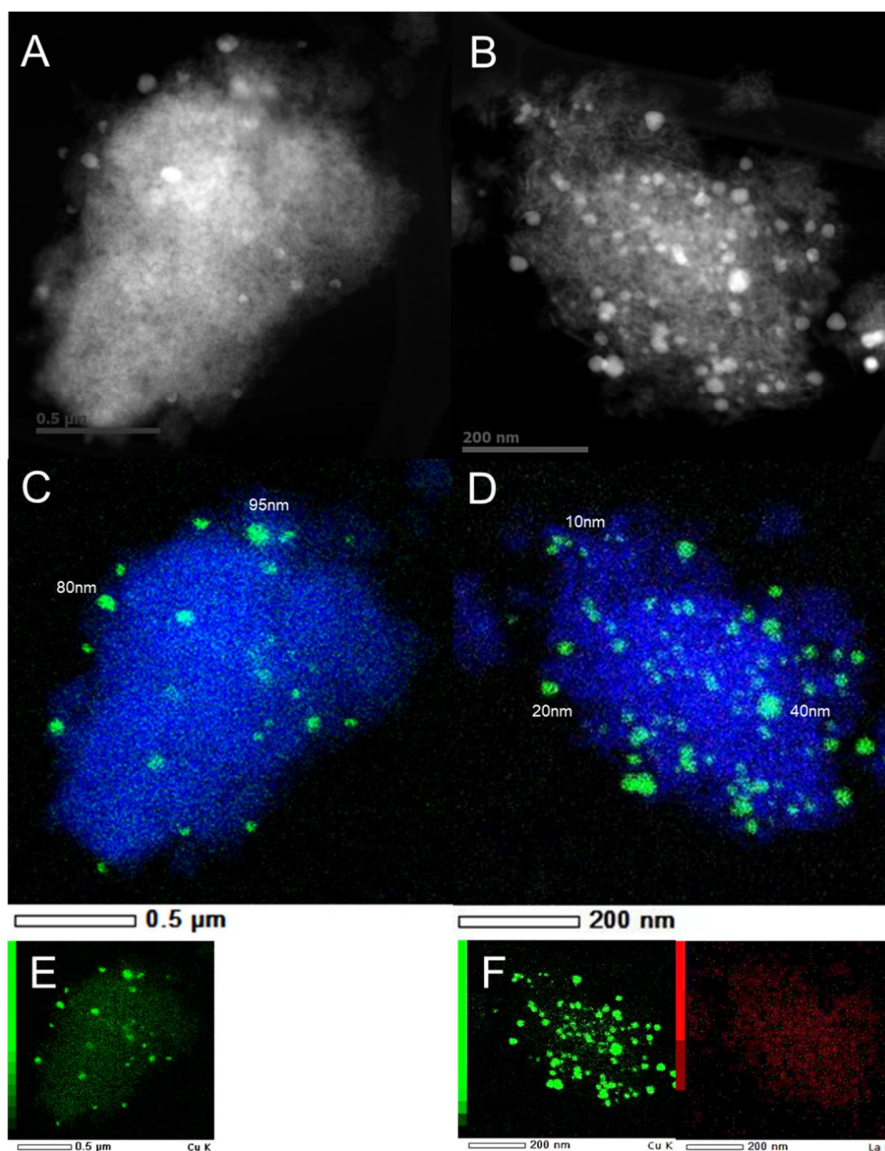
486 sintering of not only Cu^0 , but of all Cu species in the catalyst as it is impossible to distinguish different
487 oxidation states in STEM. As discussed in section 3.1.4, the La-Cu interactions also increased the
488 amount of Cu^+ species, reducing again the extent of Cu species sintering.



489

490 **Figure 11. Effect of La/Cu mass ratio on the spent Cu particle size, d_{Cu^0} , determined by dissociative N_2O**
491 **adsorption (full bars), Scherrer equation (striped bars) and STEM (dotted bars) of 10Cu (black), 1.5La-20Cu**
492 **(dark grey), 2.0La-20Cu (dark blue), 1.0La-10Cu (yellow), 1.5La-10Cu (light grey) and 2.0La-10Cu (light blue)**
493 **catalyst.**

494 Figure 12 shows the dark-field STEM images of the spent 10Cu and spent 1.0La-10Cu catalyst.
495 Whereas in the calcined (Figure SI.3) and reduced catalysts (Figure 4), Cu was highly dispersed, there
496 is a clear presence of large Cu particles after reaction. Notwithstanding that, a population of highly
497 dispersed Cu was still present, see Figure 15F. For the unpromoted catalyst, larger agglomerates
498 were observed (taking notice to the difference in scale between Figure 15E and F), while for the La-
499 Cu catalysts the majority of the Cu particles form agglomerates of *ca.* 20-30 nm (see Figure SI.12).



500

501 **Figure 12. Dark-field STEM image of spent 10Cu (A) and 1.0La-10Cu (B) catalyst. The corresponding EDX**
 502 **elemental map with the distribution of Al (blue), Cu (green) and La (red) is shown in C and D. The**
 503 **individual EDX maps of Cu and La are shown in E, corresponding to the dark-field image A, and in F,**
 504 **corresponding to the dark-field image B.**

505 The surface state of the spent Cu and La-Cu catalysts was probed by XPS. A small satellite peak
 506 between 942 and 944 eV was detected and ascribed to Cu^{2+} , see Figure SI.13, implying some
 507 reoxidation compared to the reduced catalysts, as was observed with XRD (Figure 10). The
 508 percentage of $(\text{Cu}^0 + \text{Cu}^+)$ present in the spent catalysts (Figure SI.14), increased with the La/Cu mass

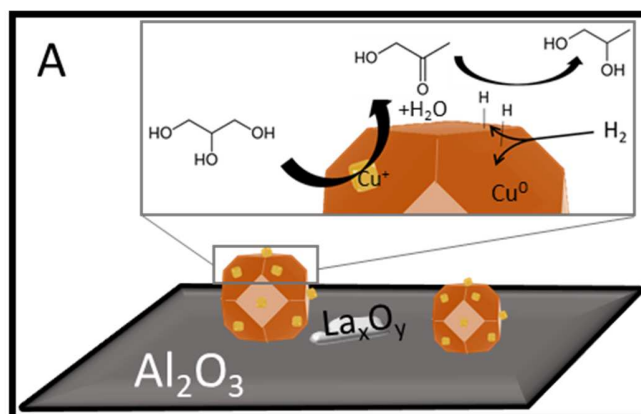
509 ratio. Due to the strong La-Cu interactions, it was assumed that Cu^+ was present on the surface of
510 the reduced catalyst, as discussed in section 3.1.5, and remained in the spent catalysts.

511 It is concluded that the La-Cu catalysts showed a better stability (see Figure 9A) as result of the
512 strong La-Cu interactions, which reduced the extent of Cu sintering.

513 **3.3 Proposed reaction mechanism over La-Cu/ γ - Al_2O_3 catalysts**

514 As mentioned in the introduction, the most accepted mechanism for the formation of 1,2-
515 propanediol is the dehydration-hydrogenation one. In the first step, glycerol is dehydrated over an
516 acid site, induced by the support, to acetol, while in the second step, these intermediates undergo
517 hydrogenation, which is catalyzed by a metallic site, to 1,2-propanediol. Combining the observed
518 characteristics and catalytic performance, our work allows to propose a more specific mechanism
519 for glycerol hydrogenolysis over La-Cu/ γ - Al_2O_3 . This mechanism, hypothesizes that Cu particles,
520 rather than the support, are the active sites for the dehydration to acetol. Figure 13 illustrates the
521 role of the different surface Cu species in this reaction mechanism.

522 As evidenced by STEM, both the La and Cu agglomerates are well dispersed in the reduced
523 catalysts. The Cu-loading affected mostly the size of the Cu^0 particles (1.3 – 5.5 nm). XPS indicated
524 the co-existence of Cu^0 and Cu^+ , as represented in Figure 14. At higher La/Cu mass ratios, more Cu^+
525 is available on the surface.



526

527 **Figure 13. Schematic representation of proposed role of La-Cu/ γ -Al₂O₃ in glycerol hydrogenolysis. (A) La-**
 528 **Cu/ γ -Al₂O₃ surface and the interaction between Cu⁺ and Cu⁰ in 1,2-propanediol formation.**

529 As shown in Figure 13, H₂ adsorbs dissociative on any Cu⁰ surface with the formation of two
 530 adsorbed hydrogen atoms. The adsorption of glycerol then occurs on Cu⁺, induced by the La-Cu
 531 interaction. It is assumed, inspired by the mechanism proposed by Alhanash *et al.*[39], that a
 532 primary hydroxyl group of glycerol interacts with the Cu⁺, which has Lewis acidity, and an O atom of
 533 Cu₂O abstracts a proton on the adjacent carbon. Cu⁺ weakens the electron density of the C-O
 534 bond[28, 87], accelerating its cleavage; yielding acetol and water by regeneration of the active site
 535 (dehydration). Finally, acetol reacts with two of the hydrogen atoms on the Cu⁰ surface, leading to
 536 the formation of 1,2-propanediol. An acid site in the proximity of a Cu⁰ site contributed to side
 537 product formation.

538 **4 Conclusions**

539 In this work, the effect of La-promotion on γ -Al₂O₃ supported Cu catalyst for glycerol
 540 hydrogenolysis towards 1,2-propanediol was assessed. Different promoter ratios were employed,
 541 leading to varying amounts of Cu⁺ and Cu⁰ species.

542 The La/Cu mass ratio had no significant effect on the textural properties (*e.g.* surface area, average
543 pore size and pore volume) of the calcined catalysts. After the reduction of the catalysts, Cu⁺ and
544 Cu⁰ co-existed. It was found that La/Cu mass ratio, affected the amount of Cu⁺ and consequently the
545 acid site distribution.

546 The activity seemingly decreased with promotion ratio, causing a tradeoff between stability and
547 activity. Sintering of the Cu particles occurred, but its extent was reduced by the presence of La
548 thanks to the La-Cu interaction. It was shown that product selectivity in glycerol hydrogenolysis on
549 La-Cu/Al₂O₃ catalysts depends on both acid and metal sites. The weak-moderate Cu⁺ acid sites in La-
550 Cu catalysts, rather than the support, enhanced the dehydration of acetol, and consequently to the
551 1,2-propandiol selectivity. The insights gained in this work provide a new view on the role of Cu⁺ and
552 therefore the complexity of glycerol hydrogenolysis. Additional *operando* characterization could
553 provide fundamental understanding of the glycerol conversion and facilitating rational catalyst
554 design.

555 **Acknowledgements**

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