

# Influence of acid–base properties of calcined MgAl and CaAl layered double hydroxides on the catalytic glycerol etherification to short-chain polyglycerols

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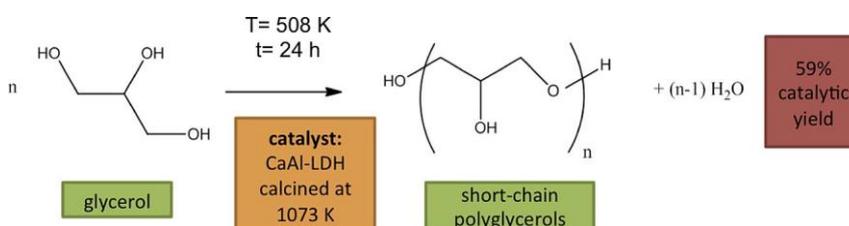
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## h i g h l i g h t s

- One-pot etherification reaction of glycerol towards short-chain polyglycerols.
- Calcined MgAl-LDH and calcined CaAl-LDH were used as catalysts.
- Basicity and acidity of the catalysts influenced the catalytic results.
- Stronger basic sites and lower acidity favoured short-chain polyglycerols.
- Higher temperature of calcination favoured a higher degree of polymerisation.

## g r a p h i c a l a b s t r a c t



## a b s t r a c t

Several MgAl-LDHs (HT) and CaAl-LDHs (HC) were synthesized in different conditions and later calcined at 723 K, resulting in catalysts (cHT and cHC), with different acid–base properties. Calcined samples were tested in the etherification reaction of glycerol towards short-chain oligomers (di- to pentaglycerol). All catalysts were characterised by XRPD, ICP, N<sub>2</sub> physisorption and TEM techniques. The basicity was evaluated using the CO<sub>2</sub>-TPD technique and the acidity by cyclohexylamine adsorption. Catalytic results were correlated with catalysts properties. Catalysts with higher acidity showed higher conversion (96% for a cHT and 75% for a cHC) but also higher selectivity to other products, with main contribution of acrolein (88% for a cHT and 58% for a cHC). In contrast, catalysts with lower acidity resulted in lower conversion (24% for a cHT and 40% for a cHC) but higher selectivity towards di- and triglycerol (100% and 64%, respectively). The formation of triglycerol and other low-weight polyglycerols (tetra- and pentaglycerol) was favoured in catalysts with low acidity and strong basic sites. When the temperature of calcination was raised to 1073 K for one cHC, the acidity decreased and the number of strong basic sites increased, resulting in higher selectivity to triglycerol (20%), the formation of tetra- and pentaglycerol (15% and 6%, respectively) and the decrease of the acrolein amount.

### Keywords:

Glycerol etherification  
Short-chain polyglycerol  
CaAl layered double hydroxides  
MgAl layered double hydroxides  
Acid–base properties

## 1. Introduction

Glycerol (1,2,3-propanetriol) has gained increasing attention from the big expansion of biodiesel industry since it is obtained

as by-product (10 wt%) in the transesterification of vegetable oils with methanol or ethanol. The use of glycerol as raw material has industrial applications in food, cosmetic and tobacco industries amongst others, but in the last years there is a glycerol surplus in the market and, consequently, its price has fallen dramatically [1,2]. Considering that glycerol is a highly functionalized molecule, an important number of compounds can be obtained using glycerol as a starting building block [1–6].

The catalytic oligomerization of glycerol to di- and triglycerol and other low-weight polyglycerols, as they are usually called, have a remarkable presence in published literature but especially notorious is the number of registered patents [4,7–9]. Low-weight polyglycerols have wide applications in cosmetics, food, polymer and plastic industry [5,10,11]. When reactions are performed at temperatures higher than 493 K, double dehydration of glycerol can lead to acrolein, a secondary undesired and toxic product [1–3].

Traditionally, the industrial process uses epichlorohydrin as starting material for the production of oligoglycerols [12,13]. Unfortunately, there are many purification steps; overall, it is an expensive process. Catalytic etherification of glycerol can be an interesting alternative to obtain oligoglycerols although is a rather complex reaction to control the oligomerization degree, which can be catalysed by basic and acid sites [14]. However, acid sites also can catalyse acrolein formation [3]. Different homogeneous and heterogeneous catalysts have been tested for this reaction.

The use of homogeneous  $\text{Na}_2\text{CO}_3$  led to high conversion (87.5%) and selectivity towards di- and triglycerol of 50% and 26%, respectively at 533 K [15]. When testing LiOH, NaOH, KOH catalysts, the best results were found for LiOH catalyst with total conversion and selectivity to diglycerol of 33% at 513 K after 6 h of reaction [16]. Richter and co-workers achieved full conversion with catalyst  $\text{C}_6\text{H}_5\text{CO}_3$  at 533 K after 24 h of reaction [17]. Total selectivity towards diglycerol was achieved at low glycerol conversion (between 10% and 20%), depending on the amount of catalyst used.

Clacens and Barrault used microporous and mesoporous solids exchanged or impregnated with different elements (Cs, La, Mg) [15,18–20]. The most significant result yielded selectivity values to di- and triglycerol of 62% and 33%, respectively, for a 79% of conversion at 533 K after 24 h for the caesium-based mesoporous catalyst. Recently, Barrault et al. tested several materials with Mg incorporated in the structure in order to avoid Mg leaching: Mg-MCM-41 in a pilot scale, and Mg-clays in a lab scale. Bulk and supported MgO were also tested for comparison [21]. (Di- + tri-)glycerol selectivity and conversion values did not change after scale up when using MCM-41 powder catalysts (70% and 100%, respectively at 533 K after 20 h of reaction) whereas Mg-clays presented high selectivity towards (di- + tri-)glycerols (80%) for a conversion of 85% at 533 K after 7 h of reaction. The use of MgO led to high conversion (77% at 533 K after 4 h of reaction), but inactive magnesium glyceroxide was identified in the catalyst after reaction. The same behaviour was observed when using CaO and BaO. In general, the use of Mg-containing catalysts resulted in a higher degree of polymerisation, since (tetra + penta)glycerol selectivity was detected for these catalysts (between 15% and 21%) [21].

Ruppert et al. performed the reaction at 493 K using basic metal oxides [22]. They found that conversion increased with basicity but also Lewis acidity was involved in the mechanism. Maireles-Torres et al. used calcined Mg/Al and Mg/Fe layered double hydroxides [23,24]. The highest conversion (50%) was found for a catalyst prepared using  $\text{NaOH}/\text{Na}_2\text{CO}_3$  as precipitant agent, with selectivity to di- and triglycerol of 85% and 15%, respectively at 493 K after 24 h of reaction. Regarding Mg/Fe calcined layered double hydroxides, the best result was obtained for the catalyst with a molar ratio of 4, achieving total selectivity towards di- + triglycerol at a conversion around 40%. More recently, Abdullah and co-workers obtained 53% and less than 25% of selectivity towards di and triglycerol,

respectively, for a conversion of 98% at 513 K for 12 h using calcined LiOH-modified montmorillonite [25,26]. These authors also reported a selectivity of 74% to di + triglycerol for a conversion of 91% at 523 K for 8 h using Ca–La oxide supported on MCM-41 although some metal leaching was observed [27].

Layered double hydroxides (LDH) have general formula  $[\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}\cdot m\text{H}_2\text{O}$ , where M(II) and M(III) are divalent and trivalent metals of positively charged layers and  $\text{A}^{n-}$  the anion that in the interlayer space neutralizes the positive charge. These compounds are also known as hydrotalcites-like compounds, being the most representative the hydrotalcite mineral  $(\text{Mg}_6\text{Al}_2(\text{OH})_{16}\cdot\text{CO}_3\cdot 4\text{H}_2\text{O})$ . When M(II) is  $\text{Ca}^{2+}$ , the compounds are included in a subgroup known as hydrocalumite group, in which the most representative compound is the hydrocalumite mineral  $\text{Ca}_2\text{Al}(\text{OH})_6\cdot\text{Cl}\cdot 3\text{H}_2\text{O}$ . On the whole, they have basic characteristics whilst the mixture of the oxides obtained after their calcination present interesting acid–base properties [28,29] and applications, as widely reported [30–34]. The use of microwave heating for the ageing treatment in the synthesis and modification of materials such as zeolites, clays and hydrotalcites-like compounds increases crystallinity and modifies their properties, apart from saving costs of time and energy during their preparation [35–38]. In general, hydrotalcites-like compounds are extensively reported in the literature. However, compounds of the hydrocalumite group are less reported. The stronger basicity of calcined LDHs with Ca and Al (CaAl-LDHs), when compared to calcined LDHs with Mg and Al (MgAl-LDHs), and the presence of Lewis acidity make them promising catalysts for the glycerol oligomerization.

The aim of this work was to test a series of calcined layered double hydroxides for the etherification reaction of glycerol towards short-chain polyglycerols (diglycerol (DG), triglycerol (TG), tetraglycerol (TTG) and pentaglycerol (PG)) (Scheme 1). The differences between catalysts were obtained using (a) MgAl-LDHs or CaAl-LDHs as catalytic precursors; (b) precursors prepared by modifying synthesis conditions; (c) CaAl-LDHs calcined at different temperatures (723, 923 and 1073 K). The acid–base properties of the catalysts have been studied and correlated with their catalytic activity.

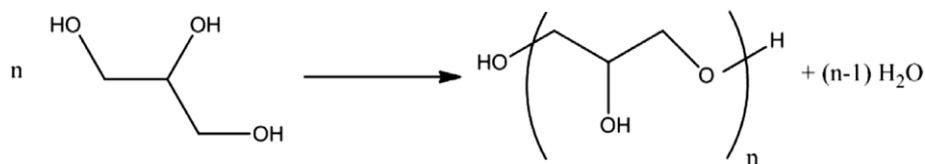
## 2. Experimental

### 2.1. Chemicals

Precursor salts  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (P98%),  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  (P98%),  $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$  (P99%), acidic test reagent cyclohexylamine (P98%), silylating reagents hexamethyldisilazane (P99%), chlorotrimethylsilane (P98), methyl laureate (P97%) and standard triglycerol (P80%) were purchased from Sigma–Aldrich. Precursor salt  $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$  (P98%) was ordered from Riedel-de Haën. Standards for chromatographic analysis diglycerol, polyglycerol-3 (considered pentaglycerol content of 8%) and polyglycerol-4 (considered tetraglycerol content of 40%) were provided from Solvay. Ethanol (absolute PBS), ammonia (sol. 28%), NaOH (P99%),  $(\text{NH}_4)_2\text{CO}_3$  (P30.0%  $\text{NH}_3$  basis), pyridine (P98%), methanol (P99%) and glycerol (P99.3%) were purchased from VWR Prolabo or Panreac. Bottled gases hydrogen (99.99%), helium (99.99%), air (99.99%), argon (99.99%) and  $\text{CO}_2$  (99.995%) were purchased from Carbueros Metálicos or Praxair.

### 2.2. Catalysts preparation

MgAl-LDHs were prepared by the well-known co-precipitation at low supersaturation method, at room temperature and at constant pH (pH = 10). Aqueous solutions containing in appropriate amounts  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  with a 2 M  $\text{NH}_3$  titrat-



Scheme 1. Glycerol etherification scheme reaction.

ing solution were simultaneously added to an aqueous solution of 0.0178 M  $(\text{NH}_4)_2\text{CO}_3$  under stirring. The Mg/Al ratio used was 3:1.

CaAl-LDHs were synthesized by co-precipitation method [39] with a Ca/Al ratio of 2:1. In a typical synthesis, a solution of 250 ml ethanol/decarbonized water mixture (2:3 v/v) was placed in a 500 ml 4-neck round-bottom flask in an oil bath at 338 K. A 100 ml solution with the salts was prepared mixing the appropriate amounts of 0.66 M  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and 0.33 M  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  solutions. A solution of 2 M NaOH was used to keep constant pH at 11.5 during precipitation. The pH electrode and the two compensated pressure funnels for addition of the salts and the NaOH solution, respectively, were connected to 3 of the necks of the round-bottom flask. A vigorous magnetic stirring and  $\text{N}_2$  bubbling through the fourth neck, to prevent from the formation of the calcite phase ( $\text{CaCO}_3$ ) were maintained during precipitation.

After complete precipitation of the salts, all gels were aged using microwave irradiation (Milestone Ethos-Touch Control) or conventional heating and in autoclave or reflux at different temperatures and times (Table 1). Samples were filtered, washed several times with decarbonized and deionized water and dried in an oven at 353 K overnight. Samples were named starting with the letters HT or HC, corresponding to MgAl-LDHs or CaAl-LDHs, respectively, followed by a number to differentiate each sample. Finally, the calcination temperature is added after the forward slash symbol (Table 1).

For the catalytic tests all samples were calcined in a muffle furnace (Carbolite CWF 1100) at 723 K for 15 h (heating rate 10 K/min). Calcined samples are called by adding a c letter before the name of the catalyst precursor.

Additionally, in order to study the effect of the calcination temperature one hydrocalumite, sample HC4 was calcined at 923 K and 1073 K, at the same furnace conditions as described before. These catalysts are named cHC4/923 and cHC4/1073, respectively.

### 2.3. Samples characterisation

XRPD (X-ray powder diffraction) measurements were made using a Siemens D5000 diffractometer (Bragg–Brentano parafocusing geometry and vertical–goniometer) fitted with a curved graphite diffracted-beam monochromator and diffracted-beam Soller slits, a  $0.06^\circ$  receiving slit, and scintillation counter as a detector. The angular  $2\theta$  diffraction range was between  $5^\circ$  and  $70^\circ$ . Sample was dusted on to a low background Si(5 1 0) sample holder. The data were collected with an angular step of  $0.05^\circ$  at 3 s per step

and sample rotation. CuK $\alpha$  (1.541 Å) radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA. In order to compare the results, JCPDS (Joint Committee on Powder Diffraction Standards) files were used to identify the phases.

Mg/Al and Ca/Al ratios were analysed in an ICP–OES analyser (Induced Coupled Plasma–Optical Emission Spectroscopy) from Spectro Arcos. Calcined samples powders (50 mg) were solubilised with  $\text{HNO}_3$  of 60 wt% (2 ml), heated if necessary, brought to 25 ml volume and finally 1 ml of the solution was diluted into 25 ml. Standards were used to perform calibration curves. All samples were analysed by triplicate.

EDX microanalysis were recorded using a JEOL 6400 electron microscope (3.5 nm resolution at 30 kV) fitted with an energy-dispersive X-ray spectrometer (Inca-Energy, Oxford Instruments) and Si(Li) detector with 1.38 eV energy resolution. From the results, Cl/Al atomic ratio was determined for all catalysts.

Brunauer–Emmet–Teller (BET) theory was applied to calculate total specific surface areas from the nitrogen adsorption isotherms at 77 K (Quantachrome Quadrasorb SI, sensitivity of the instrument is  $0.01 \text{ m}^2/\text{g}$ ). Samples, between 0.2 and 0.3 g, were previously degassed under vacuum at 423 K (Quantachrome FloVac Degasser) for 24 h.

Transmission electron microscope (TEM) images were collected using a JEOL 1011 Transmission Electron Microscope operating at 80 kV and magnification values of 12–60 k. Samples were dispersed in ethanol, and a drop of resultant suspensions was poured on carbon coated-copper grids.

TPD analysis (Belcat-M, Bel Japan Inc) was performed after activating the calcined sample (0.08 g) at 723 K for 1 h to eliminate adsorbed water. The desorption process was recorded from 313 K to the temperature at which they were previously calcined, at 10 K/min after saturation of the sample with  $\text{CO}_2$ . Argon was used as carrier gas during activation and desorption steps. TPD tests were also performed without previous adsorption of  $\text{CO}_2$  for comparison.

Surface acidity was determined through cyclohexylamine adsorption followed by thermogravimetric analyses [40]. All samples were stored in a desiccator to avoid water adsorption. 100 mg of the catalyst were placed in a crucible. Cyclohexylamine was dropped with a Pasteur pipette until the liquid covered the solid particles. The crucible was sealed with parafilm but for a small overture and kept overnight inside a fume hood. Then, the mixture was heated in a furnace muffle at 523 K for 2 h, 50 mg of the mixture were then analysed by thermogravimetric analysis (Setaram, Labsys TG DTA/DSC) from 303 to 1123 K at 10 K/min

Table 1  
Ageing conditions of the catalysts precursors: MgAl-LDHs and CaAl-LDHs.

Nomenclature	Heating	Recipient	Temperature (K)	Time (h)
	Conventional/microwaves			
HT1	Conventional	Reflux	333	18
HT2	Microwaves	Autoclave	453	1
HC1	Conventional	Reflux	333	24
HC2	Conventional	Reflux	353	3
HC3	Microwaves	Reflux	353	3
HC4	Microwaves	Autoclave	453	1

under N<sub>2</sub> flow. The same test, without cyclohexylamine, was performed for every calcined sample, in order to subtract any mass loss due to decomposition. The mass loss can be associated to the chemisorbed cyclohexylamine. Results were indicated as mmol of cyclohexylamine chemisorbed per gram of catalyst. The temperature of cyclohexylamine desorption was calculated from the first derivative graph and used to compare the acidity strength of the samples.

#### 2.4. Catalytic tests

Glycerol etherification was performed at 508 K in a topaz 50 ml three-neck glass reactor, under N<sub>2</sub> atmosphere in the presence of 2 wt% catalyst under magnetic stirring. In a typical experiment, 28 g of glycerol was used. No solvent was needed. Water and acrolein were collected using a Dean–Stark system. The presence of acrolein was qualitatively checked by gas chromatography. Samples were analysed after 24 h of reaction, as seen in most of the published literature referenced in the introduction, using a gas chromatograph (Shimadzu GC-2010), equipped with autoinjector (AOC-20i) (513 K), FID detector (613 K) and capillary column HT5 (SGE forte) (from 373 to 563 K at 1 K/min). Before analysis, samples were derivatized through silylation reaction. 0.04 g of sample was introduced into a test tube. Silylating reagents hexamethyldisilazane, chlorotrimethylsilane and pyridine were added with a ratio 3:1:9 in excess. The solution was centrifuged (JP Selecta) for 5 min at 700 rpm, and then left the precipitate to settle for 30 min. An aliquot of 1000  $\mu$ L was introduced into a vial without solvent for its analysis. Methanol was used to clean the column. In order to determine conversion and selectivity, 100  $\mu$ L of methyl laureate was added as internal standard. Results were compared to calibration standards of the reagent and products.

The following are the equations used to calculate glycerol conversion (1) and polyglycerol selectivity values (2):

$$X_{\text{glycerol}} \text{ (\%)} = \frac{n_o - n_f}{n_o} \cdot 100 \quad (1)$$

where  $n_o$  is the initial amount of glycerol mols and  $n_f$  is the final amount of glycerol mols,

$$S \text{ (\%)} = \frac{X - n_d}{n_o - n_f} \cdot 100 \quad (2)$$

where  $X$  is the stoichiometric constant with the following range of values: 2 for diglycerol, 3 for triglycerol, 4 for tetraglycerol and 5 for pentaglycerol;  $n_d$  is the amount of polyglycerol mols,  $n_o$  is the initial amount of glycerol mols and  $n_f$  is the final amount of glycerol mols.

Catalytic yield was calculated as follows (3):

$$Y \text{ (\%)} = \frac{X_{\text{glycerol}} \cdot X}{100} \cdot S \quad (3)$$

where  $X_{\text{glycerol}}$  is glycerol conversion and  $RS$  the sum of short-chain polyglycerol selectivity values.

### 3. Results and discussion

#### 3.1. Catalysts characterisation

##### 3.1.1. Calcined MgAl layered double hydroxides

The two calcined MgAl-LDHs presented similar XRPD patterns. Fig. 1 shows a representative diffractogram corresponding to calcined HT cHT2/723. The peaks associated to the HT precursor disappeared. The only crystalline phase identified was periclase (MgO, JPCDS 89-4248) with a low degree of crystallinity since the peaks were quite broad. The peaks showed a certain shift compared to the pattern. This fact that can be related to the presence of mixed oxides Mg(Al)O<sub>x</sub>. However, some differences were observed in the

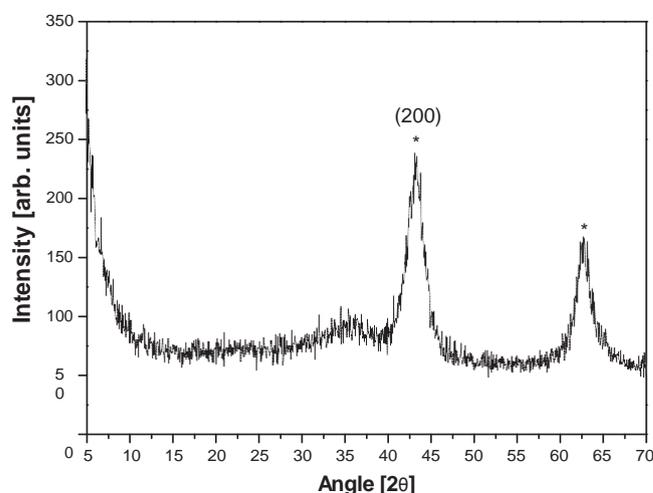


Fig. 1. XRPD of catalyst cHT2/723. (\*): MgO.

values of FWHM, measured from the reflection (2 0 0), resulting in values of 2.43° and 1.91° for samples cHT1/723 and cHT2/723, respectively. Therefore, some increase of crystallite size was obtained for the catalyst, the HT precursor of which, was aged at 453 K for 1 h with microwave irradiation.

Elemental analysis showed that the Mg/Al ratio for all calcined HC was close to 3 in agreement with the expected stoichiometry (Table 2).

BET specific surface areas of calcined HTs were high (237 and 188 m<sup>2</sup>/g, Table 2) due to the release of H<sub>2</sub>O and CO<sub>2</sub> gases during HTs calcination with generation of porosity and disaggregation/breaking of the lamellae that involve the formation of small crystallites with mesoporosity, as previously reported [36,41]. Catalyst cHT2/723 had lower BET specific surface area than cHT1/723 (Table 2) according to their higher crystallite size, as observed by XRPD.

##### 3.1.2. Calcined CaAl layered double hydroxides

The diffractograms corresponding to samples obtained after calcination of CaAl-LDHs at 723 K were similar. The diffractogram of sample cHC4/723 (Fig. 2a), which can be considered representative for the HCs calcined at 723 K, corresponded to a very amorphous material. However, a low intense peak, identified as calcite phase (CaCO<sub>3</sub>, JPCDS file 072-1652), was observed. The appearance of calcite can be attributed to the calcination conditions in static air. In order to see the effect of calcination temperature, sample HC4 was also calcined at 923 and 1073 K. For the catalyst obtained by calcination at 923 K (cHC4/923) a new crystalline phase, identified as mayenite (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, JPCDS file 48-1882), was observed in the diffractogram (Fig. 2b). This is in agreement with the results previously reported for hydrocalumite decomposition between 873 and 973 K [42]. It was also possible to identify calcite phase for this catalyst, although with less intensity than in cHC4/723 since carbonate decomposition takes place from 873 K. When the temperature of calcination was raised to 1073 K (Fig. 2c), it was possible to identify a mixture of mayenite and lime (CaO, JPCDS 04-0777). If we compare the peaks of mayenite for samples cHC4/923 and cHC4/1073, peaks were broader for sample cHC4/923, due to its lower calcination temperature, since mayenite was completely crystallized at 1073 K.

Elemental analysis showed that the Ca/Al ratio was close to 2 for all calcined samples (Table 2). Therefore, using different ageing treatments in the preparation of hydrocalumites, it was possible to obtain catalysts with the expected stoichiometry.

Table 2  
Catalysts characterisation results.

Catalysts	ICP Mg/Al Ca/Al	BET specific surface area (m <sup>2</sup> /g)	mmol cyclohexylamine/g catalyst	Temperature of cyclohexylamine desorption (K)	Chloride content (Cl/Al) atomic ratio
cHT1/723	3.00 <sup>/</sup>	237	0.79	971	–
cHT2/723	3.00 <sup>/</sup>	188	0.15	978	–
cHC1/723	1.99 <sup>/</sup>	15	0.53	1077	0.94
cHC2/723	1.94 <sup>/</sup>	22	0.18	1070	0.72
cHC3/723	2.00 <sup>/</sup>	6	0.45	1077	0.92
cHC4/723	1.84 <sup>/</sup>	3	0.27	1084	1.02
cHC4/923	1.84 <sup>/</sup>	5	0.12	1053	0.56
cHC4/1073	1.84 <sup>/</sup>	3	<0.10	1044	0.46

<sup>/</sup> Mg/Al ratio  
<sup>/</sup> Ca/Al ratio

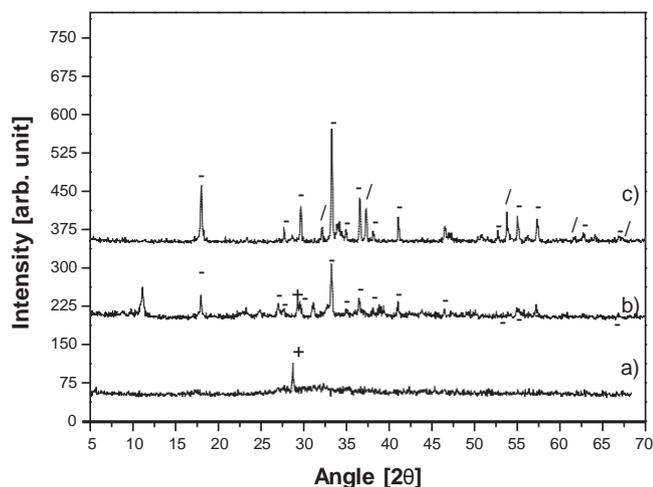


Fig. 2. XRPD of catalysts (a) cHC4/723, (b) cHC4/923, (c) cHC4/1073. (+): CaCO<sub>3</sub>, (-): Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, (/): CaO.

BET specific surface areas were lower (between 3 and 22 m<sup>2</sup>/g) than those of calcined HT (Table 2). This is surprising considering the amorphous character of the samples calcined at 723 K. However, it is important to take into account that at 723 K, dehydroxylation (loss of water) and anion decomposition (loss of chloride) is partial [29] compared to HTs [43]. This can explain their lower BET specific surface area values. However, as previously observed for cHTs, cHCs, the precursors of which were aged using microwave irradiation [44], presented lower values of BET specific surface area (Table 2). The lowest value was obtained for cHC4/723 (3 m<sup>2</sup>/g). In fact, the HC4 precursor of this sample presented the highest decomposition temperatures in the TGA analysis [44]. In this previous work, we reported that the precursors HC1, HC2 and HC3 presented lower temperatures of dehydroxylation than sample HC4. This involves a higher amount of OH<sup>-</sup> and Cl<sup>-</sup> in sample cHC4/723. These species favour interactions between crystallites, favouring agglomeration and consequently the decrease of surface area.

By increasing the temperature of calcination at 923 K, the specific surface area increased from 3 to 5 m<sup>2</sup>/g. In contrast, when the temperature of calcination was 1073 K, the value was again 3 m<sup>2</sup>/g. In fact, a certain decrease of the specific surface area should be expected for the sample calcined at higher temperature due to crystallization and sinterization processes [42]. However, the differences between specific surface areas were irrelevant.

After calcination, all catalysts presented differentiated lamellae, which remind the structure of layered double hydroxide precursors. Figs. 3 and 4a show the TEM micrographies of one HT and one HC calcined at 723 K, respectively. The sizes of particles of both

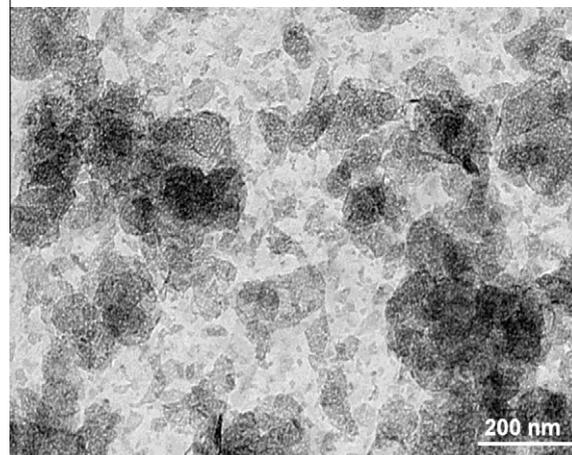


Fig. 3. TEM micrographies of catalyst cHT2/723.

materials differ enormously. Whilst cHT had sizes of less than 100 nm, the particle sizes of cHC were in the range of micrometres. These values agree with the lower BET specific surface area values observed for calcined hydroxaluminates. TEM micrographies of cHC4/923 and cHC4/1073 (Fig. 4b and c, respectively) showed smaller lamellae compared to Fig. 4a as a consequence of lamellae breakings during anion decomposition, together with a higher degree of agglomeration.

The different ageing conditions used for MgAl and CaAl layered double hydroxides synthesis led to differences in the textural properties of the calcined samples, probably related to differences of their decomposition temperatures, studied in a previous work [44]. These differences could also affect the amount of basic and acid sites.

### 3.2. Acid–basic properties

In order to correlate the catalytic behaviour of the synthesized catalysts with their acid–base properties, a study of these properties was performed. The results are shown in Tables 2 and 3.

#### 3.2.1. Basicity determination

Table 3 shows the maximum CO<sub>2</sub>-desorption temperature peaks of calcined HTs. One peak at low temperature (T<sub>max</sub> around 368 K), corresponding to weak basic sites, was obtained for both samples. An additional less-intense peak, associated with medium basic sites, appeared at 598 for cHT1/723 and at 648 K for cHT2/723, respectively. The intensity was lower for the former sample. The first peak can be related to hydroxylated surface species whereas the second peak would correspond to oxide species

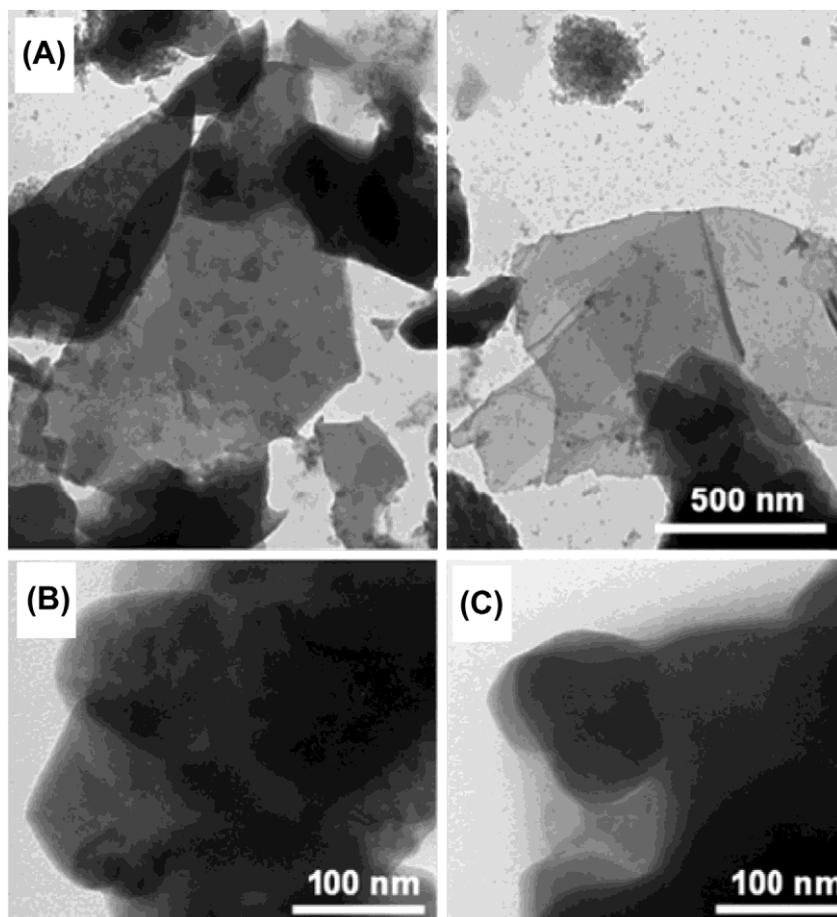


Fig. 4. TEM micrographs of catalysts (a) cHC4/723, (b) cHC4/923 and (c) cHC4/1073.

Table 3  
Distribution of the strength of basicity from CO<sub>2</sub>-TPD studies.

Catalyst	$T_{\max} < 393$ (K) Weak basic sites	$393 < T_{\max} < 693$ (K) Medium basic sites	$T_{\max} > 693$ (K) Strong basic sites
cHT1/723 <sup>a</sup>	366 m	598 vw	
cHT2/723 <sup>a</sup>	368 m	648 w	
cHC1/723 <sup>a</sup>		531 w	
cHC2/723 <sup>a</sup>		398 w	693 vw
cHC3/723 <sup>a</sup>		499 w	
cHC4/723 <sup>a</sup>		450 w, 642 w	
cHC4/923 <sup>b</sup>		461 vw	858 w
cHC4/1073 <sup>c</sup>		498 vw	928 w

Band intensities: vw (very weak), w (weak), m (medium).

<sup>a</sup> Recorded until 733 K.

<sup>b</sup> Recorded until 923 K.

<sup>c</sup> Recorded until 1073 K.

obtained after the total decomposition of the hydroxide compounds [43,45]. The higher desorption temperature (648 K) and slight higher intensity observed for cHT2/723 could be explained by the presence of some defects in this sample, the precursor of which was prepared with microwaves. This second peak cannot be associated with residual MgCO<sub>3</sub> decomposition since in the TPD performed at the same conditions but without adsorption of CO<sub>2</sub>, this peak was not observed.

For the HCs calcined at 723 K, the maximum CO<sub>2</sub> desorption temperature values were mainly between 499 and 642 K corresponding to medium basic sites (Table 3) [42]. These medium basic sites could correspond to O<sup>2-</sup> ions adjacent to OH surface groups [42], which in our samples could be adjacent to chlorine species.

Additionally, a less-intense peak at 693 K was also observed for sample cHC2/723. This can be related to the lower anion decomposition temperature observed for this sample in a previous work [44] that could justify a more extended decomposition with loss of higher amount of chlorine. This is in agreement with the lower amount of chlorine detected for this sample (Table 2). The higher basicity of cHC compared to cHT can be interpreted by the presence of CaO, which has higher basicity than MgO. Actually, at 723 K a mixture of CaOHCl, CaO and Al<sub>2</sub>O<sub>3</sub> in a ratio of 2:2:1 could be expected, as proposed in the literature from TGA experiments of Cl-hydrocalumites [44,46]. Higher temperatures are necessary for a total dehydroxylation and anion decomposition, with the subsequent increase of the number of strong basic sites. The maximum

CO<sub>2</sub> desorption temperature values for cHC4/923 and cHC4/1073 (Table 3) confirmed the presence of strong basic sites in these samples. The CO<sub>2</sub> desorption graphs of cHC4/723, cHC4/923 and cHC4/1073 are shown in Fig. 5(A and B). These profiles were obtained by subtraction of the peaks recorded with and without CO<sub>2</sub>, since a certain overlapping of the CO<sub>2</sub> desorption from the strong basic sites and CaCO<sub>3</sub> decomposition took place for the samples calcined at 923 and 1073 K. The stronger basicity of these samples agrees with the higher calcination temperature used that involves the formation of isolated O<sup>2-</sup> species in the mayenite and/or calcium oxide obtained phases (Fig. 2b and c) [42,47].

### 3.2.2. Acidity determination

The mass loss, in a TG experiment, associated with disruption of the base from acid sites was used to calculate the acid content in mmol of cyclohexylamine (CHA) per gram of sample following the method reported by Mokaya et al. [40]. From the first derivative of the thermogram, differences in the interaction CHA-acid site can be evaluated. The temperature corresponding to the minimum of the curve related to CHA loss can be considered a measure of the acid strength (Table 2). The acidity of calcined samples is a consequence of the presence of amorphous oxides with aluminium. The strength of the acidity can be modified by the amount of chlorine present in the amorphous material, due to its electronegative behaviour [48].

For cHT, the acid values were 0.79 and 0.15 mmol cyclohexylamine/g cat, for cHT1/723 and cHT2/723, respectively (Table 2). The higher crystallinity of cHT2/723 could explain its lower acidity, which is associated with aluminium with more saturated coordination. The temperature of CHA loss is low (971 and 978 K, respectively) and can be related to low acidity strength.

The acidity values for cHC were between 0.53 and <0.1 mmol cyclohexylamine/g cat (Table 2). The lowest values (<0.1 and 0.12 mmol cyclohexylamine/g cat) corresponded to the samples cHC4/923 and cHC4/1073, which were calcined at 923 and 1073 K, respectively. An increase in the temperature of calcination supposed a decrease in the acidic content. Additionally, the

amount of chlorine and the temperature of CHA loss also decreased when the calcination temperature increased (Table 2). These effects combined resulted in lower acidity content and lower acidity strength for cHC4/1073. The differences observed between the HC calcined at 723 K are difficult to explain, since all samples were very amorphous. However, in this group of samples, the catalyst with the lowest acidity cHC2/723, 0.18 mmol cyclohexylamine/g cat) was synthesised from the HC with the lowest temperature of dehydroxylation [44] and probably with a faster formation of a microcrystalline aluminium oxide with less acidity. This sample also presented the lowest acid strength. Its lower amount of chlorine could justify again this fact. In the four samples of this group it is possible to establish a direct correlation between the chlorine content and the temperature of cyclohexylamine desorption cHC4/723 > cHC1/723 > cHC3/723 > cHC2/723.

The content of acidity will affect to the selectivity of the products of reaction, as acid sites catalyse the formation of acrolein, amongst other products (Scheme 2), and favour this parallel reaction. Since the differences of basicity were not significant for the samples calcined at 723 K, catalysts with lower acid content will favour, a priori, the selectivity towards the products of interest di- and triglycerol.

### 3.3. Catalytic activity

All catalysts were active for the etherification reaction of glycerol towards diglycerol (DG) and triglycerol (TG) (Scheme 1, Table 4).

#### 3.3.1. Calcined MgAl layered double hydroxides

Catalyst cHT1/723 showed almost total glycerol conversion (96%) and low selectivity towards the products of interest (12% DG + TG). This behaviour can be related to an important contribution of the acidic content (0.79 mmol cyclohexylamine/g cat) of this catalyst that favours acrolein formation. In contrast, catalyst cHT2/723 exhibited lower conversion (24%) and 100% selectivity towards (DG + TG) (with a selectivity to TG of 11%), that resulted

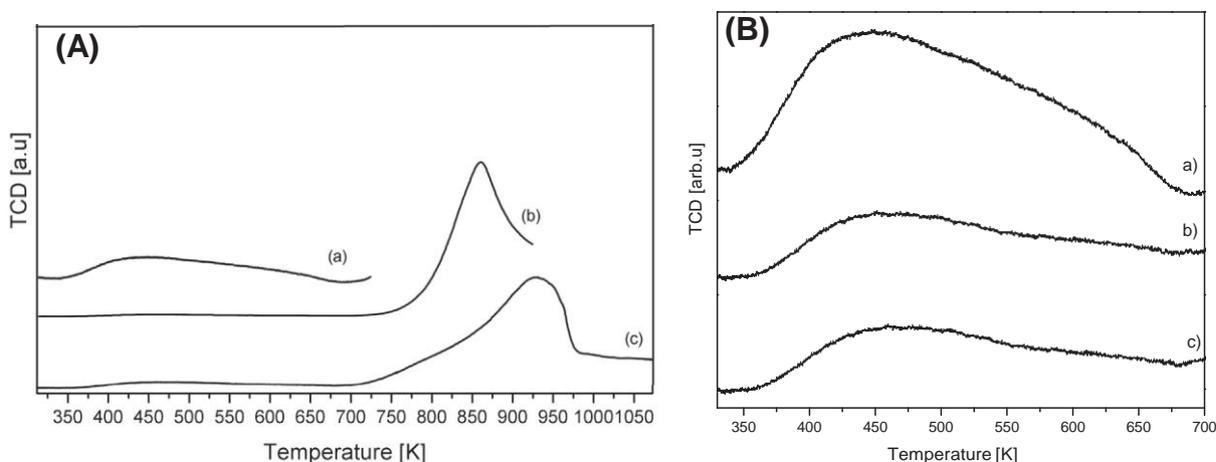
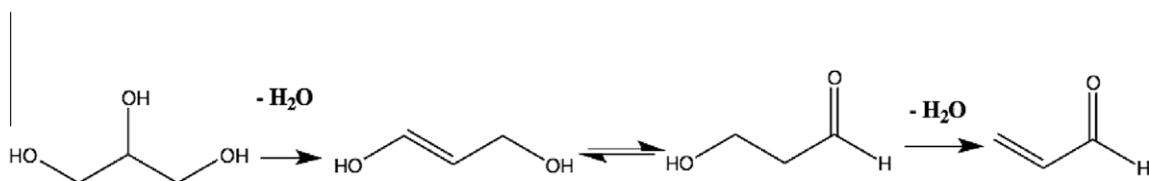


Fig. 5. (A) CO<sub>2</sub>-TPD of catalysts (a) cHC4/723, (b) cHC4/923 and (c) cHC4/1073. (B) Detailed CO<sub>2</sub>-TPD graph until 700 K.



Scheme 2. Acrolein formation scheme reaction.

Table 4  
Catalytic test results.

Catalysts	Conversion (%)	Selectivity (%)			Catalytic yield (DG + TG + TTG + PG) (%)
		DG	TG	Other products	
cHT1/723	96	9	3	88 <sup>a</sup>	12
cHT2/723	24	89	11	0	24
cHC1/723	75	36	6	58 <sup>a</sup>	32
cHC2/723	40	50	14	36 <sup>a</sup>	26
cHC3/723	64	35	10	55 <sup>a</sup>	29
cHC4/723	60	44	11	45 <sup>a</sup>	33
cHC4/923	59	38	13	49 <sup>b</sup> (8% TTG)	35
cHC4/1073	84	29	20	51 <sup>c</sup> (15% TTG + 6% PG) 6% <sup>c</sup>	59

DG: diglycerol, TG: triglycerol, TTG: tetraglycerol, PG: pentaglycerol.

<sup>a</sup> Mainly acrolein.

<sup>b</sup> Acrolein and tetraglycerol.

<sup>c</sup> Acrolein, tetraglycerol and pentaglycerol.

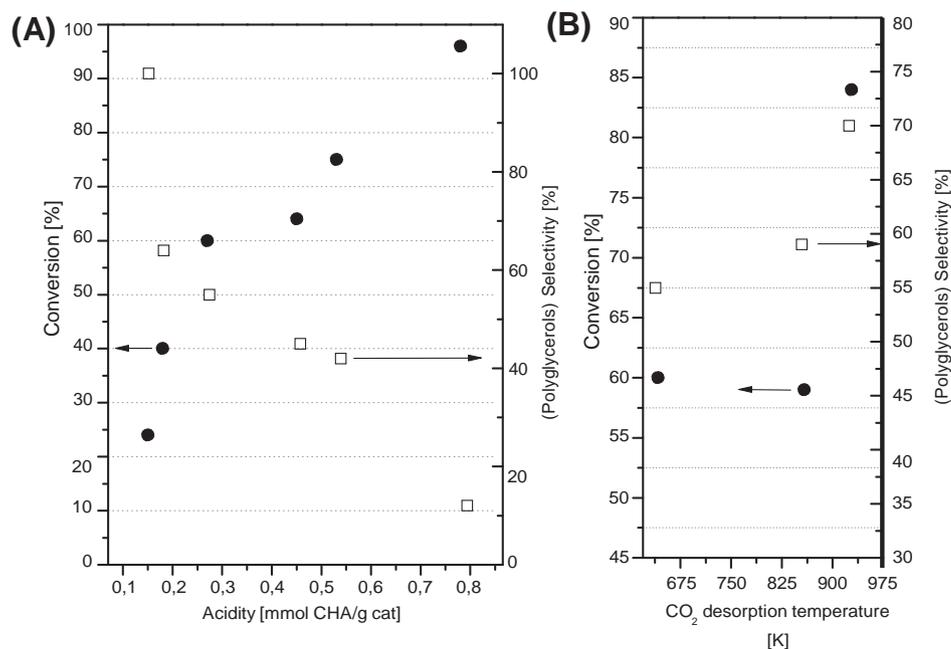


Fig. 6. (A) Acidity vs. glycerol conversion and selectivity to polyglycerols for MgAl-LDHs and CaAl-LDHs calcined at 723 K; (B) CO<sub>2</sub> desorption temperature vs. glycerol conversion and selectivity to polyglycerols for CaAl-LDHs calcined at 923 and 1073 K. In filled circles, glycerol conversion (%). In squares, polyglycerols selectivity (%).

in a higher catalytic yield towards the products of interest. This catalyst showed less acidic content (0.15 mmol cyclohexylamine/g cat) and the presence of higher amounts of medium strength basic sites than cHT2/723 (Tables 2 and 3).

### 3.3.2. CaAl layered double hydroxides calcined at 723 K

The highest conversion (75%) was obtained for catalyst cHC1/723. In spite of the presence of medium basic sites, the high acidic content of this catalyst (0.53 mmol cyclohexylamine/g cat) favoured mainly the formation of acrolein (selectivity to other products of 58%) rather than DG + TG selectivity (42%). Catalyst cHC2/723 led the highest value of DG + TG selectivity (64%). For this catalyst, the low acidic content (0.18 mmol cyclohexylamine/g cat) and the presence of strong basic sites, favoured the formation of the products of interest (DG and TG). It is important to remark that cHC2/723 exhibited the highest % of TG selectivity (14%) of all catalysts calcined at 723 K.

In contrast, catalysts cHC3/723 and cHC4/723 showed similar conversion values (64% and 60%, respectively) but cHC4/723 presented higher selectivity to DG + TG (55%) than cHC3/723 (45%) (Table 4). The different acidic content (0.45 and 0.27 mmol CHA/

g cat), together with the presence of medium basic sites with higher strength (maximum CO<sub>2</sub> desorption temperature at 642 K, Table 3) for catalyst cHC4/723 justify these results.

Fig. 6A shows the correlation between acidity (mmol CHA/g cat), glycerol conversion (%) and short chain polyglycerol (DG + TG + TTG + PG) selectivity (%) for all catalysts. It is possible to observe that an increase of acidity involved an increase of conversion and a decrease of selectivity towards short chain polyglycerols for the catalysts calcined at the same temperature (723 K).

### 3.3.3. Effect of the calcination temperature

In order to increase the basicity of the catalyst, HC4 was calcined at higher temperatures (923 and 1073 K). Catalyst cHC4/923 presented a slight decrease of conversion (59%), similar selectivity towards DG + TG (51%), higher TG selectivity (13%) and the formation of tetraglycerol (8%) when compared to cHC4/723. The differences in the catalytic results can be explained by the lower acidic content and the presence of stronger basic sites in the catalyst cHC4/923 (Table 3). Interestingly, the conversion increased (84%) for catalyst cHC4/1073, with respect to cHC4/723 and cHC4/923, and the selectivity towards triglycerol was the highest

observed (20%). The selectivity values for tetra- and pentaglycerol were 15% and 6%, respectively, with a total % yield to short-chain polyglycerols of 59%. For this catalyst, the amount of acidic content was the lowest (<0.1 mmol CHA/g cat), and presented the strongest basic sites (Table 3), which could explain the formation of higher weight polyglycerols. However, the acrolein formation was not totally avoided for catalyst cHC4/1073, since its low acidity content corresponded to medium acid sites, as deduced from its cyclohexylamine desorption temperature (Table 2).

### 3.3.4. Catalyst stability

In order to study the stability of the catalysts, XRD of the used catalysts were performed. The resulting patterns were similar to the patterns of the corresponding fresh catalysts. Calcium glycerolate phase was not observed in any case [49]. In order to discard homogeneous catalytic contribution to the results in our study, ICP tests were performed to the solution of the reaction, after its completion. The catalyst was recovered by ultracentrifugation. Leaching was discarded since calcium and aluminium were not detected as part of the final solution.

The results shown in this work, regarding (DG + TG) catalytic yield, are similar to those published recently. In those results, the best catalytic yields towards (DG + TG) ranged between 33% using homogeneous LiOH as catalyst [16], around 33% using homogeneous CsHCO<sub>3</sub> [17], 40% with a Mg/Al calcined layered double hydroxide [23] and 50% using a Mg/Fe calcined layered double hydroxide [24]. However, it is remarkable the high catalytic activity of calcined HCs considering their low values of BET specific surface area (Table 2). In light of our results more research needs to be done, such as altering the physicochemical properties for HCs calcined at high temperatures (1023 K) in order to increase selectivity to the products of interest or to higher-weight polyglycerols.

## 4. Conclusions

A series of calcined MgAl and calcined CaAl layered double hydroxides (cHT and cHC, respectively) were synthesized, characterised and tested for the etherification reaction of glycerol towards polyglycerols. The acid–base properties were correlated with their catalytic behaviour. All samples were active for the etherification reaction of glycerol towards short-chain polyglycerols. For the HCs calcined at 723 K, the highest catalytic yield (DG + TG 33%) was obtained for sample cHC4/723 after 24 h of reaction. This sample presented low acidity content, lower acidity strength in comparison with other HCs calcined at the same temperature and stronger basic sites. Increasing the temperature of calcination supposed a decrease in chloride and acidity content, decrease in the acid strength and an increase of the basicity strength. Catalyst cHC4/1073 achieved the highest catalytic yield to short chain polyglycerols (DG + TG + TTG + PG 59%) of all samples. Regarding catalytic yield, results are similar to those published before for mixed oxides considering DG and TG % and higher when TTG and PG are included. It is important to remark the low values of BET specific surface area of the calcined HCs. The higher acidity strength of the HCs calcined at higher temperature with respect to that of the calcined MgAl layered double hydroxide HT2, justifies the acrolein obtained in those samples in spite of their lower total acidity content. Catalysts were stable after reaction since glycerolate phase was not detected, by XRD, in any case. Contribution of homogeneous catalysis was discarded.

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