



## Research paper

# Boosted selectivity towards glycerol carbonate using microwaves vs conventional heating for the catalytic transesterification of glycerol

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## ARTICLE INFO

## Keywords:

Microwaves  
Glycerol  
Glycerol carbonate  
Hydrocalumite-type materials  
Transesterification

## ABSTRACT

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

## 1. Introduction

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

Glycerol carbonate has been traditionally produced by reacting glycerol with phosgene but due to the high toxicity and corrosive nature of this reagent, new alternative routes have been investigated (Teng et al., 2014). An interesting catalytic route to obtain glycerol carbonate is the transesterification reaction of glycerol with organic cyclic carbonates (ethylene carbonate or propene carbonate) or with non-cyclic carbonates (diethyl carbonate or dimethyl carbonate). Dimethyl carbonate (DMC) is preferred since the reaction can be performed at milder conditions, and the methanol formed as by-product can be easily separated. Ochoa-Gómez et al. (2009) tested several homogeneous and heterogeneous catalysts with different acidity and basicity at different reaction conditions. The best results were obtained using basic heterogeneous catalysts. CaO catalyst led to 70% of

conversion and 70% of yield to glycerol carbonate at 75 °C after 15 min of reaction (Simanjuntak et al., 2011). However, when reused, CaO deactivated due to the contact with air between catalytic runs, and because of particle agglomeration (Ochoa-Gómez et al., 2009).

Hydrocalcite-based catalysts have been widely employed for this reaction (Hemasri, 2009; Kumar et al., 2012; Liu et al., 2014, 2015; Malyaadri et al., 2011; Parameswaram et al., 2013; Takagaki et al., 2010; Yadav and Chandan, 2014). Calcined Mg/Al/Zr (Malyaadri et al., 2011), calcined Mg/Zr/Sr (Parameswaram et al., 2013) and doping transition metals cations into Mg/Al hydrocalcites resulting in yields to glycerol carbonate between 55 and 94% at reaction temperatures in the range 75–100 °C for this transesterification reaction (Liu et al., 2014). Liu et al. reported full conversion of glycerol and 96% yield of glycerol carbonate at 80 °C for 1.5 h with Li/Mg<sub>4</sub>AlO<sub>5.5</sub> obtained by impregnating calcined Mg/Al hydrocalcite with LiNO<sub>3</sub> (Liu et al., 2015). More recently, calcined silicates, guanidine ionic liquids, sulfonated imidazolium ionic liquid, Li/ZnO catalysts and Ba-mixed metal oxide catalysts have been also tested for this reaction (Fan et al., 2017; Kondawar et al., 2017; Song et al., 2017; Wang et al., 2017a,b). In previous works, we studied the catalytic behaviour of several Ca/Al hydrocalumite-type compounds, synthesized using microwaves and ultrasounds, and some of their calcined forms for the transesterification of glycerol with DMC by conventional heating (Granados-Reyes et al., 2016, 2017). We concluded that calcined hydrocalumites catalysts were more stable with time than CaO catalysts.

Microwave radiation heats more rapid and more homogeneously than conventional heating, as widely reported in the literature (Caddick and Fitzmaurice, 2009; Appukkuttan et al., 2010; Fernández et al.,

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2010; Henry et al., 2009; Kappe, 2004; Kappe and Van der Eycken, 2010; Kreamsner and Kappe, 2006; Larhed and Hallberg, 1996; Polshettiwar and Varma, 2010). The main advantages observed when microwaves are applied to catalytic reactions are the reduction of the reaction time, the decrease of side reactions, which usually improves the selectivity values, and the use of lower solvent amounts (Henry et al., 2009; Kreamsner and Kappe, 2006; Zhou et al., 2013). There are only two recent studies in which microwaves have been used for the transesterification of glycerol to glycerol carbonate (Prakruthi et al., 2015; Teng et al., 2016). In one of them, high reaction temperature was applied during reaction (Prakruthi et al., 2015) and, in the other, only one commercial catalyst has been tested using different types of crude glycerol (Teng et al., 2016). However, the effect of microwaves on the distribution of the reaction products has not been studied yet.

The aim of this work was to study the effect of using microwaves for the transesterification of glycerol with dimethyl carbonate, on the conversion and selectivity to glycerol carbonate employing several Ca/Al hydrocalumite-type compounds and their calcined forms as catalysts (Granados-Reyes, 2015).

## 2. Experimental

### 2.1. Preparation of catalysts

Hydrocalumite-type compounds were synthesized by the co-precipitation method from the corresponding Ca and Al chlorides (HC1) or Ca and Al nitrates (HC2) in a  $\text{Ca}^{2+}/\text{Al}^{3+}$  molar ratio of 2, as described elsewhere (Granados-Reyes et al., 2014). The pH was kept constant at  $11.5 \pm 0.1$ , by the simultaneous addition of an aqueous solution of 2 M NaOH (Panreac) to the corresponding salts at 60 °C. Magnetic stirring or ultrasounds were used for mixing during precipitation (US is added to notation for the samples prepared with ultrasounds). Then, samples were aged by refluxing under conventional heating at 60 °C for 24 h (HC1R<sub>24</sub>, HC2R<sub>24</sub>, HC1USR<sub>24</sub>, HC2USR<sub>24</sub>) or under microwaves (Milestone ETHOS-TOUCH CONTROL) at 60 °C for 6 h (HC1RMw<sub>6</sub>, HC2RMw<sub>6</sub>, HC1USRMw<sub>6</sub>, HC2USRMw<sub>6</sub>). The corresponding catalysts were obtained after filtration, washing with deionized and decarbonated water, and drying at 80 °C overnight. Several of these hydrocalumite-type compounds were calcined in a furnace Carbolite CWF11/5P8 at 450 °C for 15 h (cHC1R<sub>24</sub>, cHC2R<sub>24</sub>, cHC1RMw<sub>6</sub>, cHC2RMw<sub>6</sub>), and at 750 °C for 4 h (cHC1R<sub>24</sub>-750, cHC1RMw<sub>6</sub>-750).

### 2.2. Characterization methods

Powder X-ray diffraction patterns of the samples were obtained with

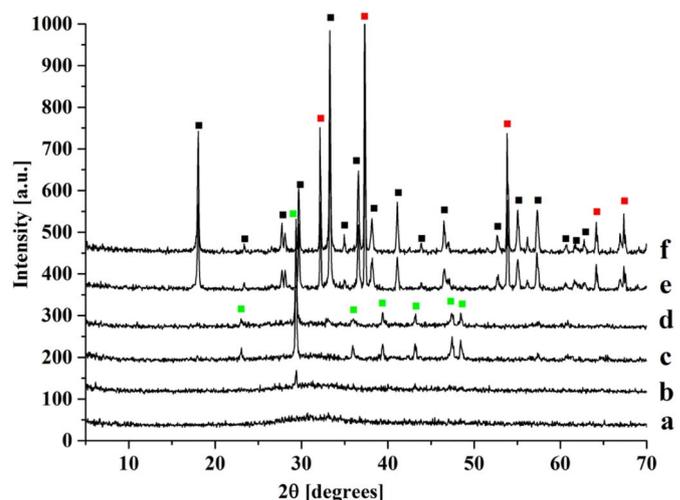


Fig. 1. XRD patterns of the samples a) cHC1R<sub>24</sub>, b) cHC1RMw<sub>6</sub>, c) cHC2R<sub>24</sub>, d) cHC2RMw<sub>6</sub>, e) cHC1R<sub>24</sub>-750 and f) cHC1RMw<sub>6</sub>-750. ■ Calcite phase; ■ Mayenite phase; ■ CaO phase.

a Siemens D5000 diffractometer using nickel-filtered  $\text{CuK}\alpha$  radiation and detecting between  $2\theta$  values of 5°–70°. The Joint Committee on Powder Diffraction Standards (JCPDS) files used for the identification of the crystalline phases were: (035-0105 - Calcium Aluminium Hydroxide Chloride Hydrate -  $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$ , 089-6723 - Calcium Aluminium Nitrate Hydroxide Hydrate -  $\text{Ca}_2\text{Al}(\text{OH})_6\text{NO}_3\cdot 2\text{H}_2\text{O}$ , 089-0217 - Katoite -  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ , 086-2341 - calcite -  $\text{CaCO}_3$ , 048-1882 - mayenite -  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  and 037-1497 - Lime - CaO). Elemental analysis of the samples was obtained with an ICP-OES analyzer (Induced Coupled Plasma – Optical Emission Spectroscopy) from Spectro Arcos. The digestion of all hydrocalumites was carried out with concentrated  $\text{HNO}_3$ . Analyses were performed by triplicate. BET surface areas were calculated from the nitrogen adsorption isotherms at  $-196$  °C using a Quantachrome Quadrasorb SI surface analyzer and a value of  $0.164 \text{ nm}^2$  for the cross-section of the nitrogen molecule. Samples were degassed at 90 °C. Basicity of the catalysts was evaluated using Hammett indicators: phenolphthalein ( $\text{pK}_a = 8.2$ ), Nile blue A ( $\text{pK}_a = 10.1$ ), tropaeolin O ( $\text{pK}_a = 11$ ), thiazole yellow G ( $\text{pK}_a = 13.4$ ) and 2,4-dinitroaniline ( $\text{pK}_a = 15$ ). 25 mg of catalyst was taken along with 2.5 ml dry methanol and 1 ml of indicator, and kept in a shaker for 2 h (Sankaranarayanan et al., 2012).

Table 1  
Characterization of catalysts.

Catalysts	Crystalline phases (XRD)	Ca/Al (ICP)	BET area ( $\text{m}^2/\text{g}$ )	Basicity (Hammett indicators)
HC1R <sub>24</sub>	$\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$	1.98	13	$10.1 < H_- > 13.4$
HC1RMw <sub>6</sub>	$\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$	1.87	10	$10.1 < H_- > 13.4$
HC1USR <sub>24</sub>	$\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}^a$	1.97	6	$10.1 < H_- > 13.4$
HC1USRMw <sub>6</sub>	$\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}^a$	1.88	7	$10.1 < H_- > 13.4$
HC2R <sub>24</sub>	$\text{Ca}_2\text{Al}(\text{OH})_6\text{NO}_3\cdot 2\text{H}_2\text{O}^a$	1.79	9	$10.1 < H_- > 13.4$
HC2RMw <sub>6</sub>	$\text{Ca}_2\text{Al}(\text{OH})_6\text{NO}_3\cdot 2\text{H}_2\text{O}^a$	1.63	9	$10.1 < H_- > 13.4$
HC2USR <sub>24</sub>	$\text{Ca}_2\text{Al}(\text{OH})_6\text{NO}_3\cdot 2\text{H}_2\text{O}^a$	1.78	16	$10.1 < H_- > 13.4$
HC2USRMw <sub>6</sub>	$\text{Ca}_2\text{Al}(\text{OH})_6\text{NO}_3\cdot 2\text{H}_2\text{O}^a$	1.85	25	$10.1 < H_- > 13.4$
cHC1R <sub>24</sub>	Amorphous Ca(Al)Ox	1.98	11	$6.8 < H_- > 8.2$
cHC1RMw <sub>6</sub>	Amorphous Ca(Al)Ox + $\text{CaCO}_3^b$	1.87	12	$6.8 < H_- > 8.2$
cHC2R <sub>24</sub>	Amorphous Ca(Al)Ox + $\text{CaCO}_3^c$	1.79	9	$6.8 < H_- > 8.2$
cHC2RMw <sub>6</sub>	Amorphous Ca(Al)Ox + $\text{CaCO}_3^c$	1.63	10	$6.8 < H_- > 8.2$
cHC1R <sub>24</sub> -750	Mayenite + $\text{CaO}^d$	1.98	4	$13.4 < H_- > 15$
cHC1RMw <sub>6</sub> -750	Mayenite + CaO	1.87	5	$13.4 < H_- > 15$

<sup>a</sup> Katoite phase was detected in low amounts (5–23%) (Granados-Reyes et al., 2014).

<sup>b</sup> Calcite was detected in very low amounts.

<sup>c</sup> Calcite was more crystalline and was detected in higher amounts than in cHC1 samples calcined at 450 °C.

<sup>d</sup> CaO was detected in higher amounts than in cHC1RMw<sub>6</sub>-750.

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