



Effect of the preparation conditions on the catalytic activity of calcined Ca/Al-layered double hydroxides for the synthesis of glycerol carbonate

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ABSTRACT

The effect of the preparation conditions of several calcined Ca/Al layered double hydroxide compounds (CaAl-LDH) on the catalytic transesterification of glycerol with dimethyl carbonate to obtain glycerol carbonate has been studied. The CaAl-LDH precursors were prepared by aging under microwaves or conventional heating, and using chlorides or nitrates as interlayer anions. Calcination conditions, such as temperature, time and calcination system, were modified. After 3 h of reaction, the catalysts obtained by calcination at 450 °C for 15 h in air exhibited moderate-high glycerol conversion (46–76%) and moderate selectivity to glycerol carbonate (41–65%). Calcination at 450 °C at longer calcination time or the use of a dynamic inert-atmosphere system during calcination led to higher conversion (89–94%) and higher selectivity to glycerol carbonate (72–73%). This has been related to the higher basicity of these catalysts. Finally, calcination at 750 °C resulted in high conversion (88–98%) and high selectivity to glycerol carbonate (60–85%) due to the presence in the catalysts of highly basic CaO. Several catalytic reuses favoured the decarboxylation of glycerol carbonate resulting in the formation of higher amounts of glycidol (42%). The progressive loss of conversion and selectivity to glycerol carbonate observed has been attributed to the loss of some CaO basic centres during reaction.

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1. Introduction

During biodiesel production, by transesterification of vegetable oils with methanol, glycerol (glycerine or 1,2,3-propanetriol) is formed as by-product in high amounts (10 wt% of the total product). The price of glycerol is falling as fast as biodiesel plants are being built. Research is currently starting to find new outlets to convert the surplus of glycerol into high-added value products that improve the economy of the whole process [1–6].

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) is one of the most attractive glycerol derivatives due to its low toxicity, good biodegradability and high boiling point [7]. This compound has many applications in different industrial sectors, such as intermediate in polymer synthesis [3,8], biolubricant owing to its adhesion to metallic surfaces and resistance to oxidation, hydrolysis, and pressure [1], protector in the carbohydrates chemistry, component of gas separation membranes, in coatings, or in the

production of polyurethane foams [9], and surfactants [10]. Glycerol carbonate could also serve as a source of glycidol, which is employed in textile, plastics, pharmaceutical and cosmetics industries [11]. Traditionally, glycerol carbonate has been industrially produced by reacting glycerol with phosgene but due to the high toxicity and corrosive nature of this reagent, new routes have been investigated [7].

One alternative option consists of obtaining glycerol carbonate by the catalytic transesterification reaction of glycerol with organic cyclic carbonates (ethylene carbonate or propene carbonate) or with non-cyclic carbonates (diethyl carbonate or dimethyl carbonate) [7,12–20]. Dimethyl carbonate is preferred since the reaction can be performed at milder conditions and the co-product methanol can be easily separated.

Biocatalysts have been used in the transesterification reaction of glycerol with dimethyl carbonate to obtain glycerol carbonate. However, this method need long reaction times [21,22]. Some studies have been carried out using zeolites as catalysts for the transesterification reaction of glycerol with dimethyl carbonate [23–25]. Additionally, Ochoa-Gomez et al. [12] studied different reaction conditions with different basic and acid homogeneous and

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heterogeneous catalysts. The best results were achieved using a basic heterogeneous catalyst (CaO). The CaO showed 100% of conversion and >95% yield after 1.5 h of reaction at 95 °C. However, when reused, CaO deactivated due to the contact with air between catalytic runs, and because of particle agglomeration [12].

Hydroxalcalite-based catalysts have been widely employed for the transesterification reaction; Alvarez et al. [26] used MgAl hydroxalcalites supported on α - and γ -Al₂O₃, and also prepared hydroxalcalite-like compounds containing a Mg/Al molar ratio of 4, activated by calcination, followed by rehydration under ultrasounds [27], or by anion exchange (F⁻, Cl⁻, CO₃²⁻) [28]. Also Zheng et al. [29] studied this reaction using MgAl hydroxalcalites with different Mg/Al ratios. The sample with ratio equal to 2 showed 97% of selectivity to GC and 67% of glycerol conversion at 70 °C for 3 h. Yadav et al. [20] studied the effects of various hydroxalcalites with different Mg/Al composition loaded on hexagonal mesoporous silica for this reaction of glycerol, in autoclave at 230 °C for 3 h. They obtained a glycerol conversion of 85% and selectivity to glycerol carbonate between 84 and 88%. Other authors have studied this reaction with ZnO/La₂O₃ mixed oxides [30], Mg/Al/Zr calcined at different temperatures [16], and Mg/Zr/Sr mixed oxide base catalysts [17].

Hydroxalcalite-type compounds belong to the layered double hydroxides family (LDHs) with formula [M(II)_{1-x}M(III)_x(OH)₂][X^{q-}_{x/q}·nH₂O] where [Ca₂Al(OH)₆]⁺ represents the hydroxalcalite layer composition, and [X^{q-}_{x/q}·nH₂O] the interlayer composition [31]. Specifically, the hydroxalcalite name is used when the interlayer anion is chloride. The CaAl-LDH structure collapses at temperatures between 400 °C and 600 °C resulting in the formation of amorphous mixed oxides, Ca(Al)O_x. At higher calcination temperatures crystalline CaO and mayenite (Ca₁₂Al₁₄O₃₃) phases are obtained. These basic mixed oxides have been scarcely used as catalysts for aldol condensation, Meerwein-Ponndorf-Verley or isomerization of 1-butene reactions [32–34].

The aim of this work was to study the effect of the preparation conditions of several calcined Ca/Al hydroxalcalite-type compounds on the catalytic transesterification of glycerol with dimethyl carbonate to obtain glycerol carbonate [35]. The CaAl-LDH precursors have been prepared by aging under microwaves or conventional heating, and using chlorides or nitrates as interlayer anions. Calcination conditions, such as temperature, time and calcination system, have been modified.

2. Material and methods

2.1. Samples preparation

Ten CaAl-LDH samples were synthesized by the co-precipitation method from different starting salts under vigorous magnetic stirring using deionized/decarbonated water, as well as nitrogen atmosphere. Two aqueous solutions containing CaCl₂·2H₂O (sigma-Aldrich, ≥99%) and AlCl₃·6H₂O (Riedel-de Haën, ≥99%) (series HC1) or Ca(NO₃)₂·4H₂O (sigma-Aldrich, ≥99%) and Al(NO₃)₃·9H₂O (sigma-Aldrich, ≥98%) (series HC2), were prepared with a 2:1 Ca²⁺/Al³⁺ molar ratio by adding an aqueous solution of 2 M NaOH (Panreac, QP) at 60 °C and constant pH of 11.5 [36]. After complete addition of the metallic salts, the two mother solutions were aged by several treatments: by refluxing in conventional heating at 60 °C for 24 h (HC1R₂₄ and HC2R₂₄), by refluxing under microwaves (Milestone ETHOS-TOUCH CONTROL, 2.45 GHz) with a power of 400 W at 60 °C for 6 h (HC1RMw₆ and HC2RMw₆), in autoclave by conventional heating at 180 °C for 1 h (HC1AC₁ and HC2AC₁), and in autoclave under microwaves at 180 °C for 1 h (HC1AMw₁ and HC2AMw₁) and for 3 h (HC1AMw₃ and HC2AMw₃) (microwaves power of 600 W). All samples were filtered at room temperature, washed with deionized and decarbonated water and then dried in an oven at 80 °C overnight.

For the preparation of the catalysts, all the hydroxalcalite-type compounds were calcined in a furnace Carbolite CWF11/5P8 at 450 °C for 15 h (cHC1R₂₄, cHC2R₂₄, cHC1RMw₆, cHC2RMw₆, cHC1AC₁, cHC2AC₁, cHC1AMw₁, cHC2AMw₁, cHC1AMw₃, cHC2AMw₃). To determine the influence of the calcination time, and the effect of using a dynamic inert atmosphere system during calcination, one of the CaAl-LDH samples (HC1AMw₃) was calcined 450 °C for 24 h (cHC1AMw₃-24 h), and other sample by flowing nitrogen gas (1 mL/s) at 450 °C for 10 h in a quartz reactor (cHC1AMw₃-N₂). Finally, in order to study the effect of the calcination temperature, several samples were calcined at 750 °C for 4 h (cHC1AC₁-750, cHC1AMw₁-750, cHC1AMw₃-750, cHC2AC₁-750 and cHC2AMw₁-750). Table 1 summarizes the preparation conditions of all samples.

2.2. X-ray diffraction (XRD)

Powder X-ray diffraction patterns of the calcined samples were obtained with a Siemens D5000 diffractometer using nickel-filtered

Table 1
Preparation conditions of calcined CaAl-LDHs.

Sample ^a	Aging conditions of the precursors				Calcination		
	Heating	Technique	T (°C)	Time (h)	T (°C)	Time (h)	System
cHC1R ₂₄	conventional	refluxing	60	24	450	15	static/air
cHC1RMw ₆	microwave	refluxing	60	6	450	15	static/air
cHC1AC ₁	conventional	autoclave	180	1	450	15	static/air
cHC1AMw ₁	microwave	autoclave	180	1	450	15	static/air
cHC1AMw ₃	microwave	autoclave	180	3	450	15	static/air
cHC1AMw ₃ -24	microwave	autoclave	180	3	450	24	static/air
cHC1AMw ₃ -N ₂	microwave	autoclave	180	3	450	10	dynamic/N ₂
cHC2R ₂₄	conventional	refluxing	60	24	450	15	static/air
cHC2RMw ₆	microwave	refluxing	60	6	450	15	static/air
cHC2AC ₁	conventional	autoclave	180	1	450	15	static/air
cHC2AMw ₁	microwave	autoclave	180	1	450	15	static/air
cHC2AMw ₃	microwave	autoclave	180	3	450	15	static/air
cHC1AC ₁ -750	conventional	autoclave	180	1	750	4	static/air
cHC1AMw ₁ -750	microwave	autoclave	180	1	750	4	static/air
cHC1AMw ₃ -750	microwave	autoclave	180	3	750	4	static/air
cHC2AC ₁ -750	conventional	autoclave	180	1	750	4	static/air
cHC2AMw ₁ -750	microwave	autoclave	180	1	750	4	static/air

^a **HC1**: Chloride salts, **HC2**: Nitrate salts.

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