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Selective dehydration of glycerol on copper based catalysts

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23 **Abstract**

24 Glycerol is produced in large quantities as a byproduct of biodiesel, and among others
25 hydroxyacetone (acetol) is an important commodity obtained from glycerol. Metallic Cu has
26 been identified as active site for the dehydration of glycerol to hydroxyacetone and acid and
27 metal sites are known to influence the catalytic performance.

28 In this study, dehydration of glycerol over 5 wt.% copper supported on γ -Al₂O₃, ZrO₂ and
29 SiO₂ was investigated. Catalysts were characterized by N₂ physisorption, H₂-TPR, NH₃-TPD,
30 N₂O chemisorption, XPS, XRD, FTIR of pyridine adsorption. Cu/ZrO₂ exhibited the highest
31 hydroxyacetone yield at 20% of glycerol conversion and the highest apparent reaction rate.
32 The superior activity of Cu/ZrO₂ was attributed to the highly acidic, both Lewis and Brønsted
33 acidic, nature of the support and positive roles of the interfacial sites. The Weisz-Prater (WP)
34 criterion was applied to confirm the absence of intraparticle diffusion limitations. It was
35 assumed spherical particles and first order reaction. The WP value obtained in the worst
36 scenario was less than 0.3 ensuring no diffusion limitation.

37 Complementary DFT study indicates that both glycerol and hydroxyacetone interact
38 significantly stronger on Cu/ γ -Al₂O₃ and Cu/ZrO₂ compared to metallic Cu, suggesting that
39 the active sites are at the interface of Cu particles and the acidic support.

40

41 *Key-words: Glycerol, Dehydration, Hydroxyacetone, Copper, Catalyst*

42

43 **1. Introduction**

44 Glycerol is a relevant bio-renewable compound for its increasing availability, since it is
45 produced in large quantities as a by-product during the transesterification of ester to obtain
46 biodiesel. The glycerol produced represents 10% of the total mass of the biodiesel production.
47 Glycerol is a compound of great importance already in our daily lives, e.g. in food industry,
48 due to its non-toxic nature [2], and it could become one of the most important building blocks
49 for chemical production in the biorefinery [1]. Related to the latter, a variety of catalytic
50 conversion routes to valorise the molecule, such as hydrogenolysis to propylene glycol [3],
51 catalytic reforming [4], cracking for the production of olefins and light parafins [5], oxidation
52 towards acids (dihydroxyacetone, tartronic acid, glyceric acid) [6], oligomerization,
53 polymerization towards glycerol monoesters [7], transesterification to monoglycerides [8],
54 dehydration to acrolein or hydroxyacetone [9], carboxylation to glycerol carbonate [10], have
55 been reported to date.

56

57 This work focuses on the selective dehydration of glycerol to hydroxyacetone.
58 Hydroxyacetone is an interesting building block due to its extremely reactive multifunctional
59 structure which contains hydroxyl and carbonyl functional groups. Particularly, it is an
60 attractive intermediate of 1,2-propanediol (1,2-PDO) which is used for the synthesis of resins,
61 liquid detergents, cosmetics, and pharmaceuticals and can be produced by hydrogenation of
62 hydroxyacetone. 1,2-PDO is currently produced from fossil fuel derived propylene oxide.
63 The catalytic process for the conversion of glycerol to 1,2-PDO requires external hydrogen
64 supply. The use of external H₂ has a negative impact to the process. Direct dehydration of
65 glycerol would form hydroxyacetone molecule without the need for hydrogen consumption

66 and under moderate conditions. Thus, the synthesis of 1,2-PDO from glycerol-derived
67 hydroxyacetone offers a greener production method of 1,2-PDO and is one of the attractive
68 paths for glycerol valorisation [3]. In addition, since hydroxyacetone is a highly reactive
69 molecule, it can be used as an intermediate in organic synthesis to produce other compounds
70 such as propionaldehyde, acetone and furan derivatives. Hydroxyacetone is a compound that
71 lacks toxicity, which justifies its use in the textile, pharmaceutical and food industries.
72 Furthermore, hydroxyacetone stands out as a key reagent for the production of lactic acid
73 which has acquired significant interest since it is considered one of the 12 best molecules of
74 the biological-based platform due to its wide potential applications in pharmaceutical and
75 food industry or as biodegradable plastics among others [11].

76

77 Conventionally, hydroxyacetone has been synthesized by several ways: (i) reaction of
78 bromoacetone with sodium or potassium formate (or acetate) followed by hydrolysis of the
79 ester with methyl alcohol; (ii) direct oxidation of acetone with the Bayer-Villegier reagent
80 [12]; (iii) dehydrogenation of aqueous propylene glycol in the presence of palladium-
81 catalyzed hydrogen peroxide [13]; (iv) biosynthetic pathway which involves metabolically
82 manipulated microorganisms using various substrates [14]. However, the presence of multi-
83 step reagents in stoichiometric quantities, the low yields and the effluent disposal costs
84 restrict the commercialization of any of these methods, thus the production of
85 hydroxyacetone from inexpensive and often-wasted bio-glycerol is beneficial for
86 environmental protection [9].

87

88 Sato *et al.* [15] investigated the dehydration of glycerol in the gas phase to hydroxyacetone
89 over Ag catalysts achieving 91% conversion of glycerol with 86% selectivity to
90 hydroxyacetone at 240°C under H₂ flow, however strong catalyst deactivation was observed.
91 Chiu *et al.* [16] studied the conversion of glycerol in gas phase to hydroxyacetone in a high-
92 pressure and high temperature semi-continuous reactor by reactive distillation over copper
93 chromite catalyst. They observed 22% glycerol conversion and 70% hydroxyacetone
94 selectivity. However, the toxicity associated to the Cr species in these catalysts and the
95 deactivation due to coke formation requires further catalyst development. It has been reported
96 that acidic sites have an important role in the glycerol dehydration and they can modulate the
97 yield towards hydroxyacetone. The presence of Brønsted acid sites is reported to favor the
98 dehydration of glycerol to acrolein, whereas Lewis acid sites promote the selective formation
99 of hydroxyacetone [17].

100

101 Copper is recognized for its intrinsic ability to break preferentially the C-O primary bond of
102 alcohols [18]. It is also suggested that copper oxide species act as Lewis acid sites to polarize
103 the C-O bond of glycerol [19]. This property of copper is of vital importance for obtaining
104 hydroxyacetone since this molecule is obtained by dehydration of any primary hydroxyl
105 group of glycerol. The support material is known to participate directly on the selective
106 dehydration. According to Sato *et al.* [1] the combination of an acid oxide support such as
107 Al₂O₃ to copper effectively promotes the selectivity to hydroxyacetone in the glycerol
108 conversion. This indicates that not only the copper species play an important role in the
109 dehydration but the Lewis acid sites of the support are also important for the formation of
110 hydroxyacetone. R. Mane *et al.* [9] investigated Cu-Al catalysts prepared by co-precipitation

111 and 24% glycerol conversion and 92% hydroxyacetone selectivity in the liquid phase were
112 observed with an aqueous solution of 20 wt.% of glycerol, 220 °C and in a N₂ atmosphere.

113

114 In addition, P. Hirunsit *et al.* [20] have reported selectivity higher than 90% towards 1,2-
115 PDO with copper catalysts supported on Al₂O₃. A. Bienholz *et al.* [21] reported for Cu/SiO₂
116 catalysts prepared by ammonia evaporation, 92% glycerol conversion and 69% selectivity to
117 hydroxyacetone in gas phase with an aqueous solution of 40 wt.% glycerol in a H₂
118 atmosphere in a fixed bed reactor. It should be added that Dasari *et al.* [3] have reported that
119 Raney copper has shown in the glycerol hydrogenolysis 69% selectivity towards 1,2-PDO
120 with 49% conversion at 200°C and H₂ pressure of 14 atm.

121

122 The results outlined above may indicate that copper alone can catalyze glycerol dehydration
123 and the support may facilitate copper species to be more active in the dehydration of glycerol.
124 The present work focuses on the study of the selective dehydration of glycerol towards
125 hydroxyacetone in aqueous phase on copper catalysts supported on materials with different
126 nature of acid properties. Particularly in the present work it will be studied the effect of the
127 total amount of acid sites; dispersion of copper species and the effect of three different
128 supports (SiO₂, γ -Al₂O₃ and ZrO₂) in the selective dehydration of glycerol to hydroxyacetone.

129 **2. Experimental**

130 *2.1 Catalyst preparation*

131 Cu/ γ -Al₂O₃ and Cu/ZrO₂ catalysts were prepared by incipient impregnation with a 5% mass
132 content of copper with respect to the weight of the support. The metal precursor was an
133 aqueous solution of Cu(NO₃)₂·3H₂O. After the impregnation step, the samples were kept
134 under hood at room temperature for 4 hours and finally dried at 120 °C for 24 hours. Once
135 dried they were calcined in a muffle with a heating ramp of 5 °C min⁻¹ from room temperature
136 to 400 °C for 4 hours. Cu/SiO₂ catalyst was prepared by ammonia evaporation method [22]
137 with a mass content of 5% of copper relative to the support. Briefly 25 wt.% ammonia
138 solution was added in an aqueous solution of Cu(NO₃)₂·3H₂O under vigorous stirring until it
139 reached pH 12. The resulting solution was heated to 80 °C maintaining this temperature until
140 it reached a pH of 6.0-7.0. The final product was filtered and washed with water, followed
141 by drying at 120 °C for 24 hours. It was then calcined in a muffle furnace with a heating ramp
142 of 5°C min⁻¹ from room temperature to 400 °C for 4 hours. Finally, prior to the reaction the
143 catalysts were reduced in a quartz reactor under H₂ flow at 50 mL min⁻¹ from room
144 temperature to 400 °C with a heating ramp of 5 °C min⁻¹ and then they were kept at 400 °C
145 for 4 hours.

146

147 *2.2 Catalyst Characterization*

148 The specific surface areas of the copper-based catalysts were measured with a Micromeritics
149 ASAP 2010 physisorption apparatus with N₂ at 77 K. BET and BJH methods were used
150 respectively for the calculation of the surface areas and pore characteristics (size distribution

151 and volume). Prior to the analysis, the samples (about 100 mg) were degassed for 4 hours at
152 120 ° C using N₂ as a carrier gas.

153 X-ray powder diffraction (XRD) measurements were conducted on a Bruker X-ray
154 diffractometer model D4 Endeavor (K α Cu, 40 kV and 20 mA) operating with 2 θ range of
155 20 - 90° at a scanning rate of 0.02° for 0.3 s.

156 FTIR spectra were collected using a FTIR-Vertex 70V instrument (Bruker) equipped with a
157 Harrick cell TM (powder, ca. 30 mg). Prior to pyridine adsorption experiments, the samples
158 were pre-treated at 400°C for 1 hour in hydrogen flow. The system was then cooled down to
159 reach 150 °C under helium flow. Pyridine vapor adsorption was performed at 150 °C (30
160 spectra, 1 spectrum per minute). Finally, pyridine desorption was monitored for 1 hour under
161 He flow at 150 °C from temperature ramping up (from 150 to 400 °C). Background spectra
162 were collected before pyridine adsorption.

163 Temperature programmed desorption of NH₃ (NH₃-TPD) experiments were performed in a
164 Micromeritics AutoChem II 2920 automatic equipment. Prior to the experiments, the
165 catalysts (about 100 mg) were reduced at 400 °C for 120 min in 10% H₂/Ar at 20 mL min⁻¹,
166 and after the reduction samples were cooled to 35 °C under the same flow. Then catalysts
167 were treated with NH₃ (20 mL min⁻¹) for 10 min at 40 °C. Thus, the samples were treated in
168 He flow (50 mL/min) to purge the system. Finally, the NH₃ desorption was carried out by
169 heating the reactor with a temperature ramp of 5 °C min⁻¹ in a flow of He (20 mL min⁻¹). A
170 trap of water, ice and NaCl salt was used. The NH₃ consumption has been determined by a
171 thermal conductivity detector (TCD).

172 The amount of surface copper atoms was measured on the samples (about 100 mg) initially
173 reduced in hydrogen flow of 50 mL min⁻¹ at 400 °C. The reduced samples were cooled in He
174 flow (50 mL/min) to 60 °C and purged for 30 minutes. 20% N₂O/Ar gas was added for
175 1 hour. The selective oxidation of the copper surface to Cu₂O was performed under 20%
176 N₂O/Ar flow (50 mL min⁻¹) at 60 °C:

177



179

180 The system was then cooled to room temperature in He flow (50 mL min⁻¹) to eliminate the
181 physisorbed species of N₂O. Cu₂O_{surface} was further reduced with 5% H₂/Ar flow (50 mL min⁻¹)
182 by raising the temperature at 5 °C min⁻¹ from room temperature to 900 °C. The H₂
183 consumption was followed by TCD detector.

184



186

187 VG Escalab 200R spectrometer equipped with a hemispherical electron analyser and an Mg
188 K α (h ν =1253.6 eV, 1 eV=1.603 $\times 10^{-19}$ J) was employed for X-ray photoelectron
189 spectroscopy (XPS) measurements. The X-ray source operated at 10 mA and 12 kV. The
190 spectrometer chamber pressure during data acquisition was maintained at 1 $\times 10^{-7}$ Pa. The
191 peaks were fitted by a non-linear least square fitting program using a properly weighted sum
192 of Lorentzian and Gaussian component curves after background subtraction. The constant
193 charging of the samples was corrected by referencing all energies to the Al 2p peak at
194 74.5 eV.

195 *2.3 Catalytic Activity*

196 Dehydration of glycerol was studied in a 300 mL batch reactor with a content of 60 mL of
197 reaction mixture with an aqueous solution of 80 wt.% of glycerol, 500 mg of catalyst which
198 corresponds to a glycerol/Cu molar ratio of 1000. The reaction was carried out for 3 hours
199 under a constant stirring of 800 rpm and temperature of 190 °C. The reaction was performed
200 under N₂ atmosphere.

201 The reaction products were analysed at different reaction time by an autosystem XL gas
202 chromatograph equipped with an FID detector and Nukol Capillary column (30 m long, 0.53
203 mm internal diameter and 0.5 µm film space) with He as a carrier gas. The products were
204 also analysed with a gas chromatograph coupled to a mass spectrometer. The glycerol
205 conversion and product selectivity were calculated according to:

206
$$\text{Conversion (\%)} = \frac{(\text{moles of glycerol reacted})}{(\text{initial moles of glycerol})} \times 100 \quad (3)$$

207

208
$$\text{Product } i \text{ selectivity (\%)} = \frac{(\text{moles of } C \text{ in the product } i)}{(\text{moles of } C \text{ in the initial quantity of glycerol})} \times 100$$

209 (4)

210 To ensure the absence of intra-particle diffusion resistance the Weisz-Prater (WP) parameter
211 was calculated. According to WP criteria, if WP (φ) \leq 0.3 the internal diffusion resistance
212 can be neglected for a heterogeneous reaction. Where φ is:

213
$$\varphi = \frac{-r_{obs}\rho_c R_p^2}{D_e C_{AS}} \quad (5)$$

214

215 Where, $-r_{obs}$ = the observed rate ($\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$), ρ_c = solid catalyst density = 2.08 g.cm^{-3} , R_p =
 216 catalyst particle radius = 0.0025 cm , C_{AS} = concentration of glycerol at catalyst surface =
 217 $0,001 \text{ mol cm}^{-3}$. D_e is the effective diffusivity of glycerol to water ($2.11 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and:

$$218 \quad D_e = \frac{D_{AB} \phi \sigma}{\tau} \quad (6)$$

219 Where ϕ = porosity pellet = 0.42 , σ = constriction factor = 0.8 and τ = tortuosity = 3 [23, 24]
 220 and D_{AB} = diffusion coefficient of glycerol to water at $250 \text{ }^\circ\text{C}$ = $1.85 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ calculated
 221 by Wilke-Chang Equation:

$$222 \quad D_{AB} = \frac{1.173 \times 10^{-13} (\phi M_B)^{0.5} T}{\mu V_A^{0.6}} \quad (7)$$

223 Where ϕ is the factor for solute-solvent interaction; Temperature (K); V_A = molar volume of
 224 solute at boiling point (glycerol), M_B = molecular weight of solvent (water) and μ is the
 225 solvent viscosity.

226

227 Finally $-r_{obs}$ is:

$$228 \quad -r_{obs} = \frac{n}{V \times m_{cat} \times t} \quad (8)$$

229 Where n = moles of glycerol reacted, V = volume in L, m_{cat} = catalyst weight in g and t =
 230 reaction time in minutes.

231

232 *2.4 Computational Details*

233 The Cu(111) surface model was constructed with a supercell of 4×4 containing 4 layers of
 234 metal atoms and a vacuum region $\sim 15 \text{ \AA}$. The two atomic layers from the bottom of the slab
 235 were fixed, while the top two layers were relaxed to their lowest energy configurations. The
 236 fixed layers were set to Cu bulk bond distances according to the optimized lattice constant

237 that was determined from bulk calculation. The slab model of γ -Al₂O₃(110) surface contains
238 thirty two Al₂O₃ molecular units and ~15 Å of the vacuum region. The (110) crystalline
239 surface was chosen because it dominates in γ -alumina nanocrystallites (~70-83% of total
240 area) [25, 26]. Twelve of Al₂O₃ molecular units located in atomic layers from bottom of the
241 slab were fixed and the rest were relaxed including the Cu₁₃ cluster and adsorbates. The fixed
242 layers were set to γ -Al₂O₃ bulk bond distances in which the γ -Al₂O₃ bulk model structure was
243 taken from references [25, 27]. The tetragonal ZrO₂ bulk structure was applied followed the
244 experimental observation. The slab model of most stable ZrO₂(111) surface was modeled
245 with total thirty nine molecular units and ~15 Å of the vacuum region excluding adsorbates.
246 Seventeen ZrO₂ molecular units from the bottom of a slab were fixed and the rest were
247 relaxed including Cu₁₃ cluster and adsorbates. The structures of bare Cu(111), Cu₁₃/ γ -
248 Al₂O₃(110) and Cu₁₃/ZrO₂(111) are shown in Fig. S5 of supporting information.

249 The initial geometries of isolated Cu₁₃ cluster were modeled based on the possible M₁₃
250 nanoparticle structures reported in previous studies [28, 29]; icosahedral (ICO), face centered
251 cubic (FCC), hexagonal close packed (HCP), capped cubic (CC), buckled biplanar (BBP),
252 triangular biplanar (TBP), and cage-like (CAG). The two most stable structures of isolated
253 Cu₁₃ cluster structures were found to be ICO and BBP (Fig. S4 of supporting information).
254 Then, the optimized ICO and BBP Cu₁₃ clusters were initially placed on the γ -Al₂O₃(110)
255 and ZrO₂(111) surfaces with variations of location on the surfaces and orientations of the
256 Cu₁₃ clusters. The most stable structures found for Cu₁₃/Al₂O₃(110) and Cu₁₃/ZrO₂(111) (Fig.
257 S5 of supporting information) were then applied for glycerol and hydroxyacetone adsorption
258 study. The 13-atom Cu cluster model can represent small particle size (~ 1nm) which has an
259 average number of metal atoms in the range 11-14 atoms. The models present Cu-Cu and

260 Cu-support interaction. Cu_{13} cluster were widely applied to study catalytic reaction such as
261 CO oxidation and ammonia decomposition [30-32]. It should be noted that the copper particle
262 size and shape can affect the reactivity as well which may be due to the variation of the
263 amount of low coordinated defect sites. The supported metal-13 cluster on support such as γ -
264 Al_2O_3 surface also were previously employed to study NO oxidation [33], H_2 dissociation
265 [34], the nature of the metal-support interaction [35], and stability of clusters on support [36].

266 Hydroxyl are created and adsorbed on Al_2O_3 and ZrO_2 surfaces due to the adsorption of water
267 which is a product of glycerol dehydration [25, 37]. The effect of hydroxylation on the
268 supports were also investigated. The relationship between the hydroxyl coverage on γ -
269 $\text{Al}_2\text{O}_3(110)$ surface and temperature has been investigated previously by Digne *et al.*[25]
270 Applying this relationship, the OH coverage on γ - $\text{Al}_2\text{O}_3(110)$ surface corresponding to the
271 experimental temperature in the range of 130-230 °C is approximately 3.0-11.8 OH nm⁻².
272 The approximately 4.5 OH nm⁻² coverage corresponding to 4 H₂O molecules on the γ -
273 $\text{Al}_2\text{O}_3(110)$ and $\text{ZrO}_2(111)$ surfaces were employed in this work. The hydroxyl group
274 adsorption was particularly located nearby the copper cluster model in order to bring in the
275 effect of hydroxylation on the dual roles of support and copper cluster.

276 The Vienna *ab initio* Simulation Program [38, 39] was employed to perform fully periodic
277 plane-wave density functional theory (DFT) calculations. Spin-polarized DFT calculations
278 were performed using the GGA-PBE functional [40] implemented with the Projector
279 Augmented Wavefunction (PAW) [41, 42] method for representing the non-valence core
280 electrons. The long-range dispersion force was included using the semi empirical dispersion
281 potential correction method described by Grimme and coworkers [43, 44]. The plane-wave
282 energy cutoff was optimized at 450 eV. The Gaussian broadening [45] with a smearing width

283 of 0.1 eV was employed. The dipole correction was included only in z direction and the
 284 surface Brillouin zone was sampled with a $2 \times 2 \times 1$ Monkhorst-Pack k-point mesh [46] for all
 285 surface calculations. The results were checked for convergence with respect to energy cutoff
 286 and number of k-points. The convergence criterion for electronic self-consistent iteration was
 287 set to 10^{-7} eV and the ionic relaxation loop was limited for all forces smaller than 0.030 eV
 288 \AA^{-1} for free atoms. Bader charge analysis was performed using VASP-VTST [47–49].

289

290 **3. Results**

291 *3.1 Catalyst characterization*

292 The textural properties of the supports and copper catalysts are summarized in Table 1 and
 293 Fig. 1. Specific area (S_{BET}), pore volume (V_{pore}) and pore diameter (d_{pore}) of the catalysts
 294 decrease compared to their supports due to the introduction of copper, indicating a partial
 295 blockage of the pores. ZrO_2 and SiO_2 exhibited the smallest and the highest specific surface
 296 area, respectively.

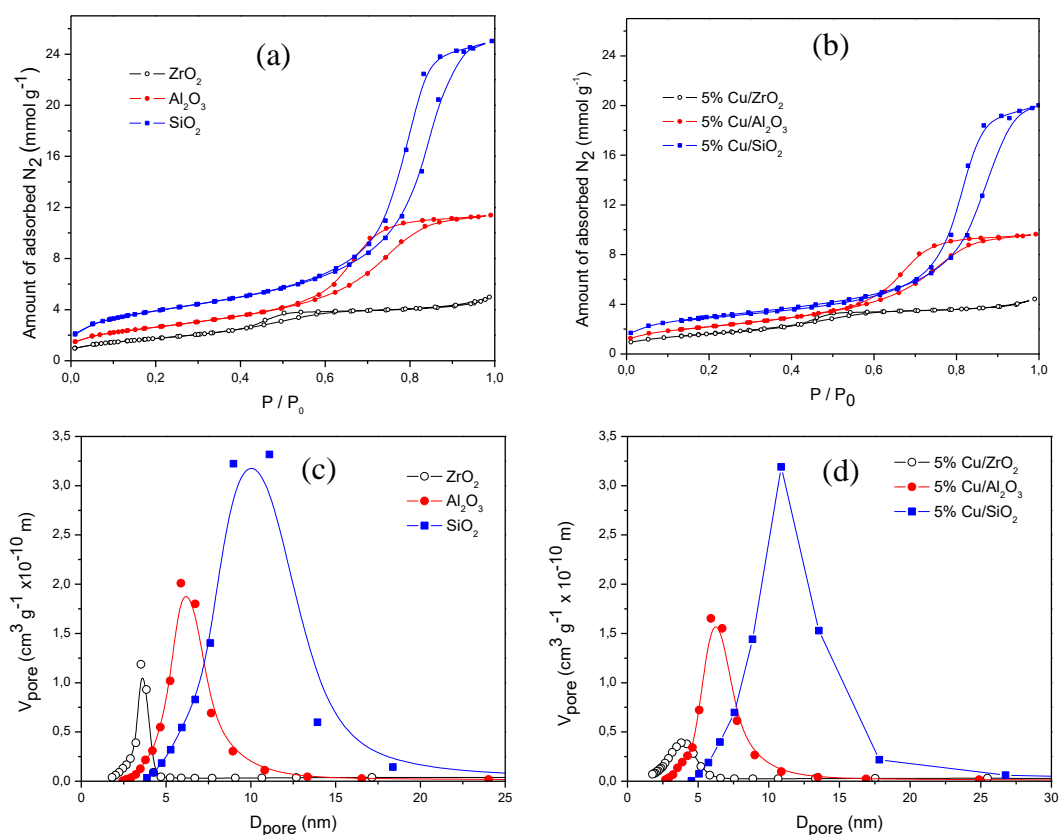
297

298 Table 1. Textural parameters of supports and copper catalysts.

299	Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{Pore} ($\text{cm}^3 \text{g}^{-1}$)	d_{pore} (nm)
300	ZrO_2	146	0.17	4.3
301	$\gamma\text{-Al}_2\text{O}_3$	212	0.39	7.4
302	SiO_2	319	0.85	10.6
303	5% Cu/ ZrO_2	131	0.13	4.0
304	5% Cu/ $\gamma\text{-Al}_2\text{O}_3$	181	0.34	7.5
305	5% Cu/ SiO_2	244	0.70	11.6

306

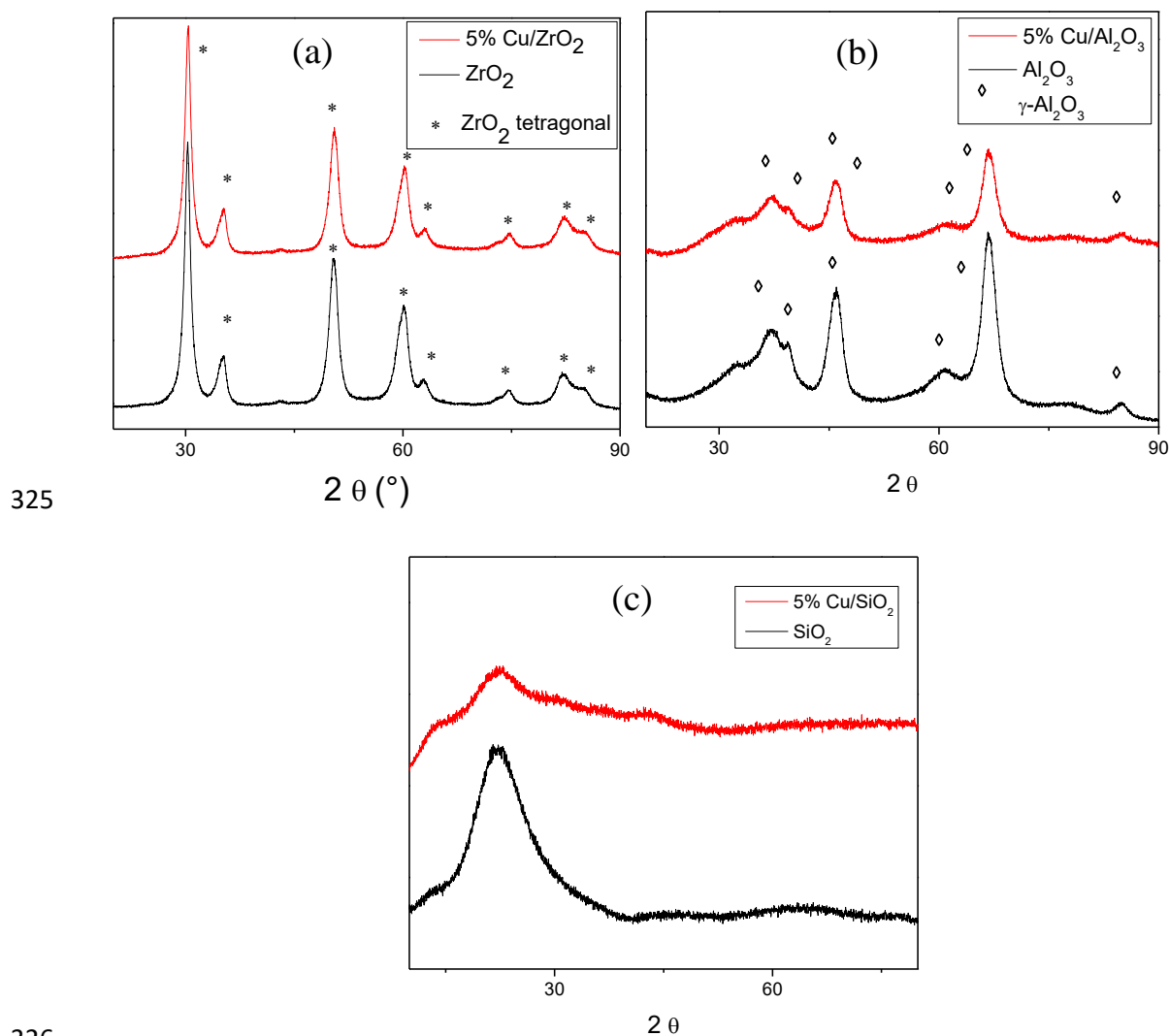
307 Fig. 1a shows N₂ sorption isotherms of the supports and Cu catalysts. Isotherms displayed a
 308 type-IV curves characteristic of mesoporous structure [50]. For SiO₂-based materials a H1-
 309 type hysteresis loop corresponding to uniform spherical pores from a regular matrix of pore
 310 size distribution centered at 10-12 nm (Fig. 1b) was found. For materials based on γ -Al₂O₃
 311 and ZrO₂ a H2-type hysteresis loop and pore size distribution centered at 4 and 7 nm were
 312 found, respectively.



313
 314 Fig. 1. (a) and (b) N₂ adsorption-desorption at 77 K and (c) and (d) Pore size distribution.

315
 316 By XRD, diffraction peaks only due to the support materials (Fig. 2) were found for all
 317 samples. Copper species are expected to exhibit reflection peaks as follows: metallic copper
 318 (Cu⁰) at 2 θ = 43, 50 and 74 ° (JCPDS 04-0836), copper (II) oxide (CuO) at 2 θ = 32.6, 35.6,

319 38.6, 48.8, 53.6, 58.3, 61.6, 66.4, 68.1, 72.3 and 75.1 ° (JCPDS 48-1548) and copper (I) oxide
320 (cuprous oxide, Cu₂O) at 2θ = 36.4, 42.3 and 61.3 ° (JCPDS 05-0667). The absence of the
321 reflection peaks due to copper species indicates their high dispersion. At 7 wt.% of copper it
322 is reported to be possible to identify Cu peaks in the XRD analysis [51]. Previous work
323 reported that the highly crystalline CuO is formed from approximately 4 wt.% of Cu for 100
324 m² g⁻¹ of γ-Al₂O₃ [52].



326

327 Fig. 2. Powder XRD patterns of (a) ZrO₂ (b) γ-Al₂O₃ and (c) SiO₂ materials.

328

329 Only tetragonal zirconia (no monoclinic) patterns were observed in ZrO₂-based materials
 330 (Table 2). For the materials based on γ -Al₂O₃ the presence of characteristic peaks of the
 331 support (JCPDS 029-0063) was observed at $2\theta = 31.9, 37.6, 39.5, 45.8,$ and 66.7° . X-ray
 332 diffraction reveals the amorphous nature of SiO₂.

333

334 Table 2. XRD pattern of monoclinic (JCPDS 37-1484) and tetragonal ZrO₂ (JCPDS 17-
 335 0923).

Monoclinic ZrO ₂		Tetragonal ZrO ₂	
2θ (°)	Crystallographic plane	2θ (°)	Crystallographic plane
24.2	(0,1,1)	30.1	(1,1,1)
28.2	(1,1,0)	35.2	(2,0,0)
31.4	(0,2,0)	50.4	(2,2,0)
34.3	(1,2,1)	59.9	(3,1,1)

336

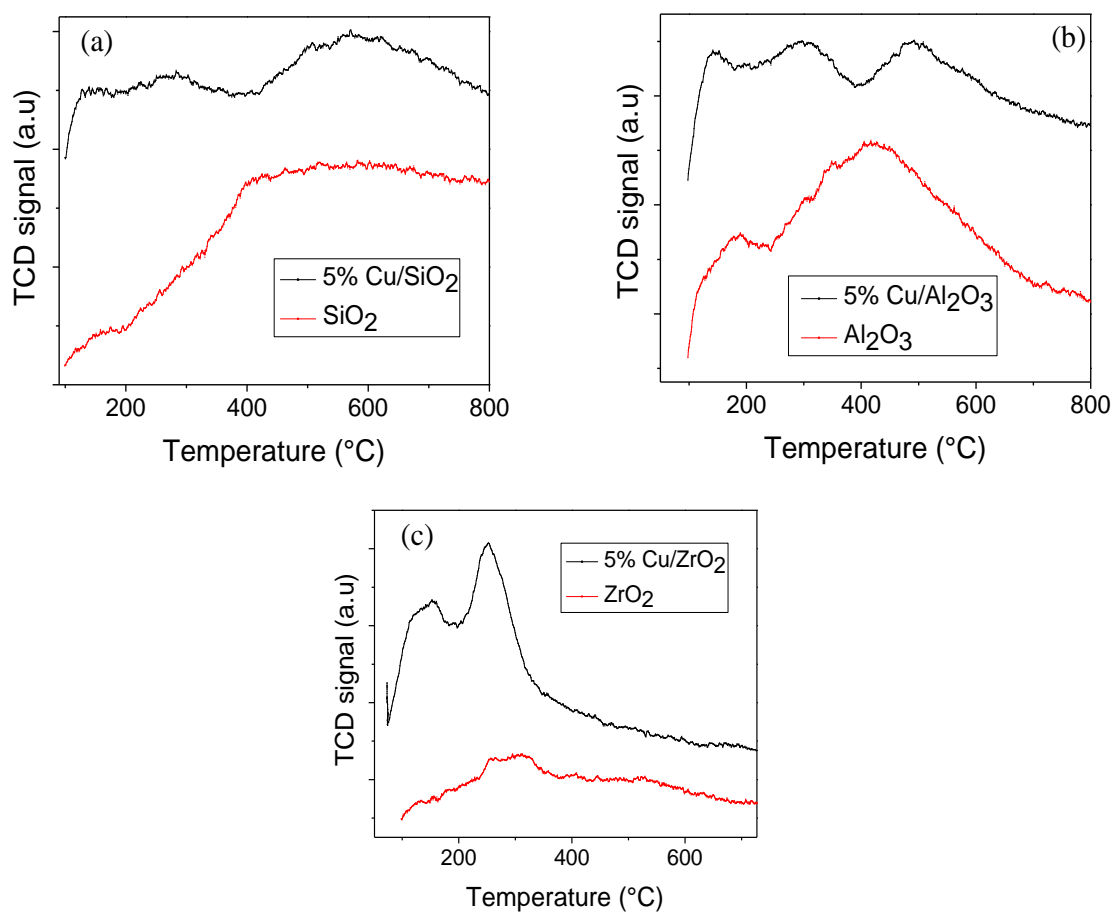
337 The evaluation of acidity of the support and catalyst materials by NH₃-TPD (Table 3 and Fig.
 338 3) showed an increase of the total acidity for the catalysts containing copper species. Cu/ZrO₂
 339 has the highest acidity ($867 \mu\text{mol g}_{\text{cat}}^{-1}$) in contrast to Cu/SiO₂ that presented the lowest total
 340 amount of acid sites ($187 \mu\text{mol g}_{\text{cat}}^{-1}$).

341 Table 3. Quantitative analysis of NH₃-TPD data of ZrO₂, γ -Al₂O₃ and Cu-based catalysts.

Sample	Total NH ₃ amount	
	($\mu\text{mol g}_{\text{cat}}^{-1}$)	($\mu\text{mol m}^{-2}$)
ZrO ₂	360	-----
γ -Al ₂ O ₃	280	-----
5% Cu/ZrO ₂	867	6.6
5% Cu/Al ₂ O ₃	591	3.3
5% Cu/SiO ₂	187	0.8

342

343 ZrO₂ support showed a signal with a maximum at 270 °C and a tail-like broad desorption
344 extending to approximately 630 °C, indicating a wide distribution of the strength of the acid
345 sites ranging from moderate (considered from 200-450 °C) to strong (> 450 °C) ones. The
346 Cu/ZrO₂ catalyst also exhibited a wide distribution of acid sites with different acid strengths
347 and the total amount of acid sites that increases with the introduction of copper species. This
348 could be attributed to the contribution of copper oxide species. Similarly, a heterogeneous
349 distribution of acid sites for the γ -Al₂O₃ system is highlighted. A minor or negligible total
350 amount of acid sites in the SiO₂ support was found.



351

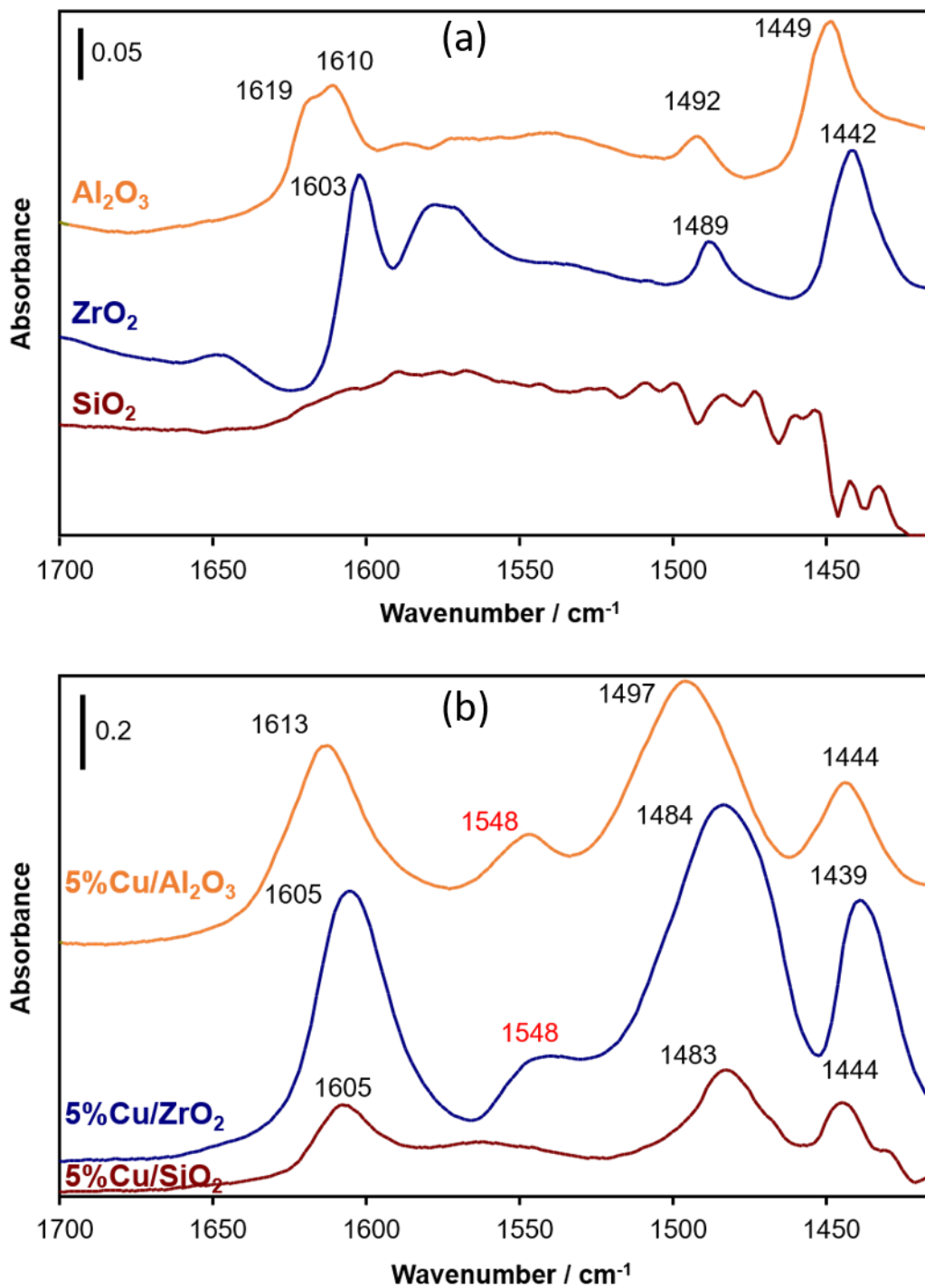
352 Fig. 3. Temperature-programmed desorption of ammonia profiles of supports and Cu-based
353 catalysts (a) SiO₂ and 5%Cu/SiO₂, (b) Al₂O₃ and 5%Cu/Al₂O₃ and (c) ZrO₂ and 5%Cu/ZrO₂.

354

355 Brönsted and Lewis acidity were identified by FTIR of pyridine as shown Fig. 4. The IR
356 spectra of the support materials and supported copper catalysts were compared in the region
357 of 1600-1400 cm⁻¹. From the IR spectra only Lewis acid sites were identified over the support
358 materials. The IR spectra of the supports (γ -Al₂O₃ and ZrO₂) show bands at about 1455, 1490
359 and 1610 cm⁻¹ after pyridine desorption at 400 °C. The band observed at 1455 cm⁻¹ is attributed
360 to the presence of hydrogen-bonded pyridine adsorbed on Lewis acid sites [53]. The observed
361 band at 1610 cm⁻¹ is ascribed to pyridine strongly bound on Lewis acid sites [54]. The band
362 observed at about 1490 cm⁻¹ is attributed to pyridine adsorbed on both Lewis and Brönsted
363 acid sites. There is no evidence for a band at about 1610 cm⁻¹ (Fig. 4) in the infrared spectra
364 of pyridine desorption on SiO₂. In addition, there is no evidence for a band at 1540 cm⁻¹
365 suggesting no Brönsted acidity for SiO₂ sample in agreement with literature [55]. It must be
366 added that the absence of the band at 1490 cm⁻¹ suggests negligible Lewis acidity in SiO₂
367 support.

368

369 Supported copper catalysts were reduced at 400 °C in hydrogen prior the pyridine
370 measurements. Impregnation of copper on ZrO₂, γ -Al₂O₃ and SiO₂ resulted in the appearance
371 of Lewis and Brönsted acid sites. The bands corresponding to Brönsted acid sites were
372 observed at 1548 cm⁻¹ for copper supported on γ -Al₂O₃ and ZrO₂ [56]. In contrast, Cu/SiO₂
373 catalyst exhibited only Lewis acid sites.



374

375 Fig. 4. FTIR of (a) supports and (b) catalyst after pyridine desorption at 400 °C.

376

377 TPR profiles of the calcined copper catalysts at 400 °C are shown in Fig. 5. Cu/SiO₂ catalyst
378 exhibits a nearly symmetrical reduction peak at ca. 200 °C. For Cu/Al₂O₃ catalyst, the main
379 reduction peak is also centred at ca. 200 °C. It is observed that the catalysts Cu/SiO₂ and
380 Cu/Al₂O₃ have an reductive event at the same temperature which suggests a homogeneous
381 copper species distribution and the corresponding reduction refers to Cu⁺²→Cu⁰ [57].

382

383

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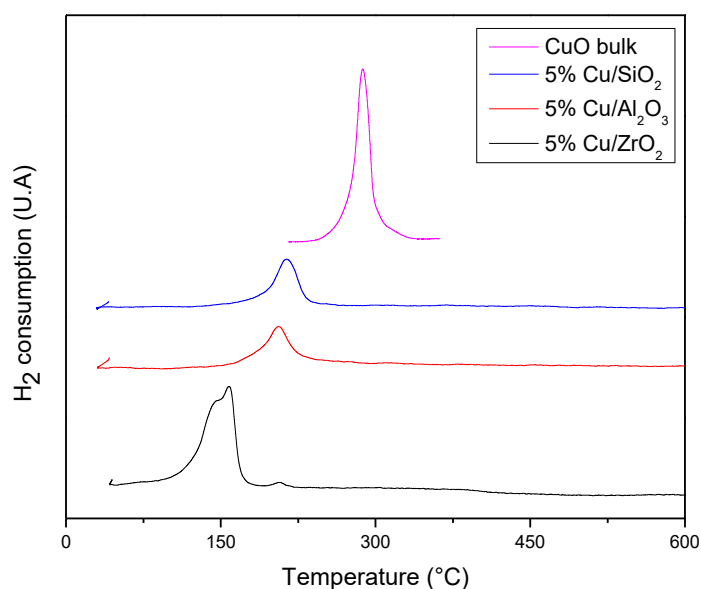
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390



391

392

Fig. 5. TPR of copper based catalysts.

393

394 For Cu/ZrO₂ sample the main reduction peak shifts to lower temperature at ca. 160°C and
395 presents a shoulder peak at ca. 140°C. Liu *et al.* [58] observed two overlapping peaks with
396 apparent maxima at 140°C and 160°C for the reduction of copper supported on tetragonal
397 zirconia. According to these authors, these peaks correspond to highly disperse Cu⁺² species
398 assigning the first peak to the reduction of Cu⁺² →Cu⁺¹, followed by a second event to Cu⁺¹
399 →Cu⁰. The reduction profile of Cu/ZrO₂ sample suggests a strong influence of the support

400 on the reduction of copper species. A shift towards lower temperatures with respect to the
401 other two supports (γ -Al₂O₃ and SiO₂) is observed. This is attributed to promoter effects of
402 ZrO₂ in the reducibility of copper species. It must be added that only a minor reduction peak
403 at 200⁰C was visible for Cu/ZrO₂. This peak can be attributed to the reduction of bulk CuO
404 [59]. The low reduction temperature strongly suggests the presence of finely dispersed copper
405 species embedded homogeneously in the ZrO₂ support. The higher reduction temperature
406 peak is assigned to the reduction of CuO crystallites [60].

407

408 The existence of vacancies on the surface of the support is a vital factor in achieving
409 dispersion of ionic species [61]. Cu⁺² species can be located at surface vacancies of ZrO₂
410 leading to a high dispersion of copper. These species are responsible for the low temperature
411 reduction peaks. Previous work reports a dispersion capacity of 8.6 ions of Cu⁺² per nm² of
412 ZrO₂. Loads of copper species higher than this dispersion capacity of ZrO₂ will result in the
413 formation of Cu⁺² ions being gradually surrounded by other Cu⁺² ions forming CuO bulk
414 species leading to an increase of the reduction temperature of these species [58]. Bulk CuO
415 exhibits a broad TPR peak at ca. 300°C (Fig. 5).

416

417 γ -Al₂O₃ is also able to stabilize Cu⁺² due to the existence of tetrahedral and octahedral
418 vacancies on its surface [62], while SiO₂ is not able due to its structurally saturated surface.
419 Previous work [63] reported the formation of bulk CuO modulated in terms of the ratio
420 Cu/SSA or “copper charge/specific support area (SSA)” of 4.5 atoms of Cu per nm² of ZrO₂
421 support. Considering that the ZrO₂ used in our work has a specific surface area of 146 m² g⁻¹
422 ¹ the appearance of bulk CuO would occur approximately in copper charges of 7 wt.%. In

423 addition, considering that the γ -Al₂O₃ used in our work has a specific surface area of 212 m²
 424 g⁻¹ it can be expected that the formation of CuO species would begin to appear with copper
 425 loading close to 10 wt.%. The detection of CuO bulk species in the XRD profiles (Fig. 2) is
 426 somewhat difficult.

427

428 Dispersion on metallic copper and the specific copper surfaces of the catalysts were
 429 determined by chemisorption of N₂O. Cu/ZrO₂ shows the highest dispersion with 38% and
 430 the largest metallic surface area of Cu⁰ (Table 4). Although ZrO₂ has the smallest specific
 431 surface it is able to disperse substantial amount of impregnated copper species due to the
 432 strong interaction between copper species and support [64]. Cu/SiO₂ shows a significantly
 433 lower copper dispersion and specific copper surface of the catalysts which are more likely
 434 due to a more intense sintering of copper particles.

435

436 Table 4. Catalysts characterization by N₂O chemisorption

Parameter \ Catalyst	5%Cu/SiO ₂	5%Cu/ γ -Al ₂ O ₃	5%Cu/ZrO ₂
N ₂ O (μ mol N ₂ O g _{cat} ⁻¹)	203	277	301
Dispersion (%)	26	35	38

437

438 XPS parameters from the reduced copper catalysts are summarized in Table 5 and Fig. 6.

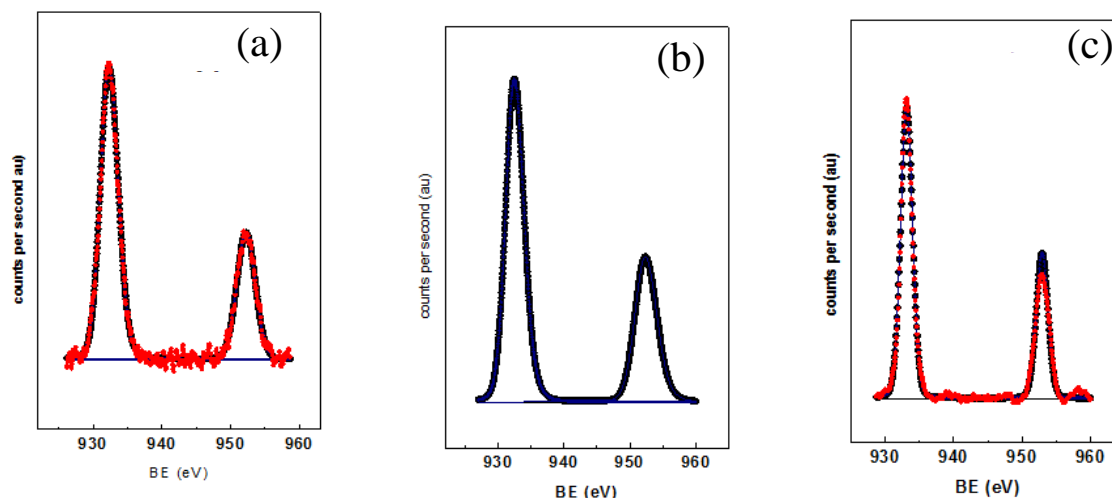


Fig. 6. XPS of (a) 5%Cu/SiO₂, (b) 5%Cu/Al₂O₃ and (c) 5%Cu/ZrO₂.

439

440

441 All reduced catalysts exhibited symmetrical Cu3p_{3/2} and Cu2p_{1/2} peaks with binding energies
 442 between 932.5 and 952.4 eV respectively. A satellite was not detected at approximately 942
 443 eV suggesting absence of Cu⁺² species [65]. Because the binding energies of Cu⁰ and Cu⁺
 444 are similar it is difficult to differentiate them based only on Cu3p_{3/2}, so we used the modified
 445 Auger parameter (α Cu) for further conclusions.

446

447 Table 5. Binding energies (eV) of internal levels, Auger parameter and atomic ratios of
 448 supported copper catalysts

Catalyst	Cu2p _{3/2}	M2p or M3d	α Cu (Auger)	Cu/M ^a atomic ratio
5%Cu/ZrO ₂	932.5	182.2	1850.9	0.016
5%Cu/Al ₂ O ₃	932.5	74.5	1851.0	0.021
5%Cu/SiO ₂	932.4	103.4	1850.8	0.027

449

450 The value of α_{Cu} at approximately 1851.0 eV for reduced copper catalysts suggests that the
451 copper species may prevail on the catalyst surface as Cu° . The value of the atomic surface
452 ratio Cu/M (M=Al, Si, Zr) determined via XPS for the reduced samples increases in the
453 following order: $\text{Cu}/\text{ZrO}_2 < \text{Cu}/\gamma\text{-Al}_2\text{O}_3 < \text{Cu}/\text{SiO}_2$. The difference in the distribution of
454 copper species on each support can be tentatively identified with the Cu/M surface atomic
455 ratio value. In this case, a lower Cu/M suggests a more homogeneous distribution of copper
456 species on ZrO_2 support in agreement with the aforementioned results via XRD (Fig. 2), TPR
457 (Fig. 5), chemisorption of N_2O (Table 4).

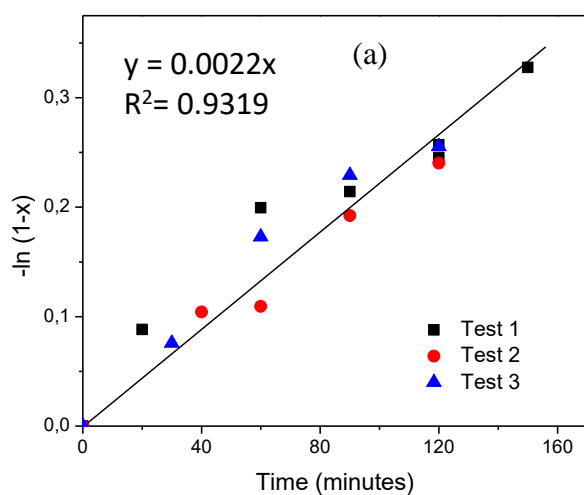
458

459 *3.2 Catalytic activity*

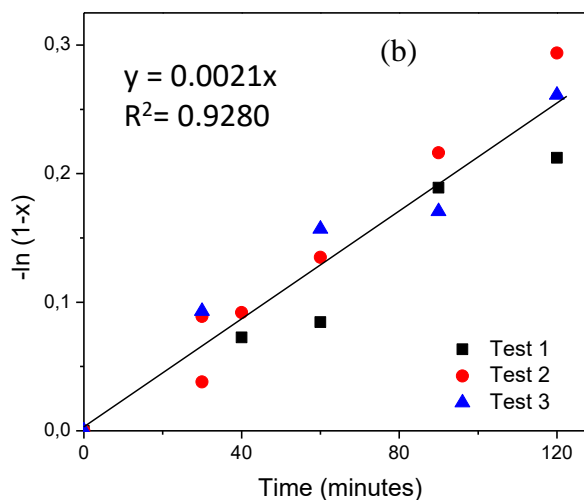
460 Glycerol conversion profile in the first 120 minutes of reaction was used to determine the
461 kinetic parameters such as the reaction order (n) and the apparent kinetic constant (k) values
462 expressed in terms of $\text{min}^{-1} \text{m}_{\text{cat}}^{-2}$. The first 120 minutes have been studied in order to ensure
463 the evaluation of the catalytic performance under conditions where the reaction is kinetically
464 controlled and there is a minimization of the influence of possible product-catalyst
465 interaction. Moreover, for the determination of the kinetic constant an isothermal process;
466 constant volume of the reaction medium and absence of mass transfer effect have been
467 considered. The Weisz-Prater (WP) criterion was used to verify the absence of intraparticle
468 diffusion limitation as well as the assumption of spherical particles and the consideration of
469 an apparent first order reaction. It was obtained a value of WP of 0.12 in the worst scenario.
470 WP values less than 0.3 ensure that there is no mass transfer, thus our system meets the WP
471 criteria. After 2 hours of reaction the conversion observed for 5%Cu/ ZrO_2 , 5%Cu/ Al_2O_3 and
472 5%Cu/ SiO_2 catalysts were at about 30%, 25% and 22%, respectively.

473 In the present study the activity results were expressed in terms of conversion (X). The same
474 catalytic test was performed multiple times to check the reproducibility. The results are
475 presented in Fig. 7 with the plot of $-\ln(1-X)$ versus *time* to demonstrate an apparent kinetic
476 of an irreversible first order reaction with a constant density system. A straight line passing
477 through the origin was obtained (Fig. 7) where the corresponding slope is equal to the
478 apparent kinetic constant of each catalyst. It was represented the results from the repeated
479 experiments for each catalyst in the corresponding plot. The highest kinetic constant was
480 found for the 5%Cu/ZrO₂ catalyst.

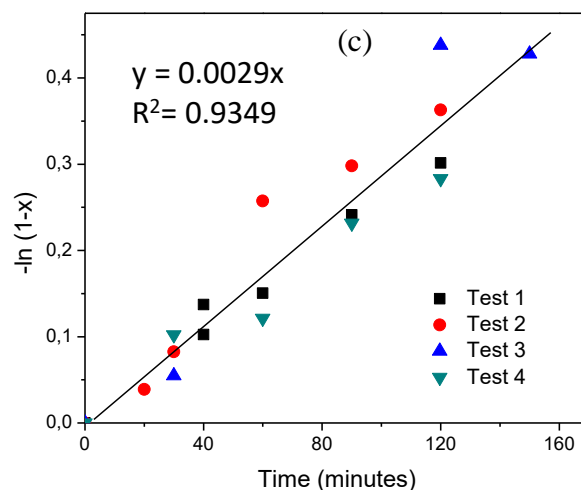
481



482



483



484

485 Fig. 7. Reaction demonstrating an apparent first order kinetic (a) 5%Cu/SiO₂, (b)
 486 5%Cu/Al₂O₃ and (c) 5%Cu/ZrO₂.

487

488 The physical-chemical properties of the support have vital influence on the dispersion of
 489 metallic copper species influencing the catalytic performance as noticed in Table 6, which
 490 represents the relationship of the kinetic constants expressed in $\mu\text{mol m}_{\text{cat}}^{-2}$ with the total
 491 quantity of N₂O chemisorbed ($\mu\text{mol m}_{\text{cat}}^{-2}$). Table 6 also shows the relationship of the
 492 corresponding kinetic constants to the total acidic sites expressed in ($\mu\text{mol m}_{\text{cat}}^{-2}$). Thus, an
 493 increase in the apparent kinetic constant with both total quantity of N₂O chemisorbed and the
 494 total quantity of acidic sites was observed.

495

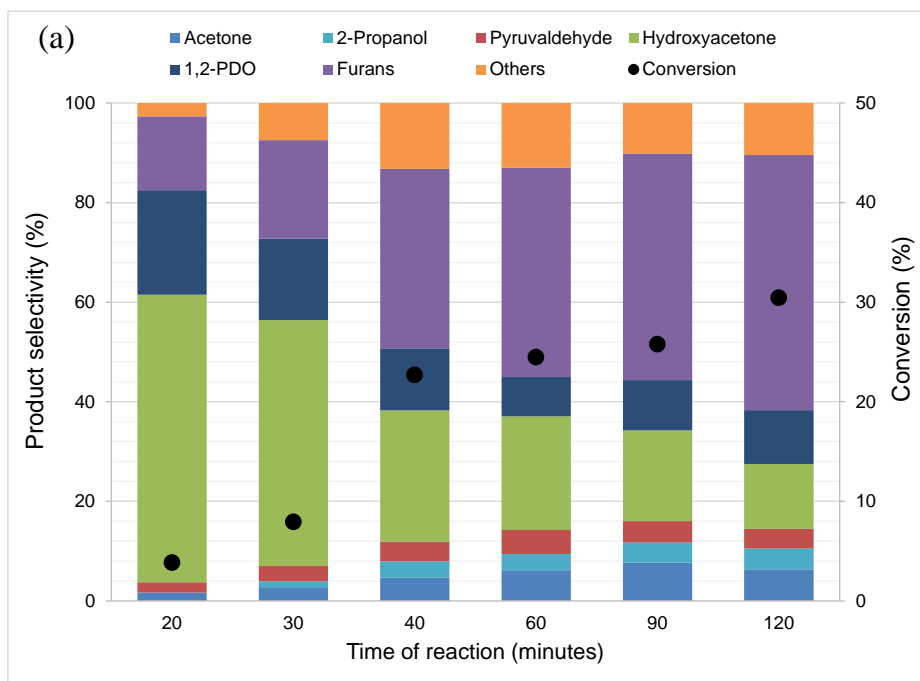
496 Table 6. Apparent kinetic constant of the copper catalysts

Apparent first order kinetic constant, k	5%Cu/SiO ₂	5%Cu/ γ -Al ₂ O ₃	5%Cu/ZrO ₂
k (min ⁻¹)	0.0022	0.0021	0.0029
k (min ⁻¹ m _{cat} ⁻²)	4.5×10 ⁻⁶	5.8×10 ⁻⁶	1.1×10 ⁻⁵

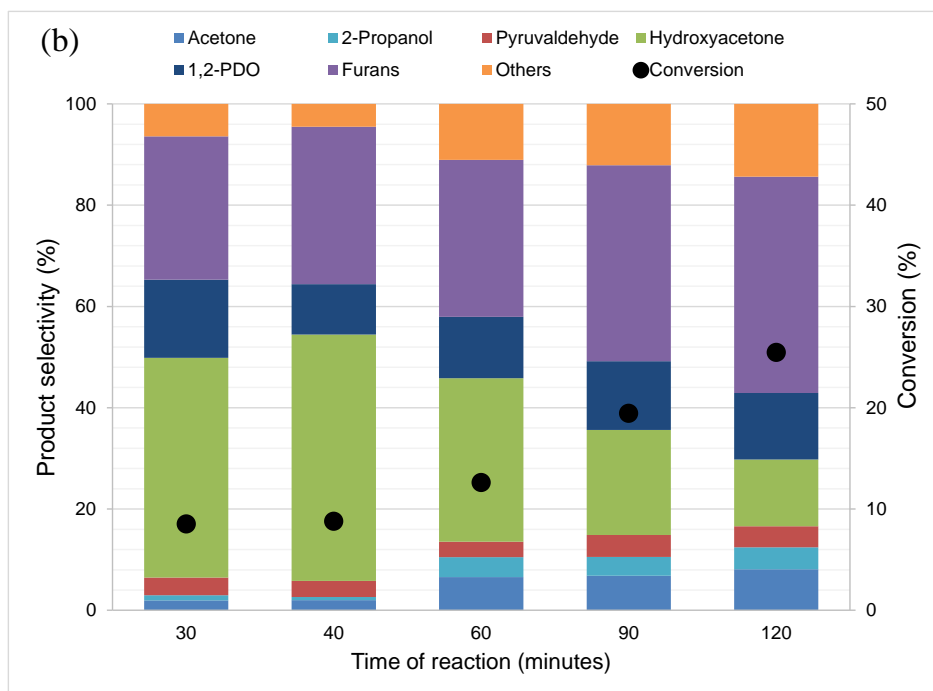
497

498 Under the experimental conditions, a negligible conversion of glycerol and hydroxyacetone
 499 selectivity were observed when the supports were directly used as catalysts in the activity
 500 tests. Fig. 8 shows their catalytic performance monitored in different times of reaction.
 501 Cu/ZrO₂ catalyst (Fig. 8a) shows a glycerol conversion of at about 4% at 20 minutes reaching
 502 at about 30% of conversion at 120 minutes of reaction. Cu/ γ -Al₂O₃ (Fig. 8b) exhibits a
 503 glycerol conversion between 8 to 25% in the range of 120 minutes of reaction. In the case of
 504 Cu/SiO₂ catalyst (Fig. 8c) it is observed a glycerol conversion of 8% at 20 minutes of reaction
 505 and at about 20% of conversion at 120 minutes of reaction.

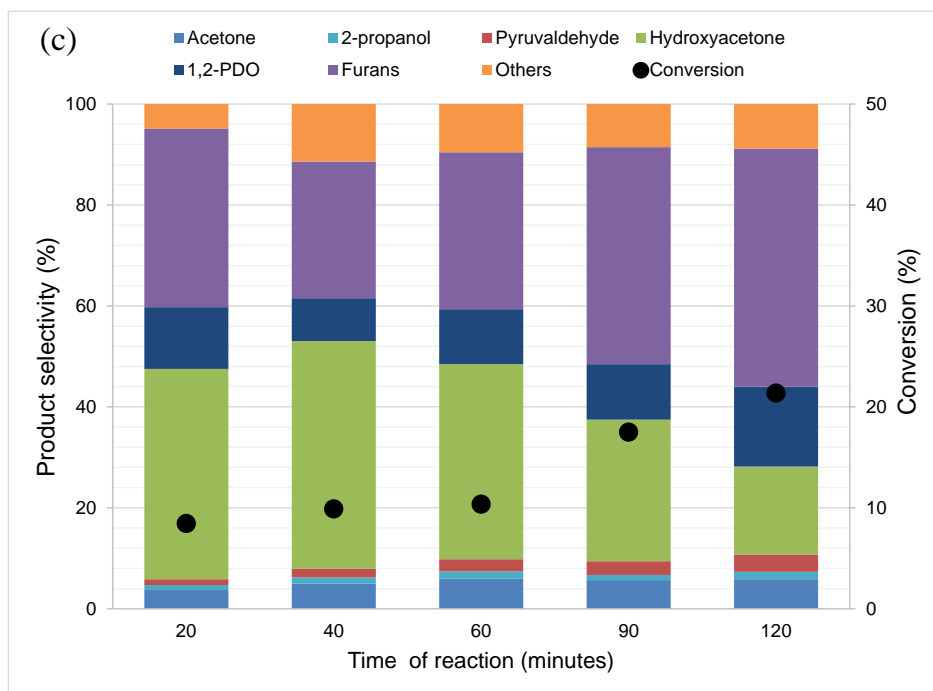
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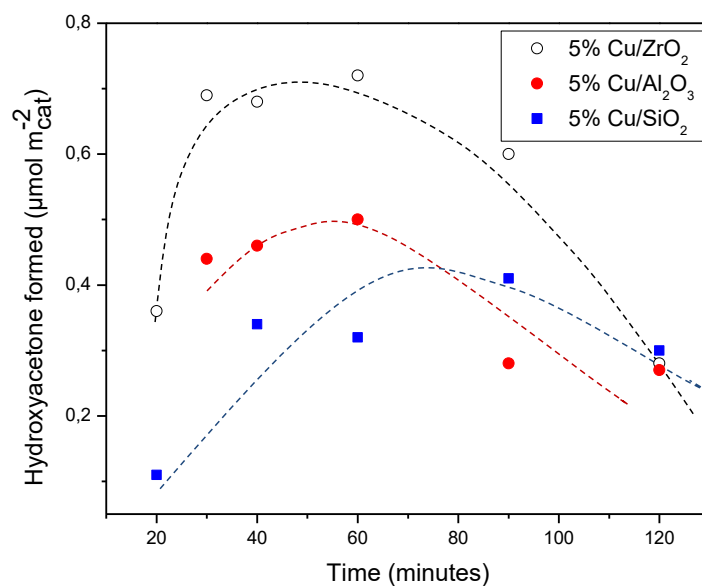
512 Figure 8. Catalytic performance of copper based catalysts. (a) 5% Cu/ZrO₂, (b) 5% Cu/Al₂O₃
 513 and (c) 5% Cu/SiO₂.

514

515 The main products observed in the reaction was acetone, 2-propanol, pyruvaldehyde,
516 hydroxyacetone, 1,2-propanediol, furan derivatives and other unidentified compounds
517 possibly produced by secondary reactions between the compounds in the reaction mixture. It
518 is noticed for the copper catalysts that the highest selectivity towards hydroxyacetone was in
519 first minutes of reaction. In this respect, hydroxyacetone selectivity of 57% and 41% was
520 observed respectively for Cu/ZrO₂ and Cu/SiO₂ catalysts at 20 minutes of reaction, whereas
521 for Cu/ γ -Al₂O₃ sample a hydroxyacetone selectivity of 43% was noticed at 30 minutes of
522 reaction. Previous work [9] reported over Cu-Al (50:50) catalyst prepared by coprecipitation
523 a hydroxyacetone selectivity of 92% and 24% of glycerol conversion at 493 K in aqueous
524 medium under N₂ atmosphere in autogenous condition. W. Suprun *et al.* [66] reported
525 hydroxyacetone selectivity of 23% and 100% of conversion in the dehydration of glycerol
526 over Al₂O₃-PO₄ catalyst at 280⁰C. Chiu *et al.*[16] reported that copper-chromite catalyzes the
527 dehydration of glycerol with a selectivity towards hydroxyacetone of 70% and 22% of
528 glycerol conversion.

529

530 Hydroxyacetone was the major product observed in the initial reaction period as shown Fig.
531 9. In addition, the highest yield towards hydroxyacetone was noticed for 5%Cu/ZrO₂.
532 Hydroxyl terminal groups of the glycerol molecule interacting with the Lewis acid sites on
533 the catalyst surface may promote the formation of an enol intermediate which rapidly
534 reorganizes to form hydroxyacetone. Thus, hydroxyacetone can be obtained by direct
535 dehydration of glycerol followed by a keto-enolic tautomerization [67]. Pyruvaldehyde was
536 also observed and it can be formed from hydroxyacetone dehydrogenation.



537

538 Fig. 9. Glycerol conversion towards hydroxyacetone. (Dashed lines only serve to guide the
539 eyes).

540

541 After 120 minutes of reaction, acetone, 2-propanol and furan derivatives were also observed.

542 These products were formed from the degradation of hydroxyacetone. Earlier works report

543 that hydroxyacetone is converted to carboxylic acids which allow acetone to be formed via

544 ketonization. Catalytic cyclisation to form furan derivatives are also observed. It must be

545 added that 1,2 propanediol (1,2-PDO) was also detected. Previous work [9] reported that

546 glycerol hydrogenolysis to 1,2-PDO proceeds through a dehydrogenation-dehydration-

547 hydrogenation mechanism. In that case hydroxyacetone is the intermediate to 1,2-PDO.

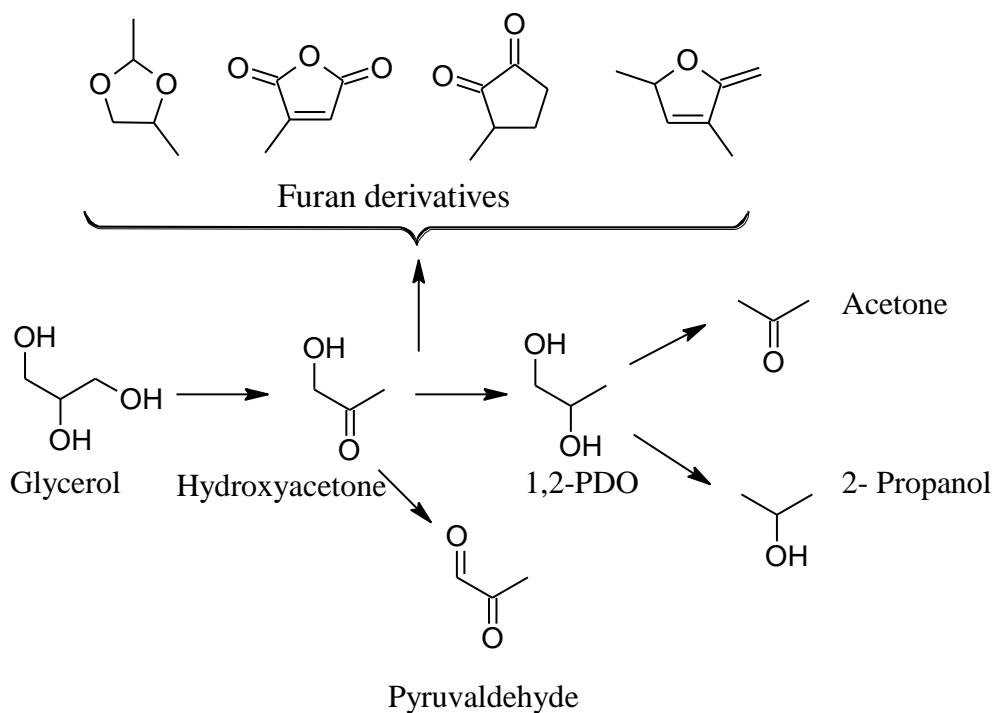
548 Copper may serve as active sites for the subsequent hydrogenation step to 1,2-PDO by the

549 formation of active hydrogen atom originating from the dehydrogenation step. The general

550 chemical route based on the main products detected by gas chromatograph and mass

551 spectrometry is shown in Scheme 1.

552



553

554

Scheme 1. Identified products in the glycerol dehydration.

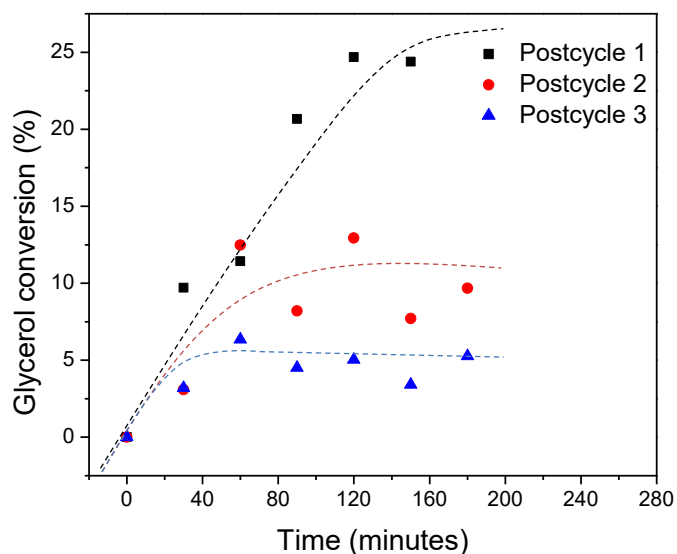
555

556 *3.3 Catalyst Recycling*

557 The recycling of 5%Cu/ZrO₂ catalyst during the selective conversion of glycerol to
 558 hydroxyacetone was investigated. After the first test (Postcycle 1), the catalyst was recovered
 559 by decantation and it was washed with a 50/50 mixture methanol-water and dried at 100°C.
 560 The dried catalysts were calcined at 400 °C for 4 hours and finally reduced at 400 °C for 4
 561 hours under hydrogen flow. The resultant reduced catalyst was used for the next cycle
 562 (Postcycle 2) under conditions that allowed to maintain the same glycerol/catalyst molar ratio
 563 used in the cycle 1. The same process of separation, washing and reactivation of the catalyst
 564 has been implemented for the Postcycle 3. As shown Fig. 10 the fresh 5%Cu/ZrO₂ gives at
 565 about 30% of glycerol conversion at 120 minutes of reaction. During the Postcycle 2 the

566 conversion of glycerol decreased to about 10% and in the third cycle the conversion
567 decreased to reach at about 5%.

568



569

570 Fig. 10. 5%Cu/ZrO₂ catalyst recycling process in the glycerol dehydration. (Dashed lines
571 only serve to guide the eyes).

572

573 To identify the origin of the deactivation, the fresh and used 5% Cu/ZrO₂ catalysts
574 (reactivated by calcination-reduction) were characterized by nitrogen physisorption (Fig. S1
575 and Table 7) and N₂O chemisorption (Fig. S2 and Table 7). In addition, X-ray diffraction
576 (Fig. S3) and scanning electron microscopy coupled to an energy dispersive X-ray
577 spectrometer (SEM-EDS) (Table 7) were performed. The EDS results indicate that copper
578 species are homogeneously distributed over ZrO₂ and there is no appreciable variation in the
579 atomic relationship Cu/Zr after each recycling (Table 7).

580

581

582

583 Table 7. Properties of the 5%Cu/ZrO₂ catalyst during the recycling process

Sample	S _{BET} (m ² g ⁻¹)	V _P (cm ³ g ⁻¹)	d _p (nm)	N ₂ O (μmol N ₂ O g _{cat} ⁻¹)	Cu/Zr ^a
Fresh	131	0.13	4.01	301	0.075
Postcycle 1	128	0.15	4.24	286	0.090
Postcycle 2	129	0.15	4.55	164	0.075
Postcycle 3	116	0.14	4.86	170	0.079

584 ^a EDS

585

586 Change of the textural properties of 5%Cu/ZrO₂ material in the recycling was negligible
 587 (Table 7). The total amount of chemisorbed N₂O was progressively reduced between each
 588 cycle (Fig. S2 and Table 7). Moreover, the X-ray diffraction of the used materials after each
 589 reactivation indicates some sintering of copper species by the appearance of copper oxide
 590 phase (Fig. S3). The observed sintering of copper particles after the catalytic cycles may
 591 result in the loss of active site which can be considered as the main factor contributing to the
 592 observed catalyst deactivation.

593

594 *3.4 DFT study*

595

596 To gain molecular insights and explain the support effects, adsorption energies of glycerol,
 597 and hydroxyacetone were computed using DFT calculations. The effect of hydroxylation on
 598 Al₂O₃ and ZrO₂ supports due to water dissociation, which is also related to Brønsted acid site
 599 were also investigated. Three possible adsorption sites were considered on each surface i.e.
 600 Cu site, Al or Zr site on support and interface site between Cu cluster and support. Here, we

601 report only adsorption at the most stable one. The adsorption energies were calculated using
 602 equation (9) and summarized in Table 8.

$$603 \quad E_{ad} = E_{total} - E_{clean\ surface} - E_{adsorbate} \quad (9)$$

604

605 where E_{ad} is adsorption energy, E_{total} is energy of structures with glycerol/hydroxyacetone
 606 adsorption, $E_{clean\ surface}$ is energy of structures without glycerol/hydroxyacetone
 607 adsorption and $E_{adsorbate}$ is energy of isolated glycerol/hydroxyacetone molecule. The more
 608 negative values of E_{ad} , the stronger adsorption.

609

610 Table 8. Adsorption energies (kJ mol^{-1}) of glycerol and hydroxyacetone on Cu(111),
 611 $\text{Cu}_{13}/\text{Al}_2\text{O}_3(110)$, $\text{Cu}_{13}/\text{ZrO}_2(111)$, $\text{Cu}_{13}/\text{hydroxylated Al}_2\text{O}_3(110)$, and $\text{Cu}_{13}/\text{hydroxylated}$
 612 $\text{ZrO}_2(111)$ surfaces and Bader charge analysis of Cu_{13} cluster. The corresponding adsorption
 613 structures are shown in Fig. 11.

614

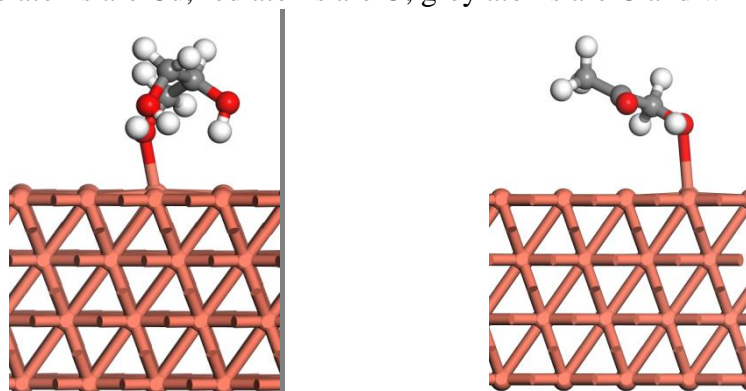
615

	Adsorption energy (kJ mol^{-1})		Charge of Cu_{13} cluster (e^-)
	glycerol	hydroxyacetone	
Cu(111)	-100.12	-102.13	
$\text{Cu}_{13}/\text{Al}_2\text{O}_3(110)$	-337.77	-252.71	+0.13
$\text{Cu}_{13}/\text{hydroxylated Al}_2\text{O}_3(110)$	-337.86	-274.01	+0.55
$\text{Cu}_{13}/\text{ZrO}_2(111)$	-151.04	-178.36	-0.28
$\text{Cu}_{13}/\text{hydroxylated ZrO}_2(111)$	-127.78	-159.66	-0.51

616

617

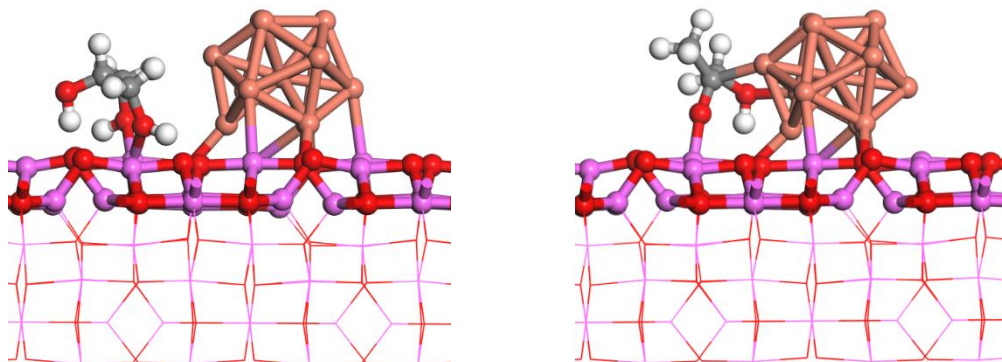
618 (a) Cu(111)
619 Orange atoms are Cu, red atoms are O, grey atoms are C and white atoms are H.



620

621

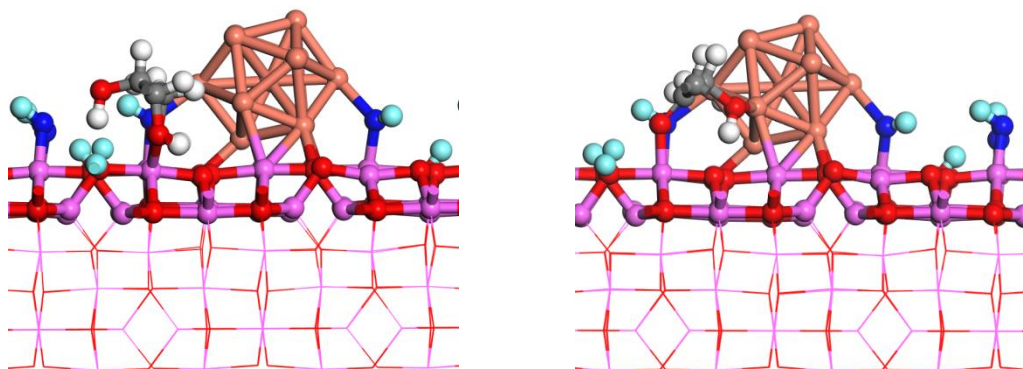
622 (b) Cu₁₃/Al₂O₃(110)
623 Purple atoms are Al.



624

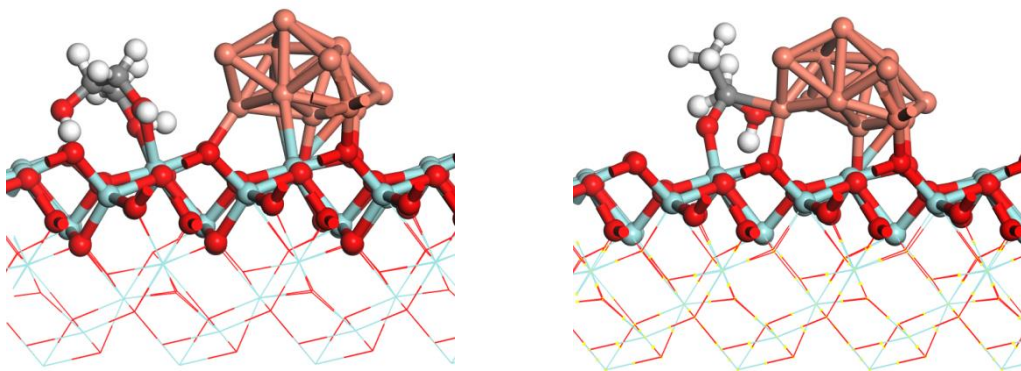
625

626 (c) Cu₁₃/hydroxylated Al₂O₃(110)
627 Blue atoms and light green atoms are O and H from hydroxylation, respectively.



628

629 (d) Cu₁₃/ZrO₂(111)
630 Light green atoms are Zr.
631

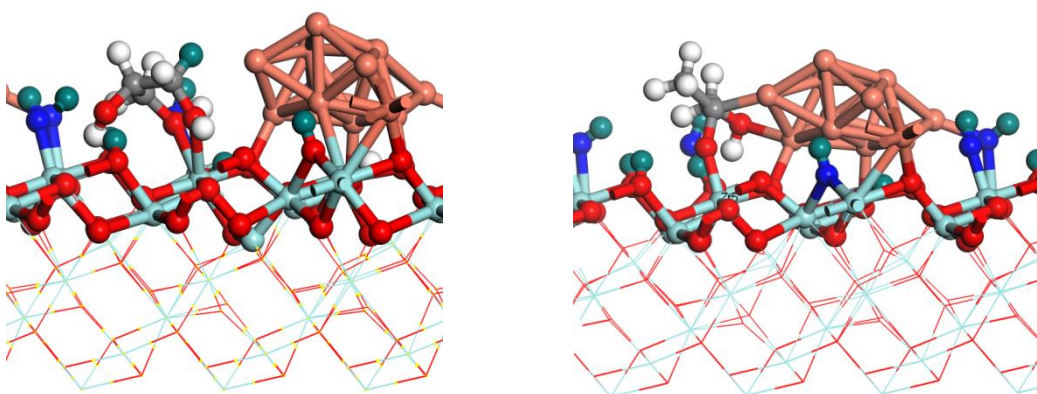


632

633

634 (e) Cu_{13} / hydroxylated $\text{ZrO}_2(111)$

635 Blue atoms and dark green atoms are O and H from hydroxylation, respectively.



636

637

638 Fig. 11. Most stable adsorption structures of glycerol (left) and hydroxyacetone (right) on (a)

639 $\text{Cu}(111)$, (b) $\text{Cu}_{13}/\text{Al}_2\text{O}_3(110)$, (c) $\text{Cu}_{13}/\text{hydroxylated Al}_2\text{O}_3(110)$, (d) $\text{Cu}_{13}/\text{ZrO}_2(111)$, and

640 (e) $\text{Cu}_{13}/\text{hydroxylated ZrO}_2(111)$ surfaces.

641

642 Glycerol and hydroxyacetone adsorption strength are in the order of $\text{Cu}(111) <$

643 $\text{Cu}_{13}/\text{ZrO}_2(111) < \text{Cu}_{13}/\text{Al}_2\text{O}_3(110)$. The relatively strong adsorption indicates that the

644 support significantly facilitate interaction with glycerol and hydroxyacetone. The strong

645 glycerol adsorption on $\text{Cu}_{13}/\text{Al}_2\text{O}_3(110)$ and $\text{Cu}_{13}/\text{ZrO}_2(111)$ surfaces could result from

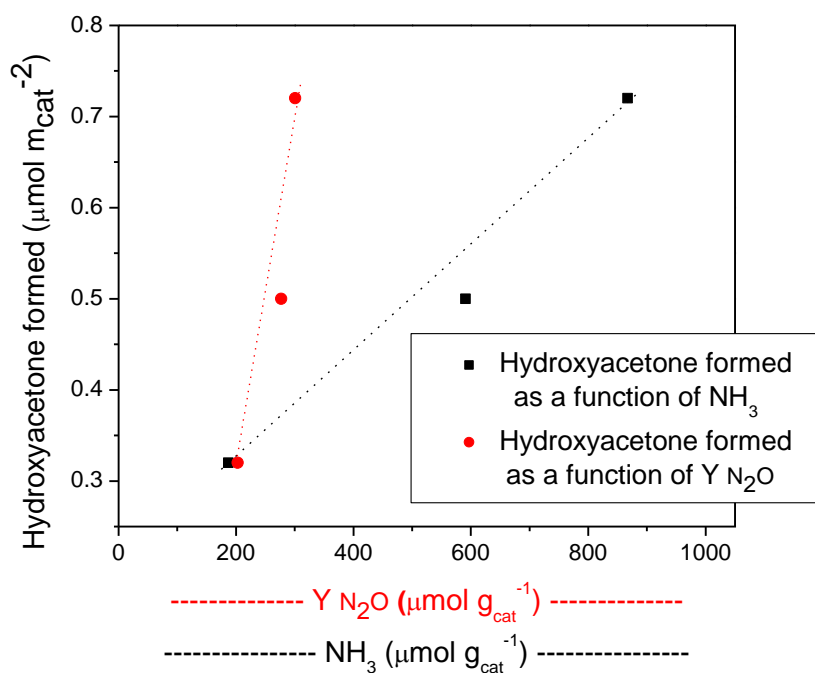
646 bidentate binding that both oxygen ends of glycerol molecule bond to the same metal atom

647 of support (Al or Zr) whereas monodentate binding occurs on Cu(111) surface (Fig. 11, left).
648 Hydroxyacetone prefers to bind through oxygen atom of hydroxyl group on Cu(111) surface
649 while it binds at the interface site where oxygen of carbonyl group interacts with metal site
650 of support and oxygen of hydroxyl group interacts with copper site (Fig. 11, right). Thus,
651 hydroxyacetone interaction on $\text{Cu}_{13}/\text{Al}_2\text{O}_3(110)$ and $\text{Cu}_{13}/\text{ZrO}_2(111)$ surfaces is significantly
652 stronger than that on Cu(111) surface. As illustrated in Fig. 11, glycerol favours to adsorb at
653 support's metal atom site locating adjacent to the Cu cluster and hydroxyacetone prefers to
654 adsorb at the interface site requiring both support's metal atom site and Cu site. This suggests
655 the vital synergistic role of the interface Cu-support as the active site and the significance of
656 high copper particles dispersion, in which turn the increase of interfacial Cu-support sites.
657 Hydroxylation on $\text{Cu}_{13}/\text{Al}_2\text{O}_3(110)$ and $\text{Cu}_{13}/\text{ZrO}_2(111)$ surfaces induce different impact on
658 binding strength. Hydroxylation on $\text{Cu}_{13}/\text{Al}_2\text{O}_3(110)$ facilitates hydroxyacetone adsorption
659 to be stronger while it weakens glycerol and hydroxyacetone adsorption on $\text{Cu}_{13}/\text{ZrO}_2(111)$,
660 yet the favourable adsorption site and adsorption characteristic (monodentate/bidentate) are
661 similar to those without hydroxylation.
662 Furthermore, Bader charge analysis (Table 8) of Cu_{13} cluster was performed to better
663 understand the effect of support. Cu_{13} supported on Al_2O_3 lose electrons to Al_2O_3 showing
664 positive charge while Cu_{13} supported on ZrO_2 gain electrons from ZrO_2 showing negative
665 charge. It is implied that ZrO_2 support shows stronger acidity compared to Al_2O_3 support.
666 The hydroxylation increases the degree of electrons transfer from Cu_{13} cluster to Al_2O_3 and
667 from ZrO_2 to Cu_{13} cluster resulting in higher positive charges of supported Cu_{13} on Al_2O_3
668 and higher negative charge of supported Cu_{13} on ZrO_2 .

669

670 **4. Discussion**

671 To establish relationships between activity and structural parameters the copper based
 672 catalysts were evaluated in the glycerol dehydration. Fig. 12 illustrates a plot correlating the
 673 produced hydroxyacetone expressed in terms of $\mu\text{mol m}_{\text{cat}}^{-2}$ at 20% of conversion with the
 674 total number of exposed metallic copper species expressed in terms of the total quantity of
 675 chemisorbed N_2O ($Y_{\text{N}_2\text{O}}$, $\mu\text{mol N}_2\text{O m}_{\text{cat}}^{-2}$) and with the total number of acid sites of the
 676 catalysts expressed in terms of $\mu\text{mol NH}_3 \text{m}_{\text{cat}}^{-2}$.
 677



678
 679 Fig. 12. Relationship between the total quantity of the produced hydroxyacetone versus
 680 exposed metallic copper atoms and the total quantity of acidic sites. (Dashed lines only serve
 681 to guide the eyes).
 682

683 In the formation of hydroxyacetone stands out a lower sensitivity to the total number of acidic
684 sites compared to the total number of exposed copper atoms which is reflected in the quantity
685 of chemisorbed N₂O. A lower quantity of chemisorbed N₂O exhibits a higher hydroxyacetone
686 yield when compared with the same quantity of acidic sites ($\mu\text{mol NH}_3 \text{ m}_{\text{cat}}^{-2}$).

687

688 The calculation results also reveal that hydroxyacetone and glycerol bind stronger on
689 Cu₁₃/Al₂O₃(110), Cu₁₃/ZrO₂(111) surfaces compared to Cu(111) surface. Also, glycerol is
690 favourable to adsorb at support metal site close to copper cluster and hydroxyacetone is
691 favourable to adsorb at the interface copper-support site (Fig. 11 (right)). These results
692 suggest the synergistic role of acid sites (Al or Zr) of supports and copper cluster to promote
693 hydroxyacetone and glycerol interaction with surfaces. In addition, the active role of the
694 interfacial sites suggests the positive effects of highly dispersed Cu over support on catalytic
695 reactivity. The DFT calculations also indicate that stronger acidity of ZrO₂ may better
696 promote moderate interaction with intermediates while relatively weak acidity of Al₂O₃
697 results in too strong interaction with intermediates. Furthermore, the negative charges of
698 supported Cu cluster on ZrO₂ may indicate the number of acid sites increase with copper
699 introduction on ZrO₂ support.

700

701 It should be added that the highest kinetic constant indicates that the most active catalyst is
702 the 5%Cu/ZrO₂ catalyst. Particularly, ZrO₂ has been described as a preventive element for
703 sintering copper species and it is therefore considered to be a structural promoter [68]. It is
704 important to complement that the results of TPR indicate that the presence of ZrO₂ facilitates
705 the reduction of copper species, as well as the results of XRD, N₂O chemisorption, EDS and

706 XPS which suggest that ZrO₂ support leads to a homogeneous distribution of copper species
707 and higher dispersion of the copper species compared with γ -Al₂O₃ and SiO₂. In addition,
708 pyridine infrared indicates that 5%Cu/ZrO₂ and 5%Cu/ γ -Al₂O₃ catalysts present both acidic
709 sites of Lewis and Brönsted. For 5%Cu/SiO₂ only Lewis acid sites were found.

710

711 **5. Conclusions**

712

713 The dehydration reaction of glycerol to hydroxyacetone on copper based catalysts suggests
714 apparent first order kinetics. By NH₃-TPD, it has been observed that the 5%Cu/ZrO₂
715 exhibited the highest total quantity of acidic sites and total amount of N₂O chemisorbed
716 suggesting higher dispersion of copper species compared with 5%Cu/ γ -Al₂O₃ and
717 5%Cu/SiO₂ catalysts. XRD analysis suggests that copper species are finely dispersed on the
718 support. XPS analysis identified that copper species are found in metallic state at the catalyst
719 surface and the atomic ratio (Cu/M) (M= Si, Al or Zr) suggests that copper species are more
720 homogeneously distributed on ZrO₂ surface.

721

722 Complementary study of DFT indicates that both glycerol and hydroxyacetone adsorb
723 significantly stronger on Cu₁₃/ γ -Al₂O₃ (110) and Cu₁₃/ZrO₂ (111) compared to Cu (111)
724 which further suggests that the active sites for glycerol and hydroxyacetone adsorption are
725 the metal support site and the dual site consisting of Al or Zr of the support (ZrO₂ and γ -
726 Al₂O₃) of the copper species.

727

728 The kinetic constants expressed in $\mu\text{mol m}_{\text{cat}}^{-2}$ indicate that the most active material for
729 glycerol dehydration has been the 5%Cu/ZrO₂ catalyst. A linear correlation between the yield
730 of hydroxyacetone expressed in terms of $\mu\text{mol m}_{\text{cat}}^{-2}$ with the total quantity of chemisorbed
731 N₂O and the total quantity of acidic sites suggest that the copper dispersion is a sensitivity
732 factor for the activity in the glycerol dehydration.

733

734 The sintering of copper particles between each catalyst recycling step by the thermal
735 activation process (calcination-reduction) is the main descriptor responsible for the lost in
736 the activity for the 5%Cu/ZrO₂ in the recycling study in agreement with the progressive
737 decrease in the total quantity of N₂O chemisorbed after each cycle. In addition, the
738 characterization by EDS did not indicate appreciable variation in the atomic Cu/Zr ratio
739 between each one of the reactions in the recycling process.

740

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