

1 **Boosted selectivity towards glycerol carbonate using microwaves vs**
2 **conventional heating for the catalytic transesterification of glycerol**

3
4 **Judith Granados-Reyes, Pilar Salagre, Yolanda Cesteros***

5 Departament de Química Física i Inorgànica. Universitat Rovira i Virgili.

6 C/ Marcel·lí Domingo s/n, 43007 Tarragona, Spain.

7
8 **Abstract**

9 Several hydrocalumite-type materials and some of their calcined forms have been tested
10 for the catalytic transesterification of glycerol towards glycerol carbonate under
11 microwaves, and by conventional heating for comparison. Microwaves slightly
12 increased conversion but greatly increased selectivity to glycerol carbonate for all
13 catalysts while the selectivity to glycidol was similar. Glycerol conversion values were
14 63-95% in microwaves and 61-91% by conventional heating, while selectivity to
15 glycerol carbonate values were 53-92% in microwaves and 30-80% by conventional
16 heating. Interestingly, microwaves favored transesterification since the sum of the
17 selectivity values to glycerol carbonate and glycidol was higher than when using
18 conventional heating.

19
20 Keywords: Microwaves; Glycerol; Glycerol carbonate; Hydrocalumite-type materials;
21 transesterification

23 **1. Introduction**

24 New industrial applications of glycerol have been developed in the last years due to its
25 formation as by-product in high amounts during biodiesel manufacture (Behr et al.,
26 2008; D'Aquino and Ondrey, 2007; Pagliaro et al., 2007; Rahmat et al., 2010; Sonnati
27 et al., 2013). One interesting approach is the catalytic conversion of glycerol to glycerol
28 carbonate, (4-hydroxymethyl-1,3-dioxolan-2-one), which has many applications in
29 different industrial sectors, such as organic intermediate (e.g. monomer of
30 polycarbonates, polyurethanes and polyglycerols) (Behr et al., 2008; Zhou et al., 2008),
31 biolubricant (Pagliaro et al., 2007), protector in the carbohydrates chemistry, component
32 of gas separation membranes, in coatings, or in the production of polyurethane foams
33 and surfactants (Randall and De Vos, 1991; Weuthen and Hees, 1995).

34 Glycerol carbonate has been traditionally produced by reacting glycerol with phosgene
35 but due to the high toxicity and corrosive nature of this reagent, new alternative routes
36 have been investigated (Teng et al., 2014). An interesting catalytic route to obtain
37 glycerol carbonate is the transesterification reaction of glycerol with organic cyclic
38 carbonates (ethylene carbonate or propene carbonate) or with non-cyclic carbonates
39 (diethyl carbonate or dimethyl carbonate). Dimethyl carbonate (DMC) is preferred since
40 the reaction can be performed at milder conditions, and the methanol formed as by-
41 product can be easily separated. Ochoa-Gómez et al. (2009) tested several homogeneous
42 and heterogeneous catalysts with different acidity and basicity at different reaction
43 conditions. The best results were obtained using basic heterogeneous catalysts. CaO
44 catalyst led to 70% of conversion and 70% of yield to glycerol carbonate at 75 °C after
45 15 min of reaction (Simanjuntak et al., 2011). However, when reused, CaO deactivated
46 due to the contact with air between catalytic runs, and because of particle agglomeration
47 (Ochoa-Gómez et al. 2009).

48 Hydrotalcite-based catalysts have been widely employed for this reaction (Kumar et al.,
49 2012; Liu et al., 2014; Liu et al., 2015; Malyaadri et al., 2011; Parameswaram et al.,
50 2013; Takagaki et al., 2010; Yadav and Chandan, 2014). Calcined Mg/Al/Zr (Malyaadri
51 et al., 2011), calcined Mg/Zr/Sr (Parameswaram et al., 2013) and doping transition
52 metals cations into Mg/Al hydrotalcites resulting in yields to glycerol carbonate
53 between 55-94% at reaction temperatures in the range 75-100 °C for this
54 transesterification reaction (Liu et al., 2014). Liu et al. reported full conversion of
55 glycerol and 96% yield of glycerol carbonate at 80 °C for 1.5 h with Li/Mg₄AlO_{5.5}
56 obtained by impregnating calcined Mg/Al hydrotalcite with LiNO₃ (Liu et al., 2015).
57 More recently, calcined silicates, guanidine ionic liquids, sulfonated imidazolium ionic
58 liquid, Li/ZnO catalysts and Ba-mixed metal oxide catalysts have been also tested for
59 this reaction (Fan et al., 2017; Kondawar et al., 2017; Song et al., 2017; Wang et al.,
60 2017a; Wang et al., 2017b). In previous works, we studied the catalytic behaviour of
61 several Ca/Al hydrocalumite-type compounds, synthesized using microwaves and
62 ultrasounds, and some of their calcined forms for the transesterification of glycerol with
63 DMC by conventional heating (Granados-Reyes et al., 2016; Granados-Reyes et al.,
64 2017). We concluded that calcined hydrocalumites catalysts were more stable with time
65 than CaO catalysts.

66 Microwave radiation heats more rapid and more homogeneously than conventional
67 heating, as widely reported in the literature (Caddick and Fitzmaurice, 2009;
68 Appukkuttan et al. 2010; Fernández et al., 2010; Henry et al., 2009; Kappe, 2004;
69 Kappe and Van der Eycken, 2010; Kremsner and Kappe, 2006; Larhed and Hallberg,
70 1996; Polshettiwar and Varma, 2010). The main advantages observed when microwaves
71 are applied to catalytic reactions are the reduction of the reaction time, the decrease of
72 side reactions, which usually improves the selectivity values, and the use of lower

73 solvent amounts (Henry et al., 2009; Kremsner and Kappe, 2006; Zhou et al., 2013).
74 There are only two recent studies in which microwaves have been used for the
75 transesterification of glycerol to glycerol carbonate (Prakruthi et al., 2015; Teng et al.
76 2016). In one of them, high reaction temperature was applied during reaction (Prakruthi
77 et al., 2015) and, in the other, only one commercial catalyst has been tested using
78 different types of crude glycerol (Teng et al. 2016). However, the effect of microwaves
79 on the distribution of the reaction products has not been studied yet.
80 The aim of this work was to study the effect of using microwaves for the
81 transesterification of glycerol with dimethyl carbonate, on the conversion and selectivity
82 to glycerol carbonate employing several Ca/Al hydrocalumite-type compounds and their
83 calcined forms as catalysts (Granados-Reyes, 2015).

84

85

86

87

88 **2. Experimental**

89 **2.1. Preparation of catalysts**

90 Hydrocalumite-type compounds were synthesized by the co-precipitation method from
91 the corresponding Ca and Al chlorides (HC1) or Ca and Al nitrates (HC2) in a $\text{Ca}^{2+}/\text{Al}^{3+}$
92 molar ratio of 2, as described elsewhere (Granados-Reyes et al., 2014). The pH was kept
93 constant at 11.5 ± 0.1 , by the simultaneous addition of an aqueous solution of 2 M
94 NaOH (Panreac) to the corresponding salts at 60 °C. Magnetic stirring or ultrasounds
95 were used for mixing during precipitation (US is added to notation for the samples
96 prepared with ultrasounds). Then, samples were aged by refluxing under conventional
97 heating at 60 °C for 24 h (HC1R₂₄, HC2R₂₄, HC1USR₂₄, HC2USR₂₄) or under

98 microwaves (Milestone ETHOS-TOUCH CONTROL) at 60 °C for 6 h (HC1RMw₆,
99 HC2RMw₆, HC1USRMw₆, HC2USRMw₆). The corresponding catalysts were obtained
100 after filtration, washing with deionized and decarbonated water, and drying at 80 °C
101 overnight. Several of these hydrocalumite-type compounds were calcined in a furnace
102 Carbolite CWF11/5P8 at 450 °C for 15 h (cHC1R₂₄, cHC2R₂₄, cHC1RMw₆,
103 cHC2RMw₆), and at 750 °C for 4 h (cHC1R₂₄-750, cHC1RMw₆-750).

104

105 **2.2. Characterization methods**

106 Powder X-ray diffraction patterns of the samples were obtained with a Siemens D5000
107 diffractometer using nickel-filtered CuK α radiation and detecting between 2 θ values of
108 5°-70°. The Joint Committee on Powder Diffraction Standards (JCPDS) files used for
109 the identification of the crystalline phases were: (035-0105- Calcium Aluminium
110 Hydroxide Chloride Hydrate- Ca₂Al(OH)₆Cl·2H₂O, 089-6723- Calcium Aluminum
111 Nitrate Hydroxide Hydrate- Ca₂Al(OH)₆NO₃·2H₂O, 089-0217- Katoite - Ca₃Al₂(OH)₁₂,
112 086-2341- calcite- CaCO₃, 048-1882- mayenite- Ca₁₂Al₁₄O₃₃ and 037-1497- Lime-
113 CaO). Elemental analysis of the samples was obtained with an ICP-OES analyser
114 (Induced Coupled Plasma – Optical Emission Spectroscopy) from Spectro Arcos. The
115 digestion of all hydrocalumites was carried out with concentrated HNO₃. Analyses were
116 performed by triplicate. BET surface areas were calculated from the nitrogen adsorption
117 isotherms at -196 °C using a Quantachrome Quadrasorb SI surface analyzer and a value
118 of 0.164 nm² for the cross-section of the nitrogen molecule. Samples were degassed at
119 90 °C. Basicity of the catalysts was evaluated using Hammett indicators:
120 phenolphthalein (pKa = 8.2), Nile blue A (pKa = 10.1), tropaeolin O (pKa = 11),
121 thiazole yellow G (pKa = 13.4) and 2,4-dinitroaniline (pKa = 15). 25 mg of catalyst

122 was taken along with 2.5 ml dry methanol and 1 ml of indicator, and kept in a shaker for
123 2 h (Sankaranarayanan et al., 2012).

124

125 **2.3. Catalytic Tests**

126 For the catalytic tests, 0.15 g of catalysts was used. Dimethyl carbonate and glycerol
127 were mixed in a 3.5:1 weight ratio in a 50 mL round bottom glass reactor fitted with a
128 reflux condenser and a thermocouple. The mixture was heated at 90 °C under N₂ under
129 microwaves (Milestone ETHOS-TOUCH CONTROL). After 3 h of reaction, the
130 mixture was filtered and evaporated in a rotatory evaporator. 1 µl of the concentrated
131 residue was analysed by gas chromatography. Catalytic tests were compared with those
132 performed at the same reaction conditions but using conventional heating instead
133 microwaves. Gas chromatography analyses were performed in a SHIMADSU GC-2010
134 apparatus, equipped with a split injection mode and a flame ionization detector. The
135 column was a SUPRAWAX-280 with 60 m length, a film thickness of 50 µm and an
136 internal diameter of 0.25 mm. Glycerol conversion and selectivity to glycerol carbonate
137 and glycidol were determined from calibration lines obtained from commercial
138 products.

139

140 **3. Results and Discussion**

141 **3.1. Catalysts characterization**

142 Table 1 summarizes the main characterization results of the catalysts. More detailed
143 characterization of the non-calcined CaAl-LDH can be found in a previous work
144 (Granados-Reyes et al., 2014).

145 XRD patterns of the hydrocalumite-type compounds showed the crystalline phase
146 corresponding to the CaAl-LDH structure. Crystalline katoite was also observed in

147 different amounts for the samples HC1 coprecipitated under ultrasounds and for all HC2
148 samples (Granados-Reyes et al., 2014). XRD patterns of the samples calcined at 450 °C
149 exhibited the presence of an amorphous phase due to the expected mixture of calcium
150 and aluminium oxides, $\text{Ca}(\text{Al})\text{O}_x$. Additionally, several crystalline peaks were detected
151 for most of the samples (cHC1RMw₆, cHC2R₂₄ and cHC2RMw₆), which were
152 identified as calcite (CaCO_3) (Figure 1). The presence of the calcite phase can be related
153 to the air atmosphere used during calcination. Calcite was more crystalline and was
154 observed in higher amounts for the samples the precursors of which were prepared with
155 nitrates (cHC2R₂₄ and cHC2RMw₆). For the samples calcined at 750 °C, a mixture of
156 CaO and mayenite phase was obtained, as expected (Figure 1). These samples did not
157 show the calcite phase since it decomposes at lower temperature than the calcination
158 temperature used. Sample cHC1R₂₄-750 had slight higher amounts of CaO than sample
159 cHC1RMw₆-750.

160 HC1 samples showed Ca/Al molar ratio values around 2, in agreement with the
161 theoretical value used in the starting reagents. For HC2, the Ca/Al molar ratio values
162 were lower than for HC1. This can be explained by the presence of katoite phase
163 detected in these samples. All the hydrocalumite-type compounds (HC1 and HC2) had
164 nitrogen adsorption-desorption isotherms type IV according to IUPAC classification,
165 corresponding to solids with mesoporous contribution. All samples exhibited low
166 surface areas, especially those calcined at higher temperature, as expected, due to the
167 presence of CaO and mayenite phases with higher cristallinity (Table 1).

168 Hydrocalumite-type compounds had higher basicity strength ($10.1 < \text{H}_- < 13.4$) than the
169 samples calcined at 450 °C ($6.8 < \text{H}_- > 8.2$) and lower basicity than the samples calcined
170 at 750 °C ($13.4 < \text{H}_- < 15$). The lower basicity of the samples calcined at 450 °C can be
171 related to the presence of calcite while the higher basicity of the samples calcined at 750

172 °C can be attributed to the presence of CaO, highly basic, together with the absence of
173 calcite, which decomposed at this higher calcination temperature.

174

175 **3.2. Catalytic Tests**

176 Figures 2 and 3 show the catalytic results obtained by HC1 and HC2 catalysts for the
177 transesterification of glycerol with dimethyl carbonate after 3 h of reaction using
178 microwaves and conventional heating during reaction. All these catalysts exhibited high
179 conversion and the formation of two reaction products: glycerol carbonate, as main
180 product, and glycidol, in lower amounts. The formation of glycidol is produced by
181 decarboxylation of glycerol carbonate over catalysts with high basicity strength
182 (Kondawar et al., 2017; Liu et al. 2015). Interestingly, the use of microwaves instead of
183 conventional heating clearly increased the conversion but especially the selectivity to
184 glycerol carbonate for all catalysts while the selectivity to glycidol was similar. No
185 other reaction products were detected by gas chromatography at the conditions used.
186 The formation of condensation products from glycerol or glycidol could round off the
187 total products obtained. There were not great differences between HC1 and HC2
188 catalysts. This can be explained by the similar surface and basic characteristics observed
189 for these catalysts (Table 1).

190 Figures 4 and 5 show the catalytic results obtained by the catalysts calcined at 450 °C
191 and 750 °C, respectively, for the transesterification of glycerol with dimethyl carbonate
192 after 3 h of reaction using microwaves and conventional heating during reaction. For all
193 these catalysts we observed that again the use of microwaves increased conversion and
194 especially selectivity to glycerol carbonate. Microwave irradiation is known to reduce
195 side reactions thus improving the selectivity of the reaction, increasing yields and purity
196 of the products (Henry et al., 2009; Kremsner and Kappe, 2006; Zhou et al., 2013).

197 Additionally, it has been reported that microwaves can accelerate organic reactions
198 (oxidation, polymerization, reduction) (Kingston and Haswell, 1997). This has been
199 attributed to the higher homogeneity of heating when using microwaves with respect to
200 conventional heating. Interestingly, the sum of the selectivity values to glycerol
201 carbonate and glycidol was higher when using microwaves than when using
202 conventional heating during reaction. Therefore, the use of microwaves favors the
203 transesterification reaction.

204 On the whole, the catalytic results of the samples calcined at 450 °C were worse than
205 those of the hydrocalumite-type compounds while the best catalytic results were
206 achieved with the samples calcined at 750 °C. This can be correlated with the different
207 basicity strenght of the catalysts, which varies in this order: samples calcined at 750 °C
208 > hydrocalumite-type compounds > samples calcined at 450 °C (Table 1) as a
209 consequence of the different composition of the samples.

210 By comparing the catalytic results obtained by our hydrocalumite-type catalyts, tested
211 under microwaves, with those reported by Prakruthi et al., 2015 by using Zn-Al, Mg-Al,
212 Ni-Al and Cu-Al LDH catalysts, also tested with microwaves, we observed that with the
213 Zn-Al LDH catalyst, Prakruthi et al., 2015 obtained 93% of glycerol conversion
214 (without reporting selectivity values). In our case, we obtained 86% of glycerol
215 conversion, with a selectivity to glycerol carbonate of 87% using milder reaction
216 conditions, *i.e.* lower catalyst loading (2,5 wt% vs. 52,6 wt %) and lower reaction
217 temperature (90 °C vs. 120 °C)

218 Teng *et al.*, 2016 reported the use of commercial CaO in the microwave-assisted
219 transesterification reaction of glycerol with different degree of purity. They obtained a
220 glycerol carbonate yield of 64.1% at 75 °C for 90 min using pure glycerol and 6.1 w%

221 of catalyst. Our hydrocalumite catalysts calcined at 750 °C led to glycerol carbonate
222 yields between 77-83% at 90 °C for 3 h with 2,5 wt% of catalyst loading.

223 The catalytic life of one of the catalysts (HC2USRMw₆) was evaluated in four
224 consecutive runs using the same reaction conditions under microwaves (Figure 6). After
225 each run, catalyst was recovered by filtration, washed in methanol at room temperature
226 and dried. Several catalytic reuses resulted in a progressive slight loss of conversion and
227 selectivity to glycerol carbonate, and glycidol. Interestingly, this behavior was different
228 to that observed when reusing one hydrocalumite-type compound by conventional
229 heating the results of which exhibited similar selectivity to glycerol carbonate values
230 but a significant increase of selectivity to glycidol (Granados-Reyes et al., 2016). The
231 homogeneity of the heating under microwaves could explain the similar activity values
232 obtained after reusing. The progressive loss of activity observed during reusing could be
233 attributed to the loss of some basic centres during reaction due to some modification in
234 the catalyst composition and crystallinity, as previously reported for this type of
235 catalysts for this reaction (Granados-Reyes et al., 2016).

236 Based on the previous mechanisms proposed in the literature by other authors for these
237 reactions (Ochoa-Gómez et al., 2009; Mouloungui, 2004), a plausible reaction
238 mechanism for the formation of glycerol carbonate and subsequent glycidol is proposed
239 in Scheme 1 on calcined hydrocalumites. O²⁻ groups act as base catalyst. Deprotonation
240 of hydroxyl groups of glycerol leads to generation of the alkoxy group that attacks the
241 electrophilic carbonyl group of DMC with the elimination of methanol, leading to
242 glycerol carbonate. For the formation of glycidol, two hydroxyl groups of the glycerol
243 remaining in the reaction medium are inserted into a cyclocarbonate group, followed by
244 oligomerization of glycerol carbonate, and finally followed by controlled
245 depolymerisation by the action of the catalyst.

246

247 **4. Conclusions**

248 Several CaAl-LDH and several calcined CaAl-LDH have been checked as catalysts for
249 the transesterification of glycerol to glycerol carbonate using microwaves or
250 conventional heating during reaction. The catalytic results of the samples calcined at
251 450 °C were worse than those of the hydrocalumite-type compounds while the best
252 catalytic results were achieved with the samples calcined at 750 °C and tested under
253 microwaves. This can be correlated with the different basicity strength of the catalysts.
254 The use of microwaves during reaction resulted in higher conversion and, especially,
255 higher selectivity to glycerol carbonate for all catalysts. Microwaves favor the
256 transesterification reaction since the sum of the selectivity values to glycerol carbonate
257 and glycidol was higher when using microwaves than when using conventional heating.
258 Also, the homogeneity of the heating under microwaves could explain the similar
259 activity values obtained after reusing.

260

261 **Acknowledgements**

262 Authors acknowledge Ministerio de Economía y Competitividad of Spain and Feder
263 Funds (CTQ2011-24610), and Catalan Government for FI grant (2012FI_B 00564).

264

265

266 **References**

- 267 Appukkuttan, P.; Mehta, V.P.; Van der Eycken, E., 2010. Microwave-assisted
268 cycloaddition reactions. *Chem. Soc. Rev.* 39, 1467-1477.
- 269 Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F., 2008. Improved utilisation
270 of renewable resources: New important derivatives of glycerol. *Green Chem.* 10, 13-30.
- 271 Caddick, S.; Fitzmaurice, R., 2009. Microwave enhanced synthesis. *Tetrahedron.* 65,
272 3325-3355.
- 273 D'Aquino, R.; Ondrey, G., 2007. Outlets for glycerin. *Chem. Eng.* 114, 31-37.
- 274 Fan, P.; Whang, J.; Xing, S.; Yang, L.; Yang, G.; Fu, J.; Miao, C.; Lv, P., 2017.
275 Synthesis of Glycerol-Free Biodiesel with Dimethyl Carbonate over Sulfonated
276 Imidazolium Ionic Liquid. *Energy Fuels* 31, 4090-4095.
- 277 Fernández,; Arenillas, A.; Bermúdez, J.M.; Menéndez, J.A., 2010. Comparative study
278 of conventional and microwave-assisted pyrolysis, steam and dry reforming of glycerol
279 for syngas production, using a carbonaceous catalyst. *J. Anal. Appl. Pyrolysis.* 88, 155-
280 159.
- 281 Granados-Reyes, J.; Salagre, P.; Cesteros, Y., 2014. Effect of microwaves, ultrasounds
282 and interlayer anion on the hydrocalumites synthesis. *Microporous Mesoporous Mater.*
283 199, 117-124.
- 284 Granados-Reyes, J., 2015. Hydrocalumite-based catalysts for glycerol revalorization.
285 PhD thesis.
- 286 Granados-Reyes, J.; Salagre, P.; Cesteros, Y., 2016. CaAl-layered double hydroxides as
287 active catalysts for the transesterification of glycerol to glycerol carbonate. *Appl. Clay*
288 *Sci.* 132-133, 216-222.

289 Granados-Reyes, J.; Salagre, P.; Cesteros, Y., 2017. Effect of the preparation conditions
290 on the catalytic activity of calcined Ca/Al-layered double hydroxides for the synthesis
291 of glycerol carbonate. *Appl. Catal. A. Gen.* 536, 9-17.

292 Hemasri, Y., 2009. Microwave Assisted Synthesis Of Substituted 1,2,3,4-Tetrahydro-2-
293 Pyrimidinones And 1,2,3,4- Tetrahydro-2-Pyrimidinethiones From Quinoline
294 Chalcones. *Heterocycl. Commun.* 15, 423-427.

295 Henry, C.; Haupt, A.; Turner, S.C., 2009. Microwave-Assisted Synthesis of Novel (5-
296 Nitropyridin-2-yl)alkyl and (5-Nitropyridin-3-yl)alkyl Carbamates. *J. Org. Chem.* 74,
297 1932-1938.

298 Kappe, C.O., 2004. Controlled Microwave Heating in Modern Organic Synthesis.
299 *Angew. Chemie-International Ed.* 43, 6250-6284.

300 Kappe, C.O.; Van der Eycken, E., 2010. Click chemistry under non-classical reaction
301 conditions. *Chem. Soc. Rev.* 39, 1280-1290.

302 Kingston, H.M.; Haswell, S.J., 1997. Microwave-enhanced Chemistry Fundamentals,
303 Sample Preparation and Applications., First Edit, ACS Professional Reference Book.

304 Kondawar, S. E.; Patil, C. R.; Rode, C. V., 2017. Tandem synthesis of glycidol via
305 transesterification of glycerol with DMC over Ba-mixed metal oxide catalysts. *ACS*
306 *Sustainable Chem. Eng.* 5, 1763-1774.

307 Kremsner, J.M.; Kappe, C.O., 2006. Silicon Carbide Passive Heating Elements in
308 Microwave-Assisted Organic Synthesis. *J. Org. Chem.* 71, 4651-4658.

309 Kumar, A.; Iwatani, K.; Nishimura, S.; Takagaki, A.; Ebitani, K., 2012. Promotion
310 effect of coexistent hydromagnesite in a highly active solid base hydrotalcite catalyst
311 for transesterifications of glycols into cyclic carbonates. *Catal. Today.* 185, 241-246.

312 Larhed, M.; Hallberg, A., 1996. Microwave-Promoted Palladium-Catalyzed Coupling
313 Reactions. *J. Org. Chem.* 61, 9582-9584.

314 Liu, P.; Derchi, M.; Hensen, E.J.M., 2014. Promotional effect of transition metal doping
315 on the basicity and activity of calcined hydrotalcite catalysts for glycerol carbonate
316 synthesis. *Appl. Catal. B Environ.* 144, 135-143.

317 Liu, Z.; Wang, J.; Kang, M.; Yin, N.; Wang, X.; Tan, Y.; Zhu, Y., 2015. Structure-
318 activity correlations of $\text{LiNO}_3/\text{Mg}_4\text{AlO}_{5.5}$ catalysts for glycerol carbonate synthesis from
319 glycerol and dimethyl carbonate. *J. Ind. Eng. Chem.* 21, 394-399.

320 Malyaadri, M.; Jagadeeswaraiyah, K.; Sai Prasad, P.S.; Lingaiah, N., 2011. Synthesis of
321 glycerol carbonate by transesterification of glycerol with dimethyl carbonate over
322 $\text{Mg}/\text{Al}/\text{Zr}$ catalysts. *Appl. Catal. A Gen.* 401, 153-157.

323 Mouloungui, Z., 2004. Conférence Chevreul Voies inhabituelles de synthèse de
324 composés oléophiles à partir des substrats végétaux solides (graines
325 oléoprotéagineuses), liquides (huiles végétales et dérivés, glycérol) pour l'industrie
326 chimique. *Oilseeds fats Crop. Lipids* 11, 425-435.

327 Ochoa-Gómez, J.R.; Gómez-Jiménez-Aberasturi, O.; Maestro-Madurga, B.; Pesquera-
328 Rodríguez, A.; Ramírez-López, C.; Lorenzo-Ibarreta, L.; Torrecilla-Soria, J.; Villarán-
329 Velasco, M.C., 2009. Synthesis of glycerol carbonate from glycerol and dimethyl
330 carbonate by transesterification: catalyst screening and reaction optimization. *Appl.*
331 *Catal. A Gen.* 366, 315-324.

332 Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Della Pina, C., 2007. From glycerol
333 to value-added products. *Angew. Chemie - Int. Ed.* 46, 4434-4440.

334 Parameswaram, G.; Srinivas, M.; Babu, B.H.; Prasad, P.S.S.; Lingaiah, N., 2013.
335 Transesterification of glycerol with dimethyl carbonate for the synthesis of glycerol
336 carbonate over $\text{Mg}/\text{Zr}/\text{Sr}$ mixed oxide base catalysts. *Catal. Sci. Technol.* 3, 3242-3249.

337 Polshettiwar, V.; Varma, R.S., 2010. Green chemistry by nano-catalysis. *Green Chem.*
338 12, 743-754.

339 Prkruthi, H.R.; Jai Prakash, B.S.; Bhat, Y.S., 2015. Microwave assisted synthesis of
340 glycerol carbonate over LDH catalyst: activity restoration through rehydration and
341 reconstruction. *J. Mol. Catal. A Chem.* 408, 214-220.

342 Rahmat, N.; Abdullah, A.Z.; Mohamed, A.R., 2010. Recent progress on innovative and
343 potential technologies for glycerol transformation into fuel additives: A critical review.
344 *Renew. Sustain. Energy Rev.* 14, 987-1000.

345 Randall, D.; De Vos, R., 1991. EP Patent 419114.

346 Sankaranarayanan, S.; Antonyraj, C. A.; Kannan S., 2012. Transesterification of edible,
347 non-edible and used cooking oils for biodiesel production using calcined layered double
348 hydroxides as reusable base catalysts *Bioresour. Technol.* 109, 57–62.

349 Simanjuntak, F.S.H.; Kim, T.K.; Lee, S.D.; Ahn, B.S.; Kim, H.S.; Lee, H., 2011. CaO-
350 catalyzed synthesis of glycerol carbonate from glycerol and dimethyl carbonate:
351 isolation and characterization of an active Ca species *Appl. Catal. A Gen.* 401, 220-225.

352 Sonnati, M.O.; Amigoni, S.; Taffin de Givenchy, E.P.; Darmanin, T.; Choulet, O.;
353 Guittard, F., 2013. Glycerol carbonate as a versatile building block for tomorrow:
354 synthesis, reactivity, properties and applications. *Green Chem.* 15, 283-306.

355 Song, X.; Wu, Y.; Cai, F.; Pan, D.; Xiao, G., 2017. High-efficiency and low-cost
356 Li/ZnO catalysts for synthesis of glycerol carbonate from glycerol transesterification:
357 the role of Li and ZnO. *Appl. Catal. A: Gen.* 532, 77-85.

358 Takagaki, A.; Iwatani, K.; Nishimura, S.; Ebitani, K., 2010. Synthesis of glycerol
359 carbonate from glycerol and dialkyl carbonates using hydrotalcite as a reusable
360 heterogeneous base catalyst. *Green Chem.* 12, 578-581.

361 Teng, W.K.; Ngoh, G.C.; Yusoff, R.; Aroua, M.K., 2014. A review on the performance
362 of glycerol carbonate production via catalytic transesterification: effects of influencing
363 parameters. *Energy Convers. Manag.* 88, 484-497.

364 Teng, W.K.; Ngoh, G.C.; Yusoff, R.; Aroua, M.K., 2016. Microwave-assisted
365 transesterification of industrial grade crude glycerol for the production of glycerol
366 carbonate. *Chem. Eng. J.* 284, 469-477.

367 Wang, S.; Hao, P.; Li, S.; Zhang, A.; Guan, Y.; Zhang, L., 2017. Synthesis of glycerol
368 carbonate from glycerol and dimethyl carbonate catalyzed by calcined silicates. *Appl.*
369 *Catal. A: Gen.* 542, 174-181.

370 Wang, X.; Zhang, P.; Cui, P.; Cheng, W.; Zhang, S., 2017. Glycerol carbonate synthesis
371 from glycerol and dimethyl carbonate using guanidine ionic liquids. *Chin. J. Chem.*
372 *Eng.* 25, 1182-1186.

373 Weuthen, M.; Hees, U., 1995. DE Patent 4335947.

374 Yadav, G.D.; Chandan, P.A., 2014. A green process for glycerol valorization to glycerol
375 carbonate over heterogeneous hydrotalcite catalyst. *Catal. Today.* 237, 47-53.

376 Zhou, C.-H.C.; Beltramini, J.N.; Fan, Y.-X.; Lu, G.Q.M., 2008. Chemoselective
377 catalytic conversion of glycerol as a biorenewable source to valuable commodity
378 chemicals. *Chem. Soc. Rev.* 37, 527-549.

379 Zhou, W. J.; Zhang, X.; Sun, X. B.; Wang, B.; Wang, J. X.; Bai, L., 2013. Microwave-
380 assisted synthesis of quinoxaline derivatives using glycerol as a green solvent. *Russ.*
381 *Chem. Bull.*, 62, 1244-1247.

Table 1. Characterization of catalysts

Catalysts	Crystalline phases (XRD)	Ca/Al (ICP)	BET Area (m ² /g)	Basicity (Hammet Indicators)
HC1R ₂₄	Ca ₂ Al(OH) ₆ Cl·2H ₂ O	1.98	13	10.1<H ₋ >13.4
HC1RMw ₆	Ca ₂ Al(OH) ₆ Cl·2H ₂ O	1.87	10	10.1<H ₋ >13.4
HC1USR ₂₄	Ca ₂ Al(OH) ₆ Cl·2H ₂ O ^a	1.97	6	10.1<H ₋ >13.4
HC1USRMw ₆	Ca ₂ Al(OH) ₆ Cl·2H ₂ O ^a	1.88	7	10.1<H ₋ >13.4
HC2R ₂₄	Ca ₂ Al(OH) ₆ NO ₃ ·2H ₂ O ^a	1.79	9	10.1<H ₋ >13.4
HC2RMw ₆	Ca ₂ Al(OH) ₆ NO ₃ ·2H ₂ O ^a	1.63	9	10.1<H ₋ >13.4
HC2USR ₂₄	Ca ₂ Al(OH) ₆ NO ₃ ·2H ₂ O ^a	1.78	16	10.1<H ₋ >13.4
HC2USRMw ₆	Ca ₂ Al(OH) ₆ NO ₃ ·2H ₂ O ^a	1.85	25	10.1<H ₋ >13.4
cHC1R ₂₄	Amorphous Ca(Al)Ox	1.98	11	6.8<H ₋ >8.2
cHC1RMw ₆	Amorphous Ca(Al)Ox + CaCO ₃ ^b	1.87	12	6.8<H ₋ >8.2
cHC2R ₂₄	Amorphous Ca(Al)Ox + CaCO ₃ ^c	1.79	9	6.8<H ₋ >8.2
cHC2RMw ₆	Amorphous Ca(Al)Ox + CaCO ₃ ^c	1.63	10	6.8<H ₋ >8.2
cHC1R ₂₄ -750	Mayenite + CaO ^d	1.98	4	13.4<H ₋ >15
cHC1RMw ₆ -750	Mayenite + CaO	1.87	5	13.4<H ₋ >15

383 ^a Katoite phase was detected in low amounts (5-23 %) (Granados-Reyes et
384 al., 2014); ^b Calcite was detected in very low amounts; ^c Calcite was more
385 crystalline and was detected in higher amounts than in cHC1 samples
386 calcined at 450 °C ; ^d CaO was detected in higher amounts than in
387 cHC1RMw₆-750.

388

389

390

391

392 **LEGENDS AND CAPTIONS**

393 **Figure 1.** XRD patterns of the samples a) cHC1R₂₄, b) cHC1RM_{w6}, c)cHC2R₂₄, d)
394 cHC2RM_{w6}, e) cHC1R₂₄-750 and f) cHC1RM_{w6}-750. ■ Calcite phase; ■ Mayenite
395 phase ■ CaO phase.

396 **Figure 2.** Catalytic activity of the catalysts HC1 A) under microwaves and B) by
397 conventional heating. Reaction conditions: dimethyl carbonate/glycerol = 3.5:1 weight
398 ratio; N₂ atmosphere; 0.15 g of catalyst; temperature: 90 °C; time: 3 h.

399 **Figure 3.** Catalytic activity of the catalysts HC2 A) under microwaves and B) by
400 conventional heating. Reaction conditions: dimethyl carbonate/glycerol = 3.5:1 weight
401 ratio; N₂ atmosphere; 0.15 g of catalyst; temperature: 90 °C; time: 3 h.

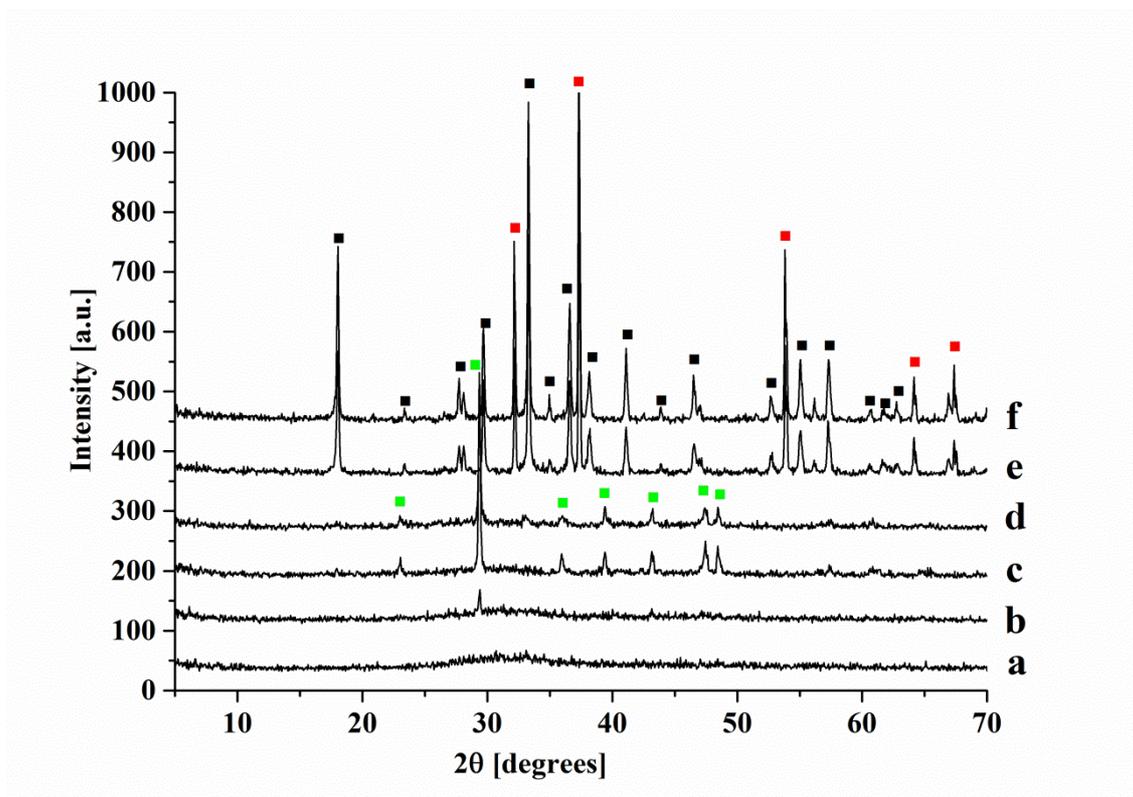
402 **Figure 4.** Catalytic activity of the samples calcined at 450 °C A) under microwaves and
403 B) by conventional heating. Reaction conditions: dimethyl carbonate/glycerol = 3.5:1
404 weight ratio; N₂ atmosphere; 0.15 g of catalyst; temperature: 90 °C; time: 3 h.

405 **Figure 5.** Catalytic activity of the samples calcined at 750 °C A) under microwaves and
406 B) by conventional heating. Reaction conditions: dimethyl carbonate/glycerol = 3.5:1
407 weight ratio; N₂ atmosphere; 0.15 g of catalyst; temperature: 90 °C; time: 3 h.

408 **Figure 6.** Reuse studies of catalyst HC2USRM_{w6} under microwaves. Reaction
409 conditions: dimethyl carbonate/glycerol = 3.5:1 weight ratio; N₂ atmosphere; 0.15 g of
410 catalyst; temperature: 90 °C; time: 3 h.

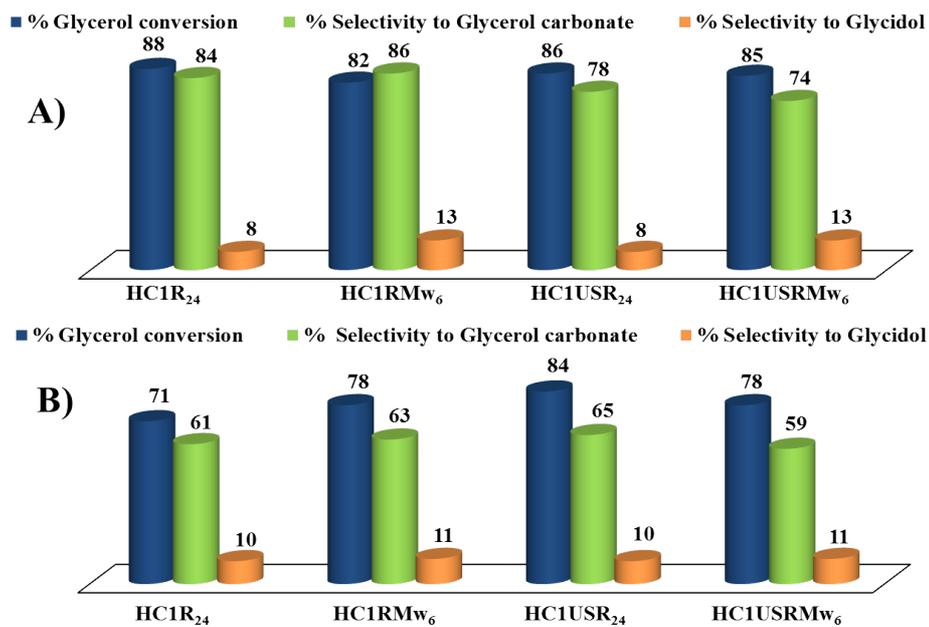
411 Scheme 1. Proposed reaction mechanism for the transesterification of glycerol with
412 dimethyl carbonate explaining the formation of glycerol carbonate and glycidol on
413 calcined hydrocalumites.

414



416

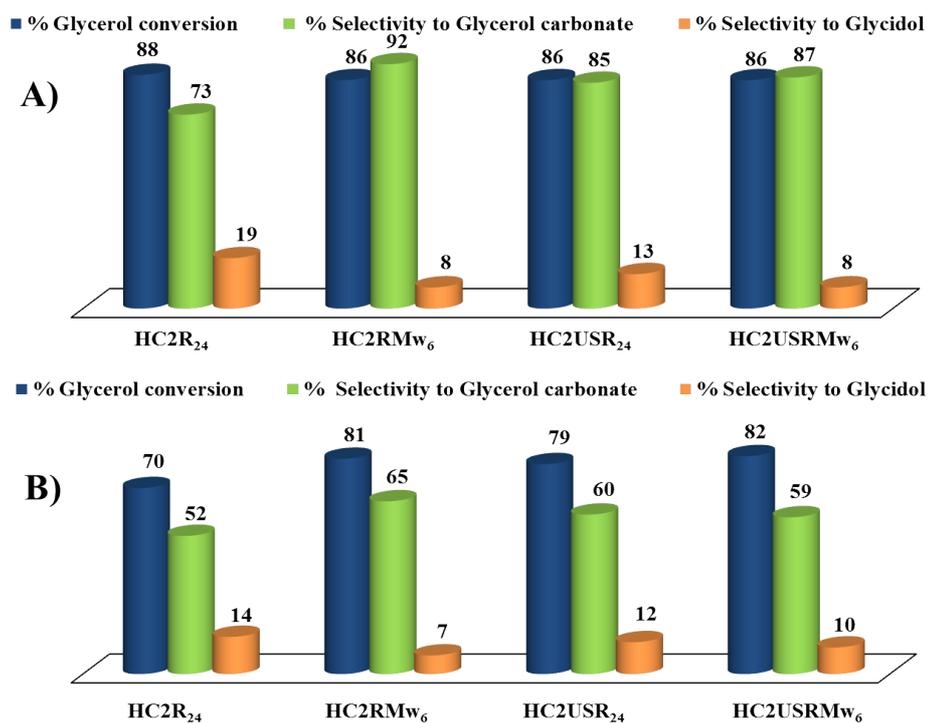
417 Figure 1.



418

419 Figure 2.

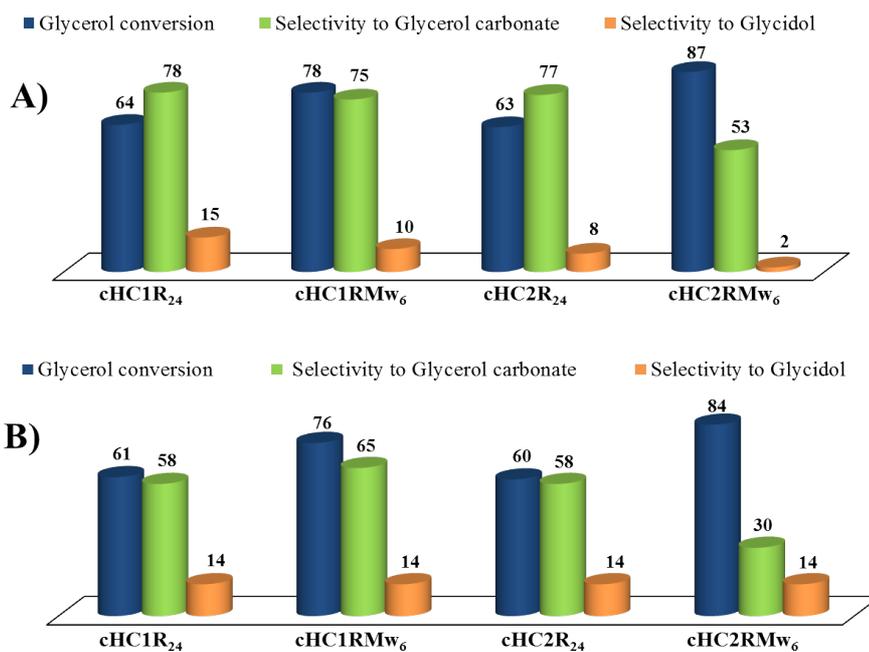
420



421

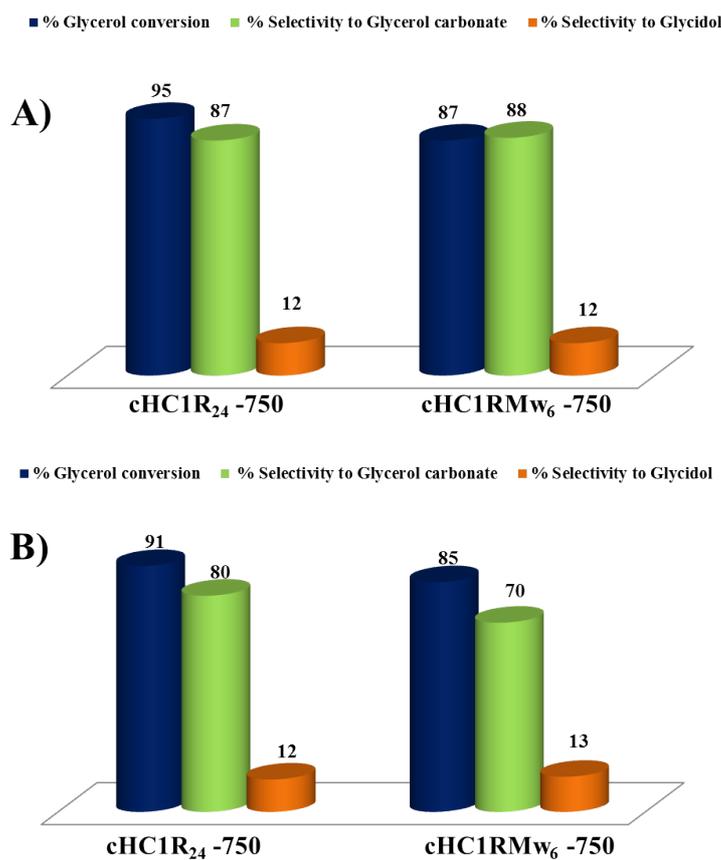
422 Figure 3.

423



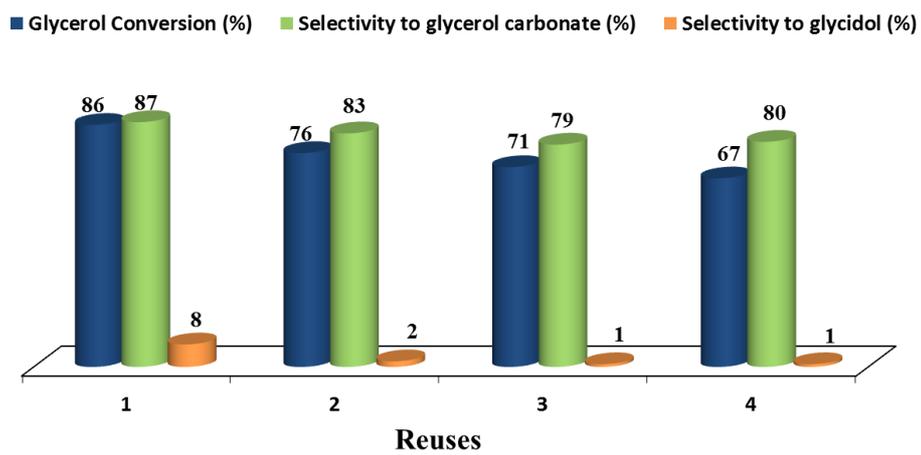
424

425 Figure 4.



426

427 Figure 5.



428

429 Figure 6.

430

431

432

