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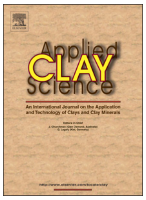

CaAl-layered double hydroxides as active catalysts for the transesterification of glycerol to glycerol carbonate

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ABSTRACT

Several hydrocalumite-type materials (CaAl-LDHs) were prepared by precipitation using nitrate or chloride salts with and without ultrasound, and aged hydrothermally in autoclave or by refluxing with and without microwaves. These samples were tested as catalysts for the transesterification of glycerol with dimethyl carbonate to glycerol carbonate. After 3 h of reaction, all catalysts showed high glycerol conversion (70–84%) and moderate selectivity values to glycerol carbonate (52–65%) accompanied by the formation of low amounts of glycidol (7–15%). These results are very interesting taking into account the low specific surface area of these catalysts (7–25 m^2/g). No significant catalytic differences were observed between the catalysts. This can be due to the similar surface and basic characteristics observed for all of them. By increasing the reaction time, an increase of conversion was observed arriving practically to total conversion after 24 h of reaction, with selectivity to glycerol carbonate in the range 65–75%. Several catalytic reuses favoured the decarboxylation of glycerol carbonate resulting in the formation of higher amounts of glycidol (30%) but still maintaining high selectivity values to glycerol carbonate (70%).

1. Introduction

Biofuels, derived from renewable raw materials, emerged as an alternative to overcome the environmental problems associated with the use of fossil fuels. During the production process of biodiesel, by transesterification of vegetable oils with methanol in the presence of basic catalysts, glycerol is formed as by-product in high amounts (10 mass% of the total product) (Pagliaro et al., 2007). The price of glycerol is falling as fast as biodiesel plants are being built. Thus, it is necessary to find new outlets to convert the surplus of glycerol into high added-value products that improve the economy of the whole process (D'Aquino and Ondrey, 2007; Pagliaro et al., 2007, 2009; Barrault and Jerome, 2008; Behr et al., 2008; Rahmat et al., 2010; Sonnati et al., 2013).

One challenging option is to obtain glycerol carbonate, (4-hydroxymethyl-1,3-dioxolan-2-one), which is a relatively new product in the chemical industry with a large potential due to its low toxicity, good biodegradability and high boiling point (Teng et al., 2014). Glycerol carbonate is a green substitute for important petro-derivative compounds such as ethylene carbonate or propylene carbonate (Shieh et al., 2002). Additionally, this compound has diverse applications in different industrial sectors. It is used as intermediate compound in organic synthesis (e.g. as monomer in the synthesis of polycarbonates, polyurethanes and polyglycerols) (Shieh et al., 2002; Barrault and Jerome, 2008; Behr et al., 2008; Zhou et al., 2008; Pagliaro et al., 2009; Rahmat et al., 2010; Sonnati et al., 2013; Teng et al., 2014), as biolubricant, due to its ability to adhere to metals and to its resistance to oxidation, hydrolysis and pressure (Pagliaro et al., 2007), as raw material of gas separation membranes, coatings and polyurethane foams (Randall and De Vos, 1991) and as surfactants (Weuthen and Hees, 1995), among other applications. Glycerol carbonate could also serve as raw material in the production of glycidol (Yoo et al., 2001), which is widely used in the textile, plastics, pharmaceutical and cosmetics industries.

Traditionally, glycerol carbonate was industrially 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). Studies were carried out on the synthesis of glycerol carbonate from glycerol and urea over zinc-containing homogeneous catalysts (Fujita et al., 2013); and over heterogeneous catalysts such as gold (Hammond et al., 2011), lanthanum oxide (Wang et al., 2011), hydrotalcite (Climent et al., 2010), tin-tungsten mixed oxides (Jagadeeswaraiah et al., 2014), and more recently, polymer-supported metal containing ionic liquid catalysts (Kim et al., 2014). High glycerol conversion and high glycerol carbonate selectivity values were achieved. However, the reaction of glycerol with urea must be

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conducted at pressures below 20–30 mbar in order to separate gaseous ammonia and avoid the formation of undesirable products such as isocyanic acid and biuret.

An alternative 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 is preferred since the reaction can be performed at milder conditions and the co-product methanol can be easily separated. Ochoa-Gómez et al. (2009) studied the influence of 12 different basic and acid homogeneous and heterogeneous catalysts, at different reaction conditions. The best results were obtained using basic heterogeneous catalysts. CaO catalyst led to 94.3% of glycerol conversion and 94% of yield to glycerol carbonate at 75 °C after 30 min of reaction. However, catalytic activity of CaO was strongly dependent on its purity, and catalyst deactivation occurred because of the formation of $Ca(OH)_2$ or $CaCO_3$ by the reaction of CaO with air (Ochoa-Gómez et al., 2009). Another study using CaO as catalyst revealed that at DMC/glycerol molar ratios less than 2, there was a leaching of calcium leading calcium species in the reaction mixture that act in a homogeneous (Simanjuntak et al., 2011). Hydrotalcite-based catalysts have been widely employed for this reaction (Takagaki et al., 2010; Malyaadri et al., 2011; Kumar et al., 2012; Parameswaram et al., 2013; Liu et al., 2014, 2015; Yadav and Chandan, 2014). In the first studies, uncalcined Mg/Al hydrotalcites with co-existent hydromagnesite phase were found to be active catalysts for this reaction but the use of a harmful solvent (N,N-dimethyl formamide) was necessary (Takagaki et al., 2010; Kumar et al., 2012). Calcined Mg/Al/Zr (Malyaadri et al., 2011), calcined Mg/Zr/Sr (Parameswaram et al., 2013) and doping transition metals cations into Mg/Al hydrotalcites (Liu et al., 2014) have been also tested as catalysts for this transesterification reaction resulting in yields to glycerol carbonate between 55–94% at reaction temperatures in the range 75–100 °C. More recently, Liu et al. (2015) reported full conversion of glycerol and 96% yield of glycerol carbonate at 80 °C for 1.5 h in the presence of $Li/Mg_4AlO_{5.5}$ obtained by impregnating calcined Mg/Al hydrotalcite with $LiNO_3$. Finally, Yadav and Chandan (2014) performed this reaction in autoclave at 170 °C for 3 h obtaining conversion values around 85% and selectivity to glycerol carbonate values between 84 and 88% when using Mg/Al hydrotalcites supported on hexagonal mesoporous silica as catalysts.

Hydrocalumite-type compounds belong to the layered double hydroxides family (LDHs) with formula $[M(II)_{1-x}M(III)_x(OH)_2][X_q^{-x/q}\cdot nH_2O]$ where $[Ca_2Al(OH)_6]^+$ represents the hydrocalumite layer composition, and $[X_q^{-x/q}\cdot nH_2O]$ the interlayer composition (Segni et al., 2006). Specifically, the hydrocalumite name is used when the anion is chloride. Hydrocalumites have been widely used in the immobilization of toxic cations (Zhou et al., 2011), optimization of concrete properties (Matschei et al., 2007), but in less extent, for catalysis (Cota et al., 2010) although the presence of Ca^{2+} instead of Mg^{2+} into the layers can provide interesting basic properties. These materials are mainly used as catalysts in their calcined forms, but hydrocalumite-type compounds have not been practically studied as catalysts. In recent years, the use of microwaves for the synthesis or modification of materials is becoming an important tool to decrease the synthesis time, with the subsequent energy saving. It is also useful to modify the sample properties, which can be of interest for catalysis (Bergadà et al., 2007; González et al., 2009, 2011; Vicente et al., 2010; Sánchez et al., 2013). Additionally, ultrasound is another interesting technique to improve the synthesis of materials since, when used for the mixing of reagents, allows obtaining materials with more homogeneous composition (Suslick, 1990; Vicente et al., 2010; Sánchez et al., 2013).

The aim of this work was to evaluate the suitability of several non-doped uncalcined hydrocalumite-type compounds, synthesized using microwaves and ultrasound, as catalysts for the transesterification of glycerol with dimethyl carbonate to obtain glycerol carbonate. Special attention was paid to study the reusability of the catalyst.

2. Experimental

2.1. Preparation of catalysts

Hydrocalumite-type compounds were synthesized by the co-precipitation method from different starting salts: chlorides (series HC1) or nitrates (series HC2). Two different aqueous solutions containing $CaCl_2\cdot 2H_2O$ (Sigma-Aldrich) and $AlCl_3\cdot 6H_2O$ (Riedel-de Haën) or $Ca(NO_3)_2\cdot 4H_2O$ (Sigma-Aldrich) and $Al(NO_3)_3\cdot 9H_2O$ (Sigma-Aldrich) were prepared with a 2:1 Ca^{2+}/Al^{3+} molar ratio. These solutions were added dropwise to a 500 ml four neck round-bottom flask in an oil bath at 60 °C previously filled with 250 ml of a mixture of water/ethanol in a 2:3 volumetric ratio. The pH was kept constant at 11.5 ± 0.1, by the simultaneous addition of an aqueous solution of 2 M NaOH (Panreac). Magnetic stirring or ultrasound was used for mixing during precipitation. After complete addition of the metallic salts, the mother solutions were aged by several treatments using microwaves or conventional heating, refluxing or autoclave at different conditions. Finally, all samples were filtered at room temperature, washed with deionized and decarbonated water and then dried in an oven at 80 °C overnight. Table 1 describes the nomenclature used to name all these samples, and summarizes the preparation conditions employed.

2.2. Characterization methods

Powder X-ray diffraction patterns of the samples were obtained using a Siemens D5000 diffractometer with nickel-filtered CuKα radiation and $\lambda = 1.45$ Å. CuKα radiation was generated in a X-ray copper tube, operating at 40 kV and 30 mA. Data were collected with 2θ values ranging between 5° and 70°, with an angular measurement of 0.05°, for 3 s in simple rotation. Crystalline phases were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) files (035-0105 — Calcium aluminium hydroxide chloride hydrate-$Ca_2Al(OH)_6Cl\cdot 2H_2O$, 089-6723 — Calcium Aluminun Nitrate Hydroxide Hydrate-$Ca_2Al(OH)_6NO_3\cdot 2H_2O$, 089-0217 — Katoite-$Ca_3Al_2(OH)_{12}$ and 086-2341 — calcite-$CaCO_3$).

Elemental analysis of the samples was obtained with an ICP-OES analyser (Induced Coupled Plasma–Optical Emission Spectroscopy) from Spectro Arcos. The digestion of all hydrocalumites was carried out with concentrated HNO_3. Analyses were performed by triplicate.

BET specific 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 nm^2 for the cross-section of the nitrogen molecule. Samples were degassed at 90 °C.

Infrared spectra were recorded on a NICOLET 380 FI-IR spectrometer. Spectra were acquired by accumulating 100 scans at 2 cm^{-1}

Table 1
Aging treatments of the precipitated samples.

Sample	Ultrasound[a]	Aging			
		Heating	Technique	T (°C)	Time (h)
$HC1R_{24}$	No	Conventional	Refluxing	60	24
$HC1RMw_6$	No	Microwaves	Refluxing	60	6
$HC1USR_{24}$	Yes	Conventional	Refluxing	60	24
$HC1USRMw_6$	Yes	Microwaves	Refluxing	60	6
$HC1AC_1$	No	Conventional	Autoclave	180	1
$HC1AMw_1$	No	Microwaves	Autoclave	180	1
$HC1AMw_3$	No	Microwaves	Autoclave	180	3
$HC2R_{24}$	No	Conventional	Refluxing	60	24
$HC2RMw_6$	No	Microwaves	Refluxing	60	6
$HC2USR_{24}$	Yes	Conventional	Refluxing	60	24
$HC2USRMw_6$	Yes	Microwaves	Refluxing	60	6
$HC2AC_1$	No	Conventional	Autoclave	180	1
$HC2AMw_1$	No	Microwaves	Autoclave	180	1
$HC2AMw_3$	No	Microwaves	Autoclave	180	3

[a] During precipitation.

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