



Journal of Nanoscience and Nanotechnology Vol. 18, 4588–4599, 2018 www.aspbs.com/jnn

# Solvent Free Transesterification of Glycerol Into Glycerol Carbonate Over Nanostructured CaAl Hydrotalcite Catalyst

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Drastic increase in green house gases due to fossil fuels usage urges the mankind to look for alternative fuel resources. Biodiesel is one of the alternative fuels which attracted the attention of many researchers. In recent years, bio-diesel drags much attention as an alternative clean fuel. Glycerol is an unavoidable byproduct in the transesterification process of vegetable oils into bio diesel and therefore market is flooded with glycerol. So it is high time to find ways of utilizing the abundant glycerol into value added products. Herein we report the catalytic transesterification of glycerol using dimethyl carbonate over MgAl-hydrotalcite (MgAl-HT), CaAl-hydrotalcite (CaAl-HT) and nano structured CaAI-HT catalysts. All the catalysts were characterized by XRD, FT-IR, TPD-CO<sub>2</sub>, BET, SEM and HR-TEM techniques. Among them Ca<sub>4</sub>AI-HT was found to be best in terms of conversion of glycerol (82.4%) and selectivity (95.9%) towards glycerol carbonate. The effect of CTAB template concentration in the nano synthesis of Ca<sub>4</sub>AI-HT on conversion and selectivity was studied and Ca<sub>4</sub>AI-HT synthesized with 0.4 moles of CTAB showed the best conversion of glycerol (98.7%) and the highest selectivity towards glycerol carbonate (97.9%). The recyclability test performed with the best catalyst showed that the catalyst was recyclable even after 5 cycles. Valorization of glycerol yields glycerol carbonate (GC) which is a very good polar solvent with high boiling point, building block in several organic syntheses and used in the production of surfactants, poly urethanes etc.

Keywords: Glycerol, Transesterification, Glycerol Carbonate, Solid Base Catalyst.

#### **1. INTRODUCTION**

The growing demand of energy due to increase in population, industrial developments and motorization have led to a steep depletion of conventional fossil fuels such as petroleum oil, coal and natural gas. The burning of these fossil fuels also affects the environment badly and is the key factor for the present global warming crises.<sup>1–3</sup> Hence the field of alternate fuels has gained much interest over the last two decades and there has been much research on the production of new, environmentally friendly fuels.

Bio-diesel, an exceptional alternative fuel can replace the primary energy sources like fossil fuels and in turn will reduce the green house gas emissions.<sup>4–6</sup> Methyl esters of fatty acids (biodiesel) produced from vegetable oils and animal fat by transesterification process leads to the formation of glycerol as an unavoidable by-product. 37 billion gallons of biodiesel was produced world wide by 2016 which implies the production of approximately 4 billion gallons of glycerol.<sup>7</sup> Glycerol is also obtained by alcoholysis, hydrolytic cleavage or saponification with alkalies of several glycerides.<sup>8-10</sup> Henceforth, there is a surplus availability of glycerol.<sup>11-13</sup> The excess availability of glycerol makes it as an affordable and adaptable building block chemical. The accumulation of crude glycerol creates economic and environmental problems.14,15 Glycerol has a broad spectrum of usage in various fields such as food, cosmetic, detergent, pharmaceutical, explosive etc., and can also be converted into value added chemicals such as esters, ethers, acetals, ketals, diols, epoxides, polyethers, polyols, triacetin, alkyd resins,

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etc.,<sup>16–18</sup> Despite the multi-dimensional usage of glycerol its surplus production urges the scientific researchers to find new applications for glycerol.

Among the various technologies for glycerol conversion, conversion through catalytic route drawn much interest and attention.<sup>19, 20</sup> Catalytic conversion of glycerol to value-added products has been done using either homogeneous catalysts or heterogeneous catalysts using various reactions such as oxidation, reduction, esterification, hydrogenolysis, etherification, polymerization, halogenation, dehydration and reforming etc.,<sup>21-24</sup> In this context, catalytic transesterification of glycerol to glycerol carbonate (GC) is also considered as an industrially important reaction. GC has received much attention in the last two decades due to versatile reactivity.<sup>25</sup> The advantageous properties such as low toxicity, excellent biodegradability and high boiling point make this compound as a very good intermediate in several organic syntheses, precursor in biomedical applications, important component in membrane used for gas separation and also in the production of poly urethanes, surfactants, high boiling polar solvents etc.8 The -OH and 2-oxo-1,3-dioxolane groups present in GC makes this molecule as a highly reactive one and therefore finds application in different domains such as solvents, polymers etc. GC readily reacts with many nucleophilic reagents such amines etc. The reaction with amino silanes yield highly branched siloxy polymers.<sup>26</sup>

Hydrotalcite is the well known layered material and finds applications as absorbents, ion exchangers, catalyst, fire retardant additives, polymer composites, controlled drug delivery, cement additives, etc.<sup>27</sup> Owing to its peculiar tunable properties (ion exchange, intercalation), structural stability at harsh conditions and cheaper availability, it has been used as a commercial solid base catalyst to carryout various industrially important reactions.<sup>28-30</sup> Hydrotalcite belongs to the class of anionic clay type with general formula of  $[M^{2+} M^{3+}(OH)_{2(n+m)}]^{m+} [A_{m/n}]^{x-}$ . YH<sub>2</sub>O, where M<sup>2+</sup>(Mg, Ca, Zn, Ni, Cu, Co), M<sup>3+</sup>(Al, Cr, Ga, Fe, Mn, etc.) and  $A^{x-}$  is a charge compensating anion ( $CO_3^{2-}$ ,  $Cl^{-}$ ,  $SO_4^{3-}$ , etc.). The anions in the interlayer compensate the positive charges arise due to the divalent and trivalent ions. In the present study transesterification of glycerol has been carried out using Mg<sub>x</sub>Al-HT and Ca<sub>x</sub>Al-HT (x = 2, 3 and 4).

GC from glycerol can be obtained by various methods such as carbonylation with phosgene or CO,<sup>31, 32</sup> Glycerolysis of urea with Lewis acid catalyst,<sup>33, 34</sup> reaction under super-critical conditions in presence of CO<sub>2</sub><sup>35, 36</sup> and using homogeneous catalysts such as NaOH, K<sub>2</sub>CO<sub>3</sub>.<sup>37, 38</sup> However these reactions have serious drawbacks like toxicity, low product yield and tedious catalyst–product separation. All these drawbacks will be overcome through heterogeneous catalytic route.<sup>39</sup> Transesterification of glycerol to GC in presence of dimethyl carbonate (DMC) has also been reported by using heterogeneous catalysts such as CaO, CaO–La<sub>2</sub>O<sub>3</sub>, KF-Hydroxyapatite, Ca<sub>2</sub>CO<sub>3</sub>–MgO, ZnO–La<sub>2</sub>O<sub>3</sub> and ionic liquids.<sup>40–45</sup> Despite the advantages of heterogeneous catalysts the above catalysts have certain limitations such as poor reusability, requiring high reaction temperature, prolonged reaction time and high molar ratio of reactants.

Hence in this article we report the transesterification process of glycerol to GC in presence of DMC under solvent free conditions using solid base catalysts such as Mg<sub>x</sub>Al-HT and Ca<sub>x</sub>Al-HT (x = 2, 3 and 4). Between these catalysts, Ca<sub>4</sub>Al-HT was found to be better in terms of conversion and selectivity. Ca<sub>4</sub>Al-HT nano catalyst were synthesized with different molar concentration of the surfactant (CTAB) and among the catalysts Ca<sub>4</sub>Al-HT 0.4CTAB was found to be the best as it converts 98.7% of glycerol with high selectivity (97.9%) towards glycerol carbonate.

# 2. EXPERIMENTAL SECTION

# 2.1. Materials

 $Mg(NO_3)_2 \cdot 6H_2O$  and  $Al(NO_3)_3 \cdot 9H_2O$  were purchased from Sigma and used as received for the synthesis of Mg-Al-HT, whereas  $Ca(NO_3)_2 \cdot 5H_2O$  (Merck) and  $Al(NO_3)_3 \cdot$  $9H_2O$  (Sigma) were used as received for the synthesis of CaAl-HT catalysts. NaOH and Na<sub>2</sub>CO<sub>3</sub> purchased from SRL and were used as received. The surfactant Cetyl trimethylammonium bromide (CTAB) was purchased from Sigma aldrich and used as received.

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# 2.1.1. Synthesis of MgAl-HT and CaAl-HT Catalysts

Magnesium-Aluminum hydrotalcite (MgAl-HT) with different Mg/Al molar ratios (2, 3 and 4) were synthesized by direct precipitation method. Solution A was prepared by dissolving 25.6 gm of Mg(NO<sub>3</sub>)<sub>2</sub>  $\cdot$  6  $\cdot$  H<sub>2</sub>O and 18.6 gm of Al(NO<sub>3</sub>)<sub>3</sub>  $\cdot$  9H<sub>2</sub>O in 70 ml deionised water (Mg/Al = 2). Solution B was prepared by dissolving sodium hydroxide and sodium carbonate of appropriate concentration. Then solution B was added slowly into solution A and stirred while maintaining the pH between 11 and 13. After 6 h, the resulting gel was stirred and transferred into an autoclave and crystallized at 393 K for 18 h. Then the resultant mass was filtered, washed several times with hot water until the washings showed neutral pH. The samples were dried in an air oven at 393 K and calcined at 823 K for 8 h to get Mg<sub>2</sub>Al-HT catalyst. Adopting similar procedure Mg<sub>x</sub>Al-HT (x = 3 and 4) catalysts were also prepared. For the synthesis of Calcium-Aluminum hydrotalcite (CaAl-HT) catalysts  $Ca(NO_3)_2 \cdot 6 \cdot H_2O$  and  $Al(NO_3)_3 \cdot 9H_2O$  were used. The same procedure described above was used to prepare Ca<sub>x</sub>Al-HT (x = 2, 3 and 4) catalysts.

#### 2.1.2. Synthesis of Nano Ca<sub>4</sub>Al-HT Catalysts

In order to improve the catalytic activity of  $Ca_4AI$ -HT catalyst, nano sized  $Ca_4AI$ -HT catalysts were prepared by using CTAB surfactant. Calculated amount of CTAB in 100 ml of distilled water were taken and added to the

white sol containing precursors of Ca and Al to prepare Ca<sub>4</sub>Al-HT yCTAB catalysts where y is the molar concentration of CTAB = 0.1, 0.2, 0.4 and 0.6. Same procedure as described in Section 2.1.1 was followed for the synthesis of nano hydrotalcites.

#### **2.2.** Characterization of the Catalysts

X-ray diffraction patterns of the MgAl-HT and CaAl-HT catalysts were recorded on a Philips X-pert diffractometer with CuK<sub> $\alpha$ </sub> radiation ( $\lambda = 1.54056$  Å) at operating voltage of 30 kv, 10 mA. The data were collected in the 2 $\theta$  range from 5° to 80° at the scan rate of 0.04°/min. The peak processing was performed using origin 8 software and was indexed in the hexagonal system on the rhombohedral lattice with the space group of R-3m (166). The standards JCPDS card No. 89-0460 was used for comparison. The interplanar spacing ( $d_{300}$ ) value was used for the identification of the basal plane. The lattice parameters a, c and V were determined by using the following equation:

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$$

Where *d*—interplanar spacing, *hkl* are the corresponding miller planes, *a* and *c* are the lattice parameters. The unit cell volume V (Å<sup>3</sup>) was calculated using,

$$V = (a^2 c) \sin 60^\circ$$

Fourier Infrared spectra (FT-IR) were recorded on an Thermo-Nicolet IR 2000 spectrophotometer in order to determine the various functional groups. The spectra were recorded in the wavenumber range of 4000–400 cm<sup>-1</sup>. Nitrogen adsorption–desorption isotherms for the calcined catalysts were constructed at 77 K using a constant volume adsorption apparatus (Micrometrics ASAP 2020) for the determination of BET surface area and other texture characteristics. Prior to the analysis, hydrotalcite samples were degassed and pretreated at 583 K for 6 h. BJH pore size distribution was also calculated from the desorption branch of the isotherms.

Quantitative determination of Ca, Mg and Al ions was done by inductively coupled plasma (ICP) technique using Perkin Elmer Optima 5300 DV. 200 mg of samples were digested in a mixture of concentrated acids for 6 h, diluted and filtered through syringe filter prior to the analysis.

Catalyst microstructure observations were performed on a Quanta 200 FEG scanning electron microscope (HR-SEM). Prior to the analysis, powdered samples were dried at 373 K for 6 h, air dispersed over the carbon tape and mounted for analysis. The high resolution transmission electron micrographs (HR-TEM) were recorded using JEOL JEM-2100JF working at the operating voltage of 200 keV. Powder samples were dispersed in absolute ethanol, ultrasonicated for 10 minutes, placed over holey carbon coated Cu grid, dried at ambient conditions and mounted for the analysis. The total basicity of the hydrotalcite catalysts was determined by Temperature programmed desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD) experiments. Prior to the analysis, 100 mg of catalyst was pre-treated at 773 K for 1 h under He stream (20 mL/min), cooled to 363 K and CO<sub>2</sub> (10 vol.%) was introduced for adsorption at this temperature for 1 h. Then the catalyst was swept with He (20 ml/min) for 60 min to remove the physisorbed CO<sub>2</sub> from the catalyst surface, the temperature was increased linearly with rate of 10 K/min in He (10 ml/min) and the signal of CO<sub>2</sub> (M/e = 44) was recorded by online mass spectrometry. The amount of CO<sub>2</sub> was quantified by a calibration curve constructed by using known amounts of NaHCO<sub>3</sub>.

#### 2.3. Catalytic Experiments and Analysis Method

The liquid phase of transesterification of glycerol (Sigma, 99%) with dimethyl carbonate (DMC, SRL, 99.5%) was investigated at atmospheric pressure under solvent free conditions. For the catalytic reaction, glycerol (0.04 mol) and dimethyl carbonate (0.16 mol) were taken in 100 ml round bottom flask fitted with stirrer and reflux condenser. The temperature of the reaction was maintained by the heating coil immersed in silicon oil integrated with the thermocouple and control unit. When the reaction temperature was reached, catalyst of 100 mg was added and stirred. After 2 h of reaction time, sample aliquots were withdrawn centrifuged and the catalysts were separated to obtain a homogeneous transparent solution. The liquid products namely glycerol carbonate with unreacted DMC and glycerol in the reaction medium was analyzed by gas chromatograph (SHIMADZU 17A) equipped with flame ionization detector (FID) using a Zebron-FFAP capillary column (30 m  $\times$  0.32 mm  $\times$  0.25  $\mu$ m). Conversion and selectivity values of the transesterification catalytic tests were calculated according to the following equations:

Molar Conversion (%) = 
$$\frac{\text{moles of glycerol converted}}{\text{moles of glycerol taken}} \times 100$$

Glycerol carbonate selectivity (%)

$$= \frac{\text{moles of glycerol converted to glycerol carbonate}}{\text{moles of converted glycerol}}$$

 $\times 100$ 

# **3. RESULTS AND DISCUSSION 3.1. Powder X-ray Diffraction**

The phase formation and crystallinity of the synthesized hydrotalcites were determined by the X-ray powder diffraction patterns. Figures 1 and 2 show the X-ray diffraction patterns of MgAl-HT and CaAl-HT with Ca/Al and Mg/Al molar ratios 2, 3 and 4.

Both the MgAl-HT and CaAl-HT catalysts show characteristic peaks in the  $2\theta$  range of 10–80. The peaks and



Figure 1. High angle X-ray diffraction patterns of  $Mg_xAl$ -HT hydrotalcites (a)  $Mg_2Al$ -HT, (b)  $Mg_3Al$ -HT and (c)  $Mg_4Al$ -HT catalysts.

their corresponding Miller planes at the corresponding  $2\theta$  at 11.64(003), 23.420(006), 34.885(012), 35.449(009), 39.444(015), 46.922(018), 53.086(1010), 60.766(110), 60.928(0015) and 62.110(113) were indexed to a hexagonal lattice with rhombohedral symmetry with the space group of R-3m (166). These peaks are in good in comparison with the standards JCPDS card No. 89-0460.<sup>46</sup> The peaks are sharp and intense indicating high degree of crystallinity and are also in good agreement with the reported literatures.<sup>47</sup> The peaks with the Miller planes of (003), (006), (009) and (0015) correspond to the basal planes while the other are assigned to the non-basal planes. The molar ratios, composition, calculated values of inter planar spacing ( $d_{300}$ ), crystallite size and lattice parameters (a, c



**Figure 2.** High angle X-ray diffraction patterns of  $Ca_xAl$ -HT hydrotalcites (a)  $Ca_2Al$ -HT, (b)  $Ca_3Al$ -HT and (c)  $Ca_4Al$ -HT catalysts.

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and V) calculated from the diffraction patterns are given in Table I.

The composition considered for the synthesis is retained in the final products on both the MgAl-HT and CaAl-HT catalysts. Both the MgAl-HT and CaAl-HT catalysts show increased basal spacing ( $d_{300}$ ) with the increase in the Mg/Al and Ca/Al ratios. This is in good agreement with previous reports.<sup>48</sup> The reason is apparent as the ionic radii of Ca<sup>2+</sup> (0.99 Å) and Mg<sup>2+</sup> (0.66 Å) are different. With increases in either Mg or Ca in the hydrotalcite the intensity of 2 $\theta$  peak corresponding to (003) plan decreases and shifts towards lower angle. The crystallite size of both MgAl-HT and CaAl-HT catalysts were also increased with the increasing  $d_{300}$ .

The effect of CTAB as template on the nano synthesis of hydrotalcite was studied using powder X-ray diffraction. Figure 3 shows the X-ray diffraction of  $Ca_4Al$ -HT prepared with different molar ratios (0.1, 0.2, 0.4 and 0.6) of CTAB.

With the increase of CTAB from 0.1 to 0.6, the  $d_{300}$ value increased indicating the increase in the interplanar spacing. This is further confirmed by the increased lattice parameters. The lattice parameters a and c were also increased. Particularly the increase along the *c*-axis was found to be high i.e., from 23.457 to 25.497 Å. Moreover the peaks corresponding to 003 and 006 planes showed slight shifting towards the lower angle. However the increase of lattice parameter along the *a*-axis was found to be minimum i.e., from 3.10 to 3.22 Å. Since both the lattice parameter a and c increase the unit cell volume also increases to 223.29 Å (Table II). The template CTAB was responsible for the increased interlayer spacing in the formation of hydrotalcites. It is also to be noted that increase in the molar concentration of CTAB up to 0.6 there was no change in the diffraction patterns, indicating the retaining of hydrotalcite structure. The results were further authenticated by SEM and HR-TEM analyses.

#### **3.2. FT-IR Spectral Analysis**

The FT-IR spectra of the MgAl-HT and CaAl-HT catalysts with molar ratios of 2, 3 and 4 are shown in Figures 4 and 5.

The broad peak observed in the region from 3800 to  $3200 \text{ cm}^{-1}$  is mainly due to the stretching mode of –OH (hydroxyls) groups of water molecules. Thus the bands at 3464 cm<sup>-1</sup> in MgAl-HT and 3482 cm<sup>-1</sup> in CaAl-HT are due to the stretching mode of the water molecules.<sup>49</sup> The band at 1636 cm<sup>-1</sup> arises due to the bending mode of the –OH group. It is evident that, with the increase in the molar ratios in MgAl-HT and CaAl-HT catalysts, the –OH stretching frequency also increase but with decreased intensity. This may be due to the weaker interaction between the hydroxyl layer and the carbonate anions. The carbonate anion gives band at 1384 cm<sup>-1</sup>, 863 cm<sup>-1</sup> and 668 cm<sup>-1</sup> due to the stretching mode of the CO<sub>3</sub><sup>2–50</sup> Thus the main peaks at 1384 cm<sup>-1</sup> for MgAl-HT and

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Catalysts	Molar ratio <sup>a</sup>		x	$d^b$	$Xs^{c}$	Lattice parameters <sup>d</sup>		$S_{\rm BET}$	$V_P$	$d_P$	Adsorbed CO <sub>2</sub>	
	$\overline{M_{t}}$	$M_{a}$	$\overline{\text{Al/Al} + M^{2+}}$	(Å)	(nm)	a (Å)	c (Å)	V (Å <sup>3</sup> )	$(m^2/g)$	(cm <sup>3</sup> /g)	(nm)	(mmol/g)
Mg <sub>2</sub> Al-HT	2	1.97	0.34	7.72	23.1	3.04	23.16	185.4	166	0.24	7.6	0.24
Mg <sub>3</sub> Al-HT	3	2.98	0.25	7.80	30.7	3.04	23.40	187.3	184	0.33	9.6	0.28
Mg <sub>4</sub> Al-HT	4	3.94	0.22	7.85	34.7	3.06	23.55	190.9	192	0.41	12.2	0.34
Ca <sub>2</sub> Al-HT	2	1.92	0.35	7.89	28.4	3.10	23.67	196.9	180	0.27	8.8	0.30
Ca <sub>3</sub> Al-HT	3	2.97	0.25	7.96	39.9	3.12	23.88	201.3	195	0.38	10.1	0.45
Ca₄Al-HT	4	3.90	0.21	8.06	43.2	3.13	24.18	205.2	234	0.42	12.6	0.57

*Notes*: <sup>a</sup>M<sup>2+</sup>/Al ratio as determined by ICP. <sup>b</sup>Inter planar spacing calculated from XRD pattern of (003) plane. <sup>c</sup>Crystallite size calculated from Scherrer equation. <sup>d</sup>Lattice parameter calculated from XRD powder pattern of (003) plane and (110) plane.

1378 cm<sup>-1</sup> for CaAl-HT are assigned to the carbonate anion within the interlayer of the hydrotalcite. A weak band at 834 cm<sup>-1</sup> may be due to the nitrate anion within the interlayer. The peaks below 1000 cm<sup>-1</sup> arise mainly due to the crystal lattice vibrations. Thus peak at 458 cm<sup>-1</sup>, 563 cm<sup>-1</sup>, 663 cm<sup>-1</sup> and 1050 cm<sup>-1</sup> are assigned to the Mg–O–Al bending, Mg–O–H stretching, Mg/Al–O–H stretching and Al–O stretching vibration respectively.<sup>51,52</sup> The peak around 2930 cm<sup>-1</sup> arises due to the interactions between the –OH and CO<sub>3</sub><sup>2–</sup> within the interlayer.<sup>53</sup>

Figure 6 Shows the FT-IR spectra of the  $Ca_4Al$ -HT catalysts prepared with different molar concentration of CTAB.

The FTIR peaks of Ca<sub>4</sub>Al-HT prepared by using CTAB surfactants getting sharper with increase in the molar concentration of CTAB. Sharpness of these peaks indian scates the formation of nanosized hydrotalcite sheets.<sup>54</sup> The broadness of the –OH stretching peaks in the region of 3200 cm<sup>-1</sup> to 3400 cm<sup>-1</sup> is not only decreased but also shifts to the higher frequency from 3432 cm<sup>-1</sup>



**Figure 3.** High angle X-ray diffraction patterns of  $Ca_4Al$ -HT hydrotalcite prepared with various CTAB concentrations (a)  $Ca_4Al$ -HT 0.1CTAB, (b)  $Ca_4Al$ -HT 0.2CTAB, (c)  $Ca_4Al$ -HT 0.4CTAB and (d)  $Ca_4Al$ -HT 0.6CTAB catalysts.

to  $3499 \text{ cm}^{-1}$  indicating the increase in the interlayer distance.

#### **3.3.** N<sub>2</sub> Adsorption Isotherm

The  $N_2$  adsorption and desorption isotherms of the MgAl-HT and CaAl-HT catalysts with molar ratios of 2, 3 and 4 are shown in Figure 7.

All the catalysts exhibit type IV isotherm with H3 hysteresis loop at relatively high relative pressure (0.6-0.9) which indicates, that the hydrotalcite prefers the layered and plate like formations.<sup>55</sup> On the basis of the IUPAC classification, N<sub>2</sub> adsorption–desorption isotherm which is typical to mesoporous materials was obtained. Hence the N<sub>2</sub> uptake forms a hysteresis loop at relatively high pressure from 0.6, which indicates the formation of easily bacessible mesopores.

The surface area, pore volume and pore diameter of the MgAl-HT and CaAl-HT catalysts are given in Table I. It is evident that with the increase in Ca and Mg molar ratios, the surface area was found to increase which may be due to the incorporation of Ca and Mg within the interlayer. The pore volume and the pore diameter were also increased with the increase in the Mg and Ca molar ratios. These results are in good agreement with the reported literatures.<sup>56</sup>

Figure 8 shows the  $N_2$  adsorption–desorption isotherm of  $Ca_4Al$ -HT catalysts synthesized using CTAB template with different molar concentrations.

The CTAB modified  $Ca_4Al$ -HT catalysts shows similar hysteresis loop at higher partial pressure indicating the formation of layered structure with porosity. It is evident that with increase in CTAB concentration, the surface area was found to increase upto the CTAB molar concentration of 0.4 and further increase in CTAB concentration, it decreased. The increase in surface area may be due to the CTAB incorporation which exfoliates laterally forming sheet like morphology whereas higher CTAB molar concentration leads to the formation of nano sized porous hydrotalcite with porous formation. As higher CTAB concentration of 0.6 decreases the surface, 0.4 was found to be the optimum CTAB concentration for the formation of nano structured hydrotalcite. Similarly the pore volume

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	$d^a$	$Xs^b$	Lattice parameters <sup>c</sup>			$S_{\rm BET}$	$V_P$	$d_P$	Adsorbed CO <sub>2</sub>
Catalyst	(Å)	(nm)	a (Å)	<i>c</i> (Å)	V (Å <sup>3</sup> )	$(m^2/g)$	$(cm^3/g)$	(nm)	(mmol/gm)
Ca <sub>4</sub> Al-HT-0.1CTAB	7.819	38.7	3.10	23.457	195.22	214	0.37	10.3	0.55
Ca <sub>4</sub> Al-HT-0.2CTAB	7.995	42.5	3.15	23.985	206.10	253	0.42	13.2	0.72
Ca <sub>4</sub> Al-HT-0.4CTAB	8.499	45.8	3.18	25.497	223.29	312	0.48	14.1	0.86
Ca <sub>4</sub> Al-HT-0.6CTAB	8.222	48.1	3.22	24.666	221.48	276	0.45	14.2	0.67

Table II.	Texture parameters	of Ca <sub>4</sub> Al-HT with	different molar	concentration of CTAB.

Notes: <sup>a</sup>Inter planar spacing calculated from XRD pattern of (003) plane. <sup>b</sup>Crystallite size calculated from Scherrer equation. <sup>c</sup>Lattice parameter calculated from XRD powder pattern of (003) plane and (110) plane.

and pore diameter was found to increase with the incorporation of CTAB (Table II).

# **3.4.** Temperature Programmed Desorption of CO<sub>2</sub>(TPD-CO<sub>2</sub>)

The basic sites were estimated from the adsorbed state of  $CO_2$  with the basic sites of hydrotalcites. The  $CO_2$ -TPD profile of the CaAl-HT and MgAl-HT catalysts are shown in Figures 9 and 10. Desorption of  $CO_2$  was monitored over a temperature range of 373 K to 773 K.

Table I shows the total amount of desorbed  $CO_2$  with increase in temperature. With the increase of Ca and Mg molar ratios, the  $CO_2$  desorption temperature was found to increase. In the case of CaAl-HT catalysts, desorption temperature from 463 K to 470 K. whereas for Mg<sub>4</sub>Al-HT it increases from 452 K to 473 K. Higher desorption temperature coupled with increase in intensity indicates stronger and higher basicity. Ca<sub>4</sub>Al-HT and Mg<sub>4</sub>Al-HT catalysts show the highest basicity among the corresponding hydrotalcites. The order of basicity as determined by  $CO_2$  desorption is as follows: Ca<sub>4</sub>Al-HT > Ca<sub>3</sub>Al-HT > Mg<sub>4</sub>Al-HT > Mg<sub>2</sub>Al-HT > Mg<sub>2</sub>Al-HT.

Figure 11 shows the CO<sub>2</sub>-TPD of Ca<sub>4</sub>Al-HT catalysts synthesized using different molar concentration of CTAB.

Here also the desorption temperature increased from 465 K to 479 K indicating stronger basicity. When



Figure 4. FT-IR spectra of  $Mg_xAI$ -HT hydrotalcites (a)  $Mg_2AI$ -HT, (b)  $Mg_3AI$ -HT and (c)  $Mg_4AI$ -HT catalysts.

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comparison was made between  $Ca_xAI$ -HT (x = 2, 3 and 4) and  $Ca_xAI$ -HT yCTAB (y = 0.1, 0.2, 0.4 and 0.6) catalysts, desorption of CO<sub>2</sub> took place at higher temperature of the hydrotalcites prepared with surfactants



Figure 5. FT-IR spectra of  $Ca_xAI$ -HT hydrotalcites (a)  $Ca_2AI$ -HT, (b)  $Ca_3AI$ -HT and (c)  $Ca_4AI$ -HT catalysts.



**Figure 6.** FT-IR spectra of Ca<sub>4</sub>Al-HT hydrotalcite prepared with various CTAB concentrations (a) Ca<sub>4</sub>Al-HT 0.1CTAB, (b) Ca<sub>4</sub>Al-HT 0.2CTAB, (c) Ca<sub>4</sub>Al-HT 0.4CTAB and (d) Ca<sub>4</sub>Al-HT 0.6CTAB catalysts.



**Figure 7.** Adsorption–desorption isotherm of  $Mg_xAl$ -HT and  $Ca_xAl$ -HT hydrotalcites (a)  $Mg_2Al$ -HT, (b)  $Mg_3Al$ -HT (c)  $Mg_4Al$ -HT (d)  $Ca_2Al$ -HT, (e)  $Ca_3Al$ -HT and (f)  $Ca_4Al$ -HT catalysts.

(CTAB). Moreover the basicity of  $Ca_xAI$ -HT yCTAB catalysts was also found to be on the higher side i.e.,  $Ca_4AI$ -HT adsorbed 0.57 mmol of  $CO_2/g$  whereas  $Ca_4AI$ -HT yCTAB (y = 0.1, 0.2, 0.4 and 0.6) catalysts adsorbed 0.55 to 0.86 mmol of  $CO_2/g$ . The higher basicity of  $Ca_4AI$ -HT yCTAB (y = 0.1, 0.2, 0.4 and 0.6) catalysts is due to the higher access of more basic sites created by CTAB template as shown in Table II. This result is further authenticated by the increase in lattice parameters observed in the XRD powder patterns and increase in surface area observed in BET adsorption–desorption isotherms.

### 3.5. Inductive Coupled Plasma (ICP) Analysis

Table I also contains composition and Mg/Al and Ca/Al molar ratios of the MgAl-HT and CaAl-HT hydrotalcites.



**Figure 8.** Adsorption–desorption isotherm of  $Ca_4AI$ -HT hydrotalcite prepared with various CTAB concentrations (a)  $Ca_4AI$ -HT (b)  $Ca_4AI$ -HT 0.1CTAB, (c)  $Ca_4AI$ -HT 0.2CTAB, (d)  $Ca_4AI$ -HT 0.4CTAB and (e)  $Ca_4AI$ -HT 0.6CTAB catalysts.



**Figure 9.** CO<sub>2</sub>-TPD profile of  $Mg_xAI$ -HT hydrotalcites (a)  $Mg_2AI$ -HT, (b)  $Mg_3AI$ -HT and (c)  $Mg_4AI$ -HT catalysts.



**Figure 10.**  $CO_2$ -TPD profile of  $Ca_x$ Al-HT hydrotalcites (a)  $Ca_2$ Al-HT, (b)  $Ca_3$ Al-HT and (c)  $Ca_4$ Al-HT catalysts.

The composition and molar ratio considered for the synthesis of MgAl-HT and CaAl-HT were retained in the solid products which are comparable to the theoretical values.



**Figure 11.**  $CO_2$ -TPD profile of  $Ca_4Al$ -HT hydrotalcites prepared with various CTAB concentrations (a)  $Ca_4Al$ -HT 0.1CTAB, (b)  $Ca_4Al$ -HT 0.2CTAB, (c)  $Ca_4Al$ -HT 0.4CTAB and (d)  $Ca_4Al$ -HT 0.6CTAB catalysts.

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Figure 12.SEM micrographs of (a) Mg4Al-HT, low magnification (b) Ca4Al-HT, low magnification (c) Mg4Al-HT, high magnification and (d) Ca4Al-HT, high magnification.HT, high magnification.IP: 93.179.90.248 On: Tue, 20 Mar 2018 09:58:09



Figure 13. SEM micrographs of Ca4Al-HT, prepared by using different CTAB molar concentration (a) 0.1, (b) 0.2 (c) 0.4 and (d) 0.6.

#### 3.6. Scanning Electron Microscope (HR-SEM)

The morphology of the  $Mg_4Al$ -HT and  $Ca_4Al$ -HT are shown through SEM images (Fig. 12).

Both Mg<sub>4</sub>Al-HT (Fig. 12(a)) and Ca<sub>4</sub>Al-HT (Fig. 12(b)) have fine plate morphology which is further confirmed at higher magnification (Figs. 12(c and d)) and both are agglomerated. Similarly the Figure 13 shows SEM images of Ca<sub>4</sub>Al-HT prepared using CTAB as template. It is evident that CTAB is responsible for the formation of nano structures in the hydrotalcite catalysts. The particle sizes became smaller and smaller when the CTAB concentration was increased. (Figs. 13(c and d)).

### 3.7. High Resolution Transmission Electron Microscope (HR-TEM)

The HR TEM images of  $Ca_4Al$ -HT hydrotalcites prepared with and without using CTAB template (0.4 molar concentrations) are shown in Figure 14.

The catalyst synthesized using CTAB with 0.4 molar concentration is designated as  $Ca_4Al$ -HT-0.4CTAB. The  $Ca_4Al$ -HT hydrotalcite synthesized without CTAB is shown in Figure 14(a). The particles have plate like morphology. However the HR TEM image of the same catalyst prepared using CTAB (Fig. 14(b)) indicate that porous

and much finer particles in nano size were formed. The individual nano particles of the Ca<sub>4</sub>Al-HT-0.4CTAB roll together with the formation of bundle like nano structures (Fig. 14(c)). At higher magnification of 20 nm the Ca<sub>4</sub>Al-HT-0.4CTAB catalyst clearly shows the particles with 10–20 nm size. These results further authenticate that Ca<sub>4</sub>Al-HT-0.4CTAB are nano sized and confirms with the XRD powder data and SEM results.

### 3.8. Catalytic Studies on Transesterification of Glycerol with DMC

#### 3.8.1. Effect of Reaction Temperature—Optimization Studies

The effect of reaction temperature on the catalytic transesterification of glycerol with dimethyl carbonate was investigated using batch reactor as shown in Scheme 1.

All the catalysts viz.,  $Mg_2Al$ -HT,  $Mg_3Al$ -HT,  $Mg_4Al$ -HT,  $Ca_2Al$ -HT,  $Ca_3Al$ -HT and  $Ca_4Al$ -HT were evaluated for their catalytic activity in the temperature range of 333–373 K. The reaction was conducted for 2 h using 1:4 molar ratio of glycerol: DMC and the results are given in Table III.

As tabulated, the conversion of glycerol increased with increase in reaction temperature for all the catalysts.



Figure 14. HR-TEM micrographs of Ca<sub>4</sub>Al-HT (a) and Ca<sub>4</sub>Al-HT 0.4CTAB (b–d) catalysts.

Solvent Free Transesterification of Glycerol Into GC Over Nanostructured CaAl Hydrotalcite Catalyst



**Scheme 1.** Transesterification of glycerol with dimethyl carbonate (DMC).

Among the Mg<sub>x</sub>Al-HT catalysts, Mg<sub>4</sub>Al-HT was found to give the best conversion of of glycerol (63.4%) with 95.7% selectivity towards glycerol carbonate. Although all the catalysts show increase in conversion, the selectivity towards GC decreases slightly with increase in reaction temperature. As a as the catalytic activity is concerned,  $Ca_xAl$ -HT catalysts show higher catalytic activity than Mg<sub>x</sub>Al-HT catalysts. In all the cases only glycidol was found to the other minor product. Among the hydrotalcites  $Ca_4Al$ -HT showed the highest glycerol conversion (82.6%) and the highest selectivity (97.9%) towards glycerol carbonate at 353 K. Hence  $Ca_4Al$ -HT hydrotalcite was chosen for further optimization studies and 353 K was found to be the optimum reaction temperature.

# 3.8.2. Effect of CTAB Concentration in Ca<sub>4</sub>Al-HT Hydrotalcites on Conversion and Selectivity

The effect of CTAB concentration in the synthesis of  $Ca_4Al$ -HT catalyst on the conversion of glycerol was investigated and the results are given in Table IV.

It is evident that the increase in CTAB molar concentration in the preparation of  $Ca_4Al$ -HT catalysts increased the conversion from 87.3% to 98.9% with very good

 Table III.
 Effect of reaction temperature on the glycerol conversion and glycerol carbonate selectivity.

			Selectivity (%)		
Catalyst	Reaction temperature (K)	Conversion (%)	Glycerol carbonate	Glycidol	
Mg,Al-HT	333	24.6	100	_	
	353	32.5	100	_	
	373	35.0	98.8	1.2	
Mg <sub>3</sub> Al-HT	333	27.5	100	_	
•••	353	39.0	98.8	0.2	
	373	38.6	98.1	1.9	
Mg <sub>4</sub> Al-HT	333	32.9	100	_	
04	353	51.6	98.8	0.2	
	373	63.4	95.7	4.3	
Ca <sub>2</sub> Al-HT	333	54.6	100	_	
-	353	71.3	99.7	0.3	
	373	73.2	98.0	2.0	
Ca <sub>3</sub> Al-HT	333	62.0	99.4	0.6	
2	353	78.3	98.6	1.4	
	373	80.7	93.8	6.2	
Ca₄Al-HT	333	67.0	98.9	1.1	
·	353	82.4	95.9	4.1	
	373	82.6	91.8	8.2	
7	353 373	82.4 82.6	95.9 91.8	4.1 8.2	

*Notes*: Reaction conditions: Temperature: 333, 353 and 373 K, catalyst weight: 100 mg, glycerol/DMC molar ratio: 1:4, reaction time: 2 h.

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**Table IV.** Effect of CTAB concentration in Ca<sub>4</sub>Al-HT on glycerol conversion and glycerol carbonate selectivity.

	Reaction		Selectivity (%)		
Catalyst	temperature (K)	Conversion (%)	Glycerol carbonate	Glycidol	
Ca₄Al-HT	353	82.4	95.9	4.1	
Ca <sub>4</sub> Al-HT-0.1CTAB	353	87.3	98.5	1.5	
Ca <sub>4</sub> Al-HT-0.2CTAB	353	92.1	98.0	2.0	
Ca <sub>4</sub> Al-HT-0.4CTAB	353	98.7	97.9	2.1	
Ca <sub>4</sub> Al-HT-0.6CTAB	353	98.9	95.1	4.9	

*Notes*: Reaction conditions: Temperature: 353 K, catalyst weight: 100 mg, glycerol/DMC molar ratio: 1:4, reaction time: 2 h.

selectivity over 95% towards GC. Among  $Ca_4Al$ -HT yCTAB catalysts,  $Ca_4Al$ -HT 0.4CTAB converts maximum glycerol with maximum selectivity. On increasing the CTAB concentration further to 0.6 molar a slight decrease in selectivity was observed.

# 3.8.3. Effect of Time on Stream on Conversion and Selectivity

In order to investigate the effect of reaction time on the glycerol conversion and selectivity towards glycerol carbonate, 100 mg of the best catalyst viz.,  $Ca_4Al$ -HT 0.4CTAB was taken and the reaction was conducted at the optimized reaction temperature of 353 K for 4 h and the results are summarized in Table V.

Chalthough the conversion increase with reaction time the selectivity decreases slightly. As maximum conversion with highest selectivity could be obtained at 2 h of reaction time, the reaction time of 2 h was optimized.

#### 3.8.4. Effect of Glycerol: DMC Molar Ratio

In order to check the effect of molar ratio of glycerol to dimethyl carbonate (DMC) on conversion and selectivity the reaction was performed with different molar ratios from 1:1 to 1:4 under the optimized conditions: Catalyst =  $Ca_4AI$ -HT 0.4CTAB, temperature = 353 K, time = 2 h and the results are given in Table VI.

The results clearly indicate that the molar ratio of 1:4 was found to be the best in terms of conversion and selectivity.

 Table V.
 Effect of reaction time on the glycerol conversion and glycerol carbonate selectivity.

			Selectivity (%)		
Catalyst	Reaction time (h)	Conversion (%)	Glycerol carbonate	Glycidol	
Ca <sub>4</sub> Al-HT-0.4CTAB	1	72.6	97.8	2.2	
Ca <sub>4</sub> Al-HT-0.4CTAB	2	98.7	97.9	2.1	
Ca <sub>4</sub> Al-HT-0.4CTAB	3	99.1	96.8	3.2	
Ca <sub>4</sub> Al-HT-0.4CTAB	4	99.5	94.2	5.8	

*Notes*: Reaction conditions: Temperature: 353 K, catalyst weight: 100 mg, glycerol/DMC molar ratio: 1:4, reaction time: 1, 2, 3 and 4 h. Table VI. Effect of glycerol to DMC molar ratio on glycerol conversion and glycerol carbonate selectivity

			Selectivity (%)		
Catalyst	Glycerol/DMC molar ratio	Conversion (%)	Glycerol carbonate	Glycidol	
Ca <sub>4</sub> Al-HT-0.4CTAB	1:2	81.9	98.2	1.8	
Ca <sub>4</sub> Al-HT-0.4CTAB	1:3	90.5	97.8	2.2	
Ca <sub>4</sub> Al-HT-0.4CTAB	1:4	98.7	97.9	2.1	
Ca <sub>4</sub> Al-HT-0.4CTAB	1:5	98.7	97.8	2.2	

Notes: Reaction conditions: Temperature: 353 K, catalyst weight: 100 mg, reaction time: 2 h.

#### 3.8.5. Recyclability of Ca<sub>4</sub>Al-HT 0.4CTAB Catalyst

In order to investigate the recyclability of Ca<sub>4</sub>Al-HT 0.4CTAB catalyst, the reaction was performed at the optimized reaction conditions of temperature (353 K), catalyst weight (100 mg), reaction time (2 h) and glycerol to DMC molar ratio (1:4) for five cycles. The results show that the Ca<sub>4</sub>Al-HT 0.4CTAB was catalytically active without much loss even after 5 catalytic cycles. The catalyst converted almost 97.8% of glycerol with selectivity of 97.0% towards glycerol carbonate. This result proves that Ca<sub>4</sub>Al-HT 0.4CTAB catalyst is stable.

#### 4. CONCLUSION

CaAl-HT and MgAl-HT with molar ratio of 2, 3 and 4 were successfully synthesized by direct precipitation ue 25. J. García, H. G. Marína, and E. Piresa, Green Chem. 12, 426 method. Based on the initial screening of both catalytic series Ca<sub>4</sub>Al-HT was found to be the best in terms of conversion of glycerol to glycerol carbonate. Ca<sub>4</sub>Al-HT nano catalyst was synthesized with different molar concentration of CTAB (0.1, 0.2, 0.4 and 0.6). XRD, BET and HR TEM studies confirm the formation of nano-structured Ca<sub>4</sub>Al-HT catalyst. The same catalyst was found to show high basicity by CO<sub>2</sub>-TPD analysis. Among the catalyst Ca<sub>4</sub>Al-HT 0.4CTAB was found to be most active as it converts glycerol (98.7%) with the highest selectivity towards glycerol carbonate (97.9%). The recyclability test performed with the best catalyst showed that the catalyst was active without much loss even after 5 cycles.

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Received: 5 July 2017. Accepted: 21 July 2017.

IP: 93.179.90.248 On: Tue, 20 Mar 2018 09:58:09 Copyright: American Scientific Publishers Delivered by Ingenta