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A green process for glycerol valorization to glycerol carbonate over heterogeneous hydrotalcite catalyst

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ABSTRACT

Biodiesel production is accompanied by 10% w/w glycerol which needs to be valorized to into bulk and specialty chemicals in order to make the biodiesel economics favorable. Glycerol carbonate is one such product from glycerol which has many potential applications. A green process using calcined hydrotalcite supported on hexagonal silica (CHT-HMS) catalyst was developed for the conversion of glycerol to glycerol carbonate using dimethyl carbonate. Effects of various Al:Mg composition and loading on hexagonal mesoporous silica (HMS) were studied. Al:Mg composition of 1:2 with 15% w/w loading on HMS was the best catalyst. . CHT-HMS catalyst was fully characterized by various techniques such as FT-IR, EDAX, SEM, TPD, XRD, etc. The effects of various parameters such as speed of agitation, catalyst concentration, mole ratio, and temperature were studied. The catalyst is robust and recyclable. The reaction follows Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism with weak adsoption of all species. Thus, a second order rate equation for the reaction was developed and the activation energy estimated.

1. Introduction

Biodiesel production is accompanied by 10% w/w glycerol as a co-product which needs to be utilized in order to make the economics favorable [1–6]. The use of bio-diesel is considered as the green alternative to reduce carbon emissions. Additionally, the needs of new economic synthetic routes for chemicals starting from non-petrochemical sources are desirable and therefore glycerol would be acceptable as a raw material. In 2011, 66.2% of the total glycerol was produced from bio-diesel industry. US consumption of biodiesel rose from 263 million gallons in 2010 to 878 million gallons in 2011 to 1 billion gallon in 2012, demand for biodiesel fell and so did prices. The EPA has mandated the use of 1.28 billion gallons of biodiesel in 2013. Production came from 112 biodiesel plants with capacity of 2.2 billion gallons per year. Increasing biodiesel demand will continue to supply glycerol abundantly and it needs to be valorized [10].

Several bulk and specialty chemicals could be produced with glycerol as platform [7–9]. Conversion of glycerol to glycerol carbonate is one of the attractive options to valorize glycerol. Glycerol carbonate is a fairly new chemical in the market, which possibly will present some new commercial applications [10].

Glycerol carbonate is an attractive starting material due to the presence of two competing sites of reactivity in it. Glycerol monoesters, glycerol carbonate esters, glycerol monourethanes, glycerol diurethanes, are obtained from glycidol or glycerol carbonate which are non-ionic glycerilic oxygenated surfactants, and non-ionic glycerilic oxygenated and nitrogenated surfactants [10]. Glycerol carbonate is an intermediate in the alkylene carbonate family with many potential areas of application such as reactive protic solvent and solvent for battery electrolyte, filming lubricants, agrosynthons, filming plasticizers, CO_2 separation from gaseous mixtures, phenolic resin preparation, synthesis of new functionalized polymers like polycarbonates and polyurethanes, medicinal and sanitary field, wetting agent ingredient for cosmetics, polymer bases for emulsions; as a surfactant component in coating and paint industry; and a substitute for ethylene carbonate and propylene carbonate, etc. [11]. The production of organic carbonates is currently 80,000 TPA and carbonate based polymers 1.1 MTPA, which is expanding continuously. The production will continue to grow, especially if their use as additives for fuels expands [7].

Enzymatic synthesis of glycerol carbonate from glycerol and dimethyl carbonate was reported with 74% conversion of glycerol and 80.3% selectivity towards glycerol carbonate [12]. Sulfur assisted carbonylation of glycerol with carbon monoxide has also been studied [13]. A few reports deal with synthesis of glycerol carbonate from glycerol and urea with liberation of ammonia gas over gold [14], lanthanum oxide [15] and hydrotalcite catalyst [16]. Urea has been used as a reagent to make glycerol carbonate with lanthanum oxide as solid base catalyst [17] and zinc containing homogeneous catalysts [18]. However, the use of urea suffers

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Nomenclature

a_p	solid–liquid interfacial area (cm^2/cm^3 of liquid phase)
A	reactant species A—glycerol
AS	chemisorbed A
B	reactant species B—DMC
BS	chemisorbed B
C_A, C_B	concentration of A and B (mol/cm^3)
C_{A0}, C_{B0}	initial concentration of A and B (mol/cm^3)
C_{AS}, C_{BS}	concentration of A and B at solid (catalyst) surface (mol/g.cat)
C_{PS}, C_{WS}	concentration of P and W at solid (catalyst) surface (mol/g.cat)
C_S	concentration of vacant sites (mol/g/cat)
C_t	total concentration of the sites (mol/g/cat)
d_P	diameter of catalyst particle (cm)
G	glycerol carbonate (product)
GS	chemisorbed product
M	methanol
$-r_A$	rate of disappearance of A ($mol.cm^{-3}.min^{-1}$)
k_{SLA}, k_{SLB}	solid–liquid mass transfer coefficients (cm/s)
K_A	equilibrium constant for adsorption of A on catalyst surface (cm^3/mol)
K_B	equilibrium constant for adsorption of B on catalyst surface(cm^3/mol)
K_{SR}	equilibrium constant for surface reaction of chemisorbed A and B
K_G	equilibrium constant for adsorption of G on catalyst surface
$K_{M(cm^3/mol)}$	equilibrium constant for adsorption of M on catalyst surface (cm^3/mol)
S	vacant site
Sh	Sherwood number
t	time (min)
w	catalyst concentration (g/cm^3 of liquid phase)
X_A	fractional conversion of A

Greek letters

ρ_p	density of catalyst particle (g/cm^3)

from reduced pressure requirements in order to separate gaseous ammonia and to avoid the formation of undesirable side products such as isocyanic acid and biuret. DMC is preferred since the severity of the process is less and the co-product methanol can be easily separated. A process for preparation of cyclic carbonates uses alkyl ammonium and tertiary amine catalysts and reports 92% conversion of glycerol with 92% selectivity to glycerol carbonate at 120 °C using tetra-butyl ammonium bromide (TBAB) as a catalyst [19]. Transesterification reaction of glycerol with dimethyl carbonate is also reported [20]. It has been reported that hydrotalcite and mixed oxides efficiently catalyze the process [20–24]. The synthesis of glycerol carobnate from glycerol and dimethyl carbonate (DMC) using several basic ionic liquids as both solvents and catalysts is reported [25]. Using *N*-methyl-*N*-butylmorpholinium dicyanamide, 95% conversion of glycerol into glycerol carbonate is achieved after four catalyst recycles at 120 °C in 13 h using a DMC/glycerol molar ratio of 3. However, the main drawbacks of this process are its long reaction time and column chromatography to separate catalyst and product.

A few of the aforesaid processes utilize carbonates and bicarbonates catalysts which are not reusable and in fact they create a lot of waste. In the current work, the synthesis of glycerol carbonate was achieved through reaction of glycerol and dimethyl carbonate by using calcinated Al–Mg hydrotalcite supported on hexagonal mesoporous silica (CHT-HMS) as a heterogeneous and reusable solid base catalyst. The results are novel and also include kinetic modeling which will be useful for reactor design and scale-up.

2. Materials and methods

2.1. Chemicals

The following chemicals were procured from reputed firms and used without further purification: dimethyl carbonate (DMC), methanol, *n*-undecane, ethanol, aluminum nitrate, magnesium nitrate, sodium carbonate, sodium hydroxide (all form S.D. Fine chem. Ltd, Mumbai, India); glycerol, tetraethylorthosilicate (Merck, Germany), hexadecylamine (Spectrochem Ltd., Mumbai, India).

2.2. Catalyst synthesis

5 g Dodecyl amine was added to 41.8 g ethanol and 29.6 g distilled water to make a homogeneous solution. Tetraethylorthosilicate (20.8 g) was added to the above solution under stirring and it was aged for 18 h at room temperature to form a white precipitate. The clear liquid above it was decanted to get hexagonal mesoporous silica (HMS) which was then dried on a glass plate. It was calcined at 550 °C in air for 3 h to remove the template [26].

5 g HMS was added to 30 cm^3 an aqueous solution of 1.28 g (5.0 mmol) magnesium nitrate and 3.75 g (10.0 mmol) aluminum nitrate. The slurry was stirred at 60 °C for 30 min. The solution was then co-precipitated by adding it slowly to a solution of 1.40 g (35.0 mmol) NaOH and Na_2CO_3 1 g (9.43 mmol) in 10 cm^3 distilled water with vigorous stirring at 30 °C for 2 h. During the addition, the pH of the solution was maintained at 9–10. The slurry was then agitated at 30 °C for 4 h, filtered, washed with distilled water repeatedly to attain pH 7 and dried in oven at 100 °C for 24 h. The catalyst was finally calcined in a muffle furnace at 450 °C for 12 h to obtain 15 wt% calcined hydrotalcite on hexagonal mesoporous silica (CHT-HMS) catalyst with Al:Mg ratio 1:2.

2.3. Catalyst characterization

2.3.1. FT-IR

FT-IR spectrum was obtained by Bruker IFS-66 single channel Fourier transform spectrophotometer. A thin pellet was prepared by mixing the catalyst with spectroscopic grade KBr. The pellet was subjected to a number of scans to record the spectra (Fig. 1). It shows absorption at 1083 cm^{-1} due to asymmetric stretching of Si–O–Si whereas peaks at ~466 cm^{-1} and 789 cm^{-1} are attributed to the internal bands of SiO_4 tetrahedra. A broad absorption band at

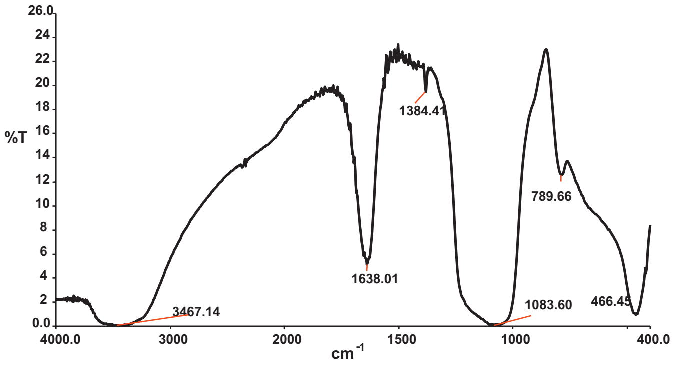

Fig. 1. FT-IR spectrum of the catalyst.

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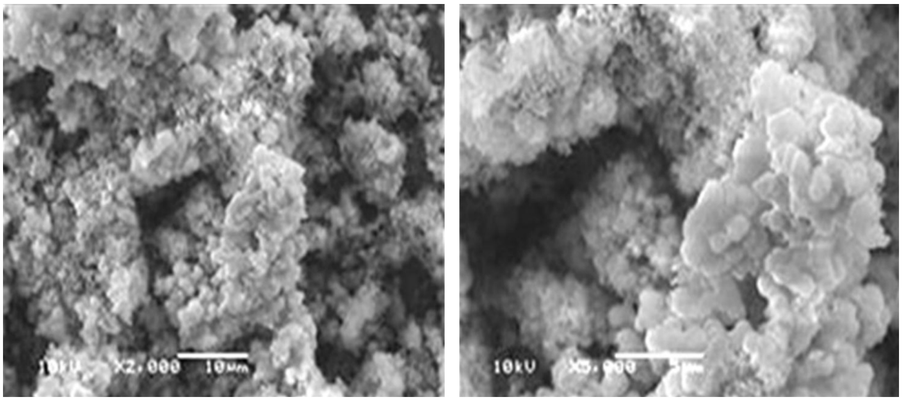

Fig. 2. SEM images of CHT-HMS catalyst with Al:Mg 1:2.

3467 cm^{-1} was due to stretching of H bonded OH group and water molecules; and thus the corresponding deformation mode are at 1638 cm^{-1}. FT-IR spectrum indicated the presence of functional group which indicated the mesoporous silica structure is intact after modifying the catalyst.

2.3.2. Surface area analysis

Surface area and pore size distribution measurements were obtained by Micromeritics ASAP 2010 instrument by N_2 adsorption at −197 °C, after subjecting the sample to high vacuum at 450 °C for 4 h. The adsorption desorption isotherms for the CHT-HMS catalyst with Al:Mg 1:2 showed characteristic of mesoporous solids. Characteristic nitrogen BET surface area for pure HMS was found to be 820 m^2/g which decreased to 250 m^2/g for CHT-HMS with Al:Mg 1:2. Pore volume for HMS and CHT-HMS were measured as 0.39 cm^3/g and 0.29 cm^3/g, respectively. This shows the accumulation of hydrotalcite on the HMS surface. The BJH adsorption pore size distribution shows that a major portion of surface area is due to pores with 4.6 nm diameter, suggesting pore sizes of the CHT-HMS in the mesoporous region (figure not shown for brevity).

2.3.3. SEM

Surface morphology of the catalyst was captured with SEM (Camera SU 30 microscope, JEOL, Japan). The dried samples were mounted on specimen studs and sputter coated with thin film of gold to prevent charring. Topographical images in SEM were formed from back scattered primary or low-energy secondary electrons (Fig. 2). A smoother surface layer is clearly seen from the images for CHT loaded HMS with particle size in the range of 0.1 μm to 2 μm. The particles were uniform with small agglomerates.

2.3.4. TPD

Temperature programmed desorption (TPD) was performed by using a Micromeritics AutoChem 2910 (USA) instrument. The basicity of CHT-HMS catalyst samples was studied by CO_2-TPD. A sample was loaded and activated at 450 °C, in a quartz cell; under continuous helium flow (20 cm^3/min) for a period of 2 h. Pre-saturation was accomplished by passing 10% v/v CO_2 in He for 1 h at 30 °C. Then the sample was flushed with He for 1 h at 50 °C to remove excess CO_2. The adsorbed CO_2 was desorbed in He flow (30 ml/min) with a heating rate of 10 °C/min and the temperature was raised from 50 °C to 450 °C. The desorbed CO_2 was detected by using a thermal conductivity detector (TCD). A broad peak with a maximum at 114 °C corresponds to desorption of adsorbed CO_2 (Fig. 3). The amount of CO_2 adsorbed was 9.7 ml/g of the catalyst at STP. This suggests the presence of basic sites in the catalyst.

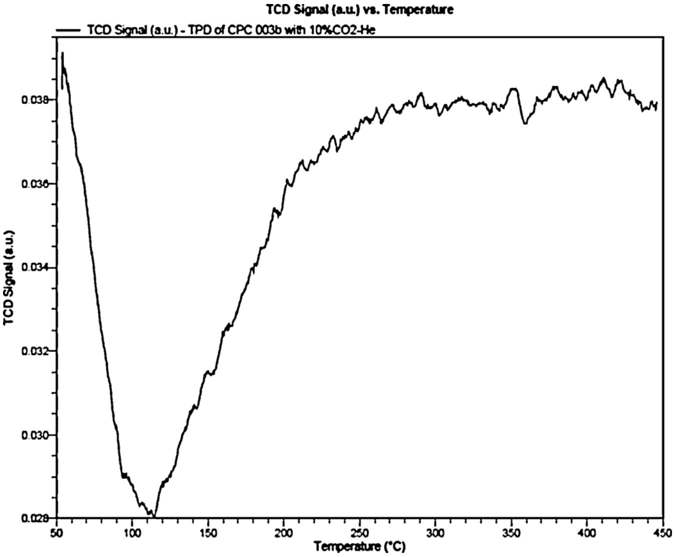

Fig. 3. Temperature programmed desorption of CO_2 for the catalyst.

2.3.5. XRD

The X-ray scattering measurements were performed by using a Philips PW 1729 powder diffractometer with Cu-*K*α (1.54 Å). The scattered intensities were collected from 10° to 60° (2θ) by scanning at 0.025° (2θ) steps with a counting time of 1 s at each step. The catalyst exhibited a strong reflection at 2θ of about 2.8° (figure not shown). In CHT-HMS catalyst with Al:Mg 1:2, the particles which were formed on the surface and/or in the pore of HMS, were very small to show an XRD pattern and pores of HMS blocked by the formed Al–Mg mixed oxide, or by the walls of HMS being partially destroyed. Hence, no peak was observed in XRD pattern of calcined HT on HMS from 10° to 70°.

2.3.6. EDAX

Elemental analysis of the catalyst was carried out which showed exact % composition of each component in the catalyst. During the synthesis, 1:2 ratio of Al:Mg was used, which was almost matching with the values obtained from EDAX results (Table 1). Around 15% loading of ($MgO + Al_2O_3$) was observed.

Table 1
Elemental analysis of CHT-HMS catalyst.

Composition, w/w	O (%)	Mg (%)	Al (%)	Si (%)
CHT-HMS	51.70	5.38	2.93	39.99

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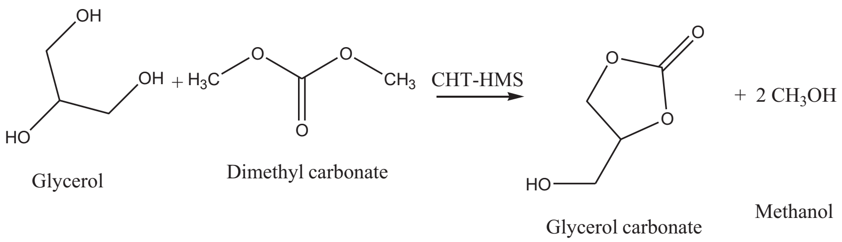

Scheme 1. Synthesis of glycerol carbonate from glycerol and DMC over CHT-HMS.

2.4. *Reaction procedure*

The experiments were carried out in a 100 cm^3 stainless autoclave (Amar equipment, Mumbai, India) with stirrer with pitched turbine impeller. For the standard reaction, the reactor was charged with 0.109 mol glycerol, 0.326 mol dimethyl carbonate (DMC), 0.002 g/cm^3 CHT-HMS catalyst with Al:Mg 1:2, 1.0 cm^3 *n*-undecane as an internal standard and methanol as a solvent to make the total volume of 55 cm^3 at 170 °C for 3 h. The autogenous pressure of the reaction mixture was about 6.5 atm to 7.0 atm. As the reaction proceeded, methanol and CO_2 were generated in the reaction and therefore the pressure reached to 17.0 atm to 18.0 atm at the end of the reaction. At the end of the reaction, the autoclave was cooled to room temperature, fewer atmospheric pressure and then opened to enable the reaction liquid to be filtered.

2.5. *Analysis*

The samples were withdrawn periodically from the autoclave, after stopping the agitation temporarily, by using a sampling valve. The samples were centrifuged to allow the catalyst particle to settle down. The upper clear liquid was taken further for the analysis. Analysis of the reaction mixture was performed by GC (Chemito, model 1000) equipped with FID and a BPX-50 capillary column (0.25 mm diameter and 30 m length). The calculations were based on the limiting reactant glycerol. The product glycerol carbonate and all the other impurities were confirmed by GC–MS instrument (Perkin Elmer Clarus 500) equipped with BP-1 capillary column (30 m length, 0.025 mm i.d.).

3. Results and discussion

When DMC was used as a solvent, two immiscible phases were formed which made the kinetic study of the reaction difficult (Scheme 1). Methanol was found to be highly miscible with the reaction mixture, hence it was taken as solvent. In methanol as a solvent, high reaction temperature was required to shift the equilibrium towards forward direction as it was also a co-product in the reaction. The other side products were 4-(methoxymethyl)-1,3-dioxolan-2-one, 3-methoxy propane-1,2-diol and bis[(2-oxo-1,3-dioxolan-4yl)methyl] carbonate in small quantity. The effect of various parameters on the conversion of glycerol was studied with glycerol as a limiting reactant. Concentration profiles of all reactants and products were measured as function of time. Over 80% conversion was obtained for 1:3 mol ratio of glycerol to DMC in standard experiment in 90 min.

3.1. *Screening of various catalysts*

Varying ratios of Al–Mg containing CHT-HMS catalysts were prepared by a standard aqueous preparation and heat crystallization process. Selection of the catalyst was based on the conversion of glycerol and selectivity towards glycerol carbonate. This catalyst contains two types of sites, acidic as well as basic. Acidic sites were fewer as compared to the basic sites. The role of both the sites is demonstrated in the reaction mechanism. HMS is slightly acidic in nature due to presence of surface –OH groups and thus the presence of intact HMS structure shown from XRD and FT-IR indicates the presence of acidic sites in the catalyst. CO_2 TPD shows the presence of basic site due to the presence of alkaline earth metal Mg in the catalyst [25,26]. The presence of silica support increases the surface area and gives uniform pore size and therefore was more advantageous to sacrifice the small activity of the catalyst due to acid neutralization of this solid base catalyst in the presence of silica. High thermal stability, larger surface area, uniform-sized pores and adsorption capacity for aromatic organic molecules turn these materials into interesting catalysts. The catalyst was found to have excellent activity towards transesterification reaction of glycerol. CHT-HMS catalysts with different Al and Mg ratios were screened for the reaction under similar experimental conditions (Table 2). The reaction was also studied with pure HMS as a catalyst to verify the role of active sites in the catalyst. 0.11 g catalyst was added to the reaction mixture. No conversion was obtained when pure HMS was used since it is an inert support. Catalyst with Al:Mg ratio of 1:2 was found to be the best for the reaction and therefore it was taken for the further reaction studies.

3.2. *Effect of speed of agitation*

The effect of speed of agitation was studied in the range of 600–1000 rpm (Fig. 4) with 0.002 g/cm^3 catalyst concentration at 170 °C. The mole ratio of glycerol to DMC was kept as 1:3. No significant change in the rate and conversion pattern was observed, which indicated the absence of any resistance to external mass transfer of

Table 2
Catalyst screening for the synthesis of glycerol carbonate[a].

Entry	Catalysts with different Al:Mg ratio	Reaction time (h)	Conversion of glycerol (%)	Selectivity to glycerol carbonate (%)
1	Al:Mg (1:3)	2.5	83.1	86.6
2	**Al:Mg (1:2)**	**2.5**	**84.7**	**84.3**
3	Al:Mg (2:1)	2.5	73.5	88.3
4	Al:Mg (3:1)	2.5	72.9	86.5
5	HMS	2.5	0	–

[a] Reaction conditions: 0.326 mol dimethyl carbonate, 0.109 mol glycerol, 0.002 g/cm^3 CHT-HMS catalyst, 1.0 cm^3 *n*-undecane as internal standard, 20 cm^3 methanol, 55.0 cm^3 total reaction volume, speed of agitation 1000 rpm, temperature 170 °C.

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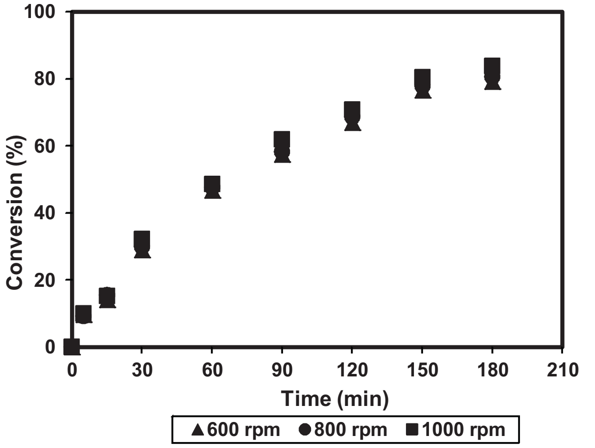

Fig. 4. Effect of speed of agitation on conversion of glycerol. Reaction conditions: 0.326 mol dimethyl carbonate, 0.109 mol glycerol, 0.002 g/cm^3 CHT-HMS catalyst, 1.0 cm^3 *n*-undecane as internal standard, 20 cm^3 methanol, 55.0 cm^3 total reaction volume, speed of agitation 1000 rpm, temperature 170 °C.

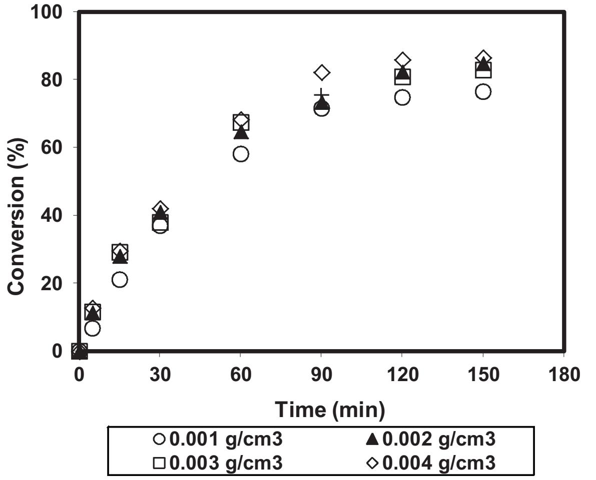

Fig. 5. Effect of catalyst loading on conversion of glycerol. Reaction conditions: 0.326 mol dimethyl carbonate, 0.109 mol glycerol, 1.0 cm^3 *n*-undecane as internal standard, 20 cm^3 methanol, speed of agitation, 55 cm^3 total reaction volume, 1000 rpm, temperature 170 °C.

reactants to the external surface of the catalyst. However, all further reactions were carried out at a speed of 1000 rpm. Theoretical calculations were also done to prove the absence of external mass transfer resistance as per some of our earlier work [27–30].

3.2.1. *Effect of solid-liquid mass transfer resistance*

The rate of mass transfer was calculated from the mass transfer coefficients for both the reactants, which were obtained from their bulk liquid phase diffusivities. The solid-liquid mass transfer resistance was calculated using the Wilke–Chang equation and Sherwood number. The values of solid to liquid phase mass transfer co-efficients k_{SLA} and k_{SLB} were calculated from Sherwood number (Sh) as 7.45×10^{-3} cm/s and 6.93×10^{-3} cm/s, respectively. To be on the safer side, the limiting value of the Sherwood number was taken as 2. The actual value was far greater than 2 due to intense agitation. The effect of mass transfer resistance due A and B was given by $1/(k_{SLA}\times a_p)$ and $1/(k_{SLB}\times a_p)$ where, a_p represents the external surface area per unit liquid volume $\left(a_p = \left(6w/\rho_p d_p\right) = 2.94\times10^4\,\text{cm}^{-1}\right)$ and the values obtained were 4.761×10^{-3} s and 4.9×10^{-4} s, respectively. The mass transfer resistances were 2.94 s/cm^3/mol and 0.82 s/cm^3/mol for transfer of A and B, respectively. Whereas the initial rate (r_A) for the standard reaction was found to be 6.7×10^{-7} mol/cm^3/s. Thus, the resistance due to reaction ($1/r_A$) 1.49×10^6 s/cm^3/mol was very much greater than mass transfer resistances of 2.94 s/cm^3/mol and 0.82 s/cm^3/mol. This confirmed that mass transfer rates are much higher than rates of reaction and hence speed of agitation had no influence on reaction rate.

3.3. *Effect of catalyst concentration*

It was observed that the rate of reaction increased with increase in catalyst quantity in the range of 0.001 g/cm^3 to 0.004 g/cm^3 (Fig. 5). This is due to the proportional increase in active sites. Beyond catalyst concentration of 0.002 g/cm^3 the effect was small to increase conversion which suggested that more number of active sites were available than required the available reactant molecules.

3.4. *Effect of mole ratio*

When the mole ratio of glycerol to dimethyl carbonate was less than 1:3 during the reaction, it was observed that both the conversion and selectivity decreased. Glycerol to DMC mole ratio of 1:3 was required to shift the reaction equilibrium towards the product and 80% conversion was obtained. Under such conditions no reaction of dimethyl carbonate with the third OH group of glycerol was seen. Due to the proximity of the carbonate group, the reactivity of the third OH group was lower than that of the first one. The intramolecular reaction with the second OH group proceeds much faster than the intermolecular one with the next dimethyl carbonate molecule and thermodynamically stable five-membered cyclic carbonate is formed exclusively. Mole ratio effect was studied in the range of 1:1 to 1:4 and 1:3 was found as the best (Fig. 6).

3.5. *Effect of temperature*

The effect of temperature was varied from 150 °C to 180 °C (Fig. 7). The rate of reaction increased with an increase in temperature. However, selectivity towards glycerol carbonate was decreased at higher temperature due to the formation of other impurities. Hence 170 °C was taken as optimum temperature for the reaction.

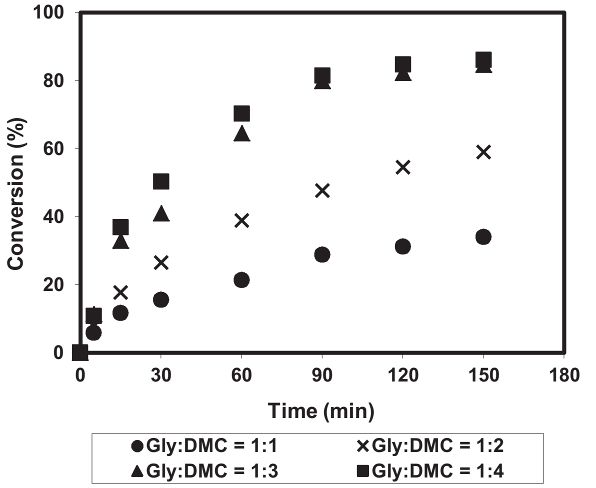

Fig. 6. Effect of mole ratio of glycerol: DMC. Reaction conditions: 0.002 g/cm^3 CHT-HMS catalyst, 1.0 cm^3 *n*-undecane as internal standard, 20 cm^3 methanol, 55 cm^3 total reaction volume, speed of agitation 1000 rpm, temperature 170 °C.

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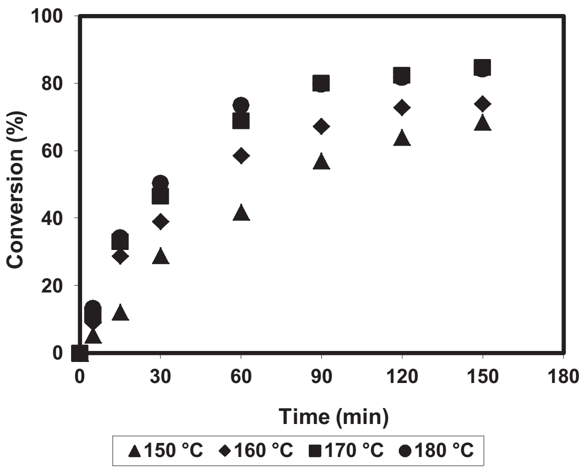


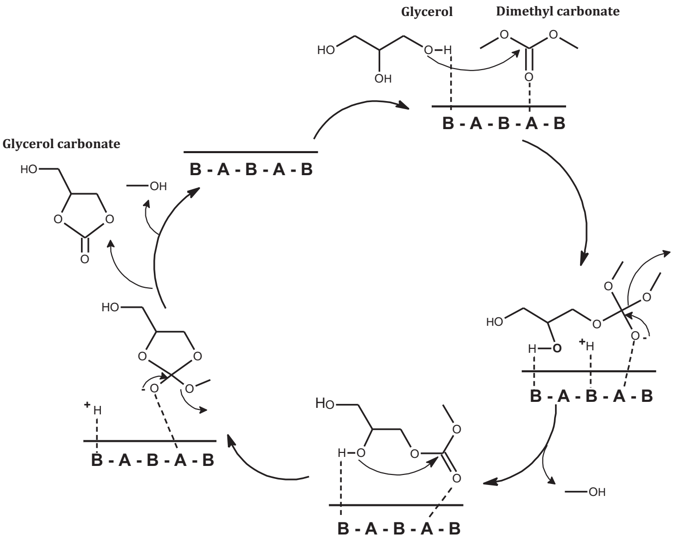
Fig. 7. Effect of temperature on conversion of glycerol. Reaction conditions: 0.326 mol dimethyl carbonate, 0.109 mol glycerol, 0.002 g/cm^3 CHT-HMS catalyst, 1.0 cm^3 *n*-undecane as internal standard, 20 cm^3 methanol, total reaction volume 55 cm^3, speed of agitation 1000 rpm.

3.6. Development of kinetic model

The above results were used to build a kinetic model. From the calculated values of mass transfer rates of A and B and the initial rate, it was evident that the reaction was devoid of inter and intra-particle diffusion resistances. Thus the reaction may be controlled by any of these 3 steps namely adsorption, surface reaction and desorption.

The catalytic mechanism is given in Scheme 2. First glycerol and dimethyl carbonate get adsorbed on the surface of the catalyst. The adsorbed species reacts to give intermediate which is adsorbed on the catalytic surface, this intermediate rearranges to form methanol and glycerol carbonate. The catalyst gets regenerated at the end of the reaction.

During the reaction dimethylcarbonate is consumed and two moles of methanol is formed and hence there is change in the total reaction volume. Initial total volume of the reaction was 55 cm^3, whereas after 84.7% conversion in 2.5 h the total volume of the reaction mixture was calculated as 54.3 cm^3. As this change in the volume was very less, it would not affect the rate and the conversion pattern based on catalyst concentration.



Scheme 2. Catalytic reaction mechanism.

The Langmuir–Hinshelwood–Hougen–Watson (LHHW) model was used. The reaction involves two reactants namely glycerol (A) and DMC (B) to give the desired product glycerol carbonate (G) and methanol (M).

Adsorption of glycerol (A) on vacant site (S) was given by

$$A + S \overset{K_A}{\longleftrightarrow} \mathrm{AS} \tag{1}$$

Adsorption of DMC (B) on vacant site was given by

$$B + S \overset{K_B}{\longleftrightarrow} \mathrm{BS} \tag{2}$$

Surface reaction of AS and BS leading to the formation of Glycerol carbonate (GS) on the site

$$\mathrm{AS} + \mathrm{BS} \overset{K_{SR}}{\longleftrightarrow} \mathrm{GS} + \mathrm{MS} \tag{3}$$

Desorption of glycerol carbonate (PS) and methanol (MS) was given by

$$\mathrm{GS} \overset{1/K_G}{\longleftrightarrow} G + S \tag{4}$$

$$\mathrm{MS} \overset{1/K_M}{\longleftrightarrow} M + S \tag{5}$$

The total concentration of the sites, C_t expressed as

$$C_t = C_S + C_{\mathrm{AS}} + C_{\mathrm{BS}} + C_{\mathrm{GS}} + C_{\mathrm{MS}} \tag{6}$$

or

$$C_t = C_S + K_AC_AC_S + K_BC_BC_S + K_GC_GC_S + K_MC_MC_S \tag{7}$$

The concentration of vacant sites,

$$C_S = \frac{C_t}{1 + K_AC_A + K_BC_B + K_GC_G + K_MC_M} \tag{8}$$

If the surface reaction (C) controls the rate of reaction, then the rate of reaction of A was given by,

$$-r_A = -\frac{dC_A}{dt} = k_{\mathrm{SR}}C_{\mathrm{AS}}C_{\mathrm{BS}} - k'_{\mathrm{SR}}C_{\mathrm{GS}}C_{\mathrm{MS}} \tag{9}$$

$$-\frac{dC_A}{dt} = \frac{k_{\mathrm{SR}}\left\{K_AK_BC_AC_B - \left(K_GK_MC_GC_M/K_{\mathrm{SR}}\right)\right\}Ct^2}{(1 + K_AC_A + K_BC_B + K_GC_G + K_MC_M)^2} \tag{10}$$

When the reaction was far away from equilibrium,

$$-\frac{dC_A}{dt} = \frac{k_{\mathrm{SR}}K_AK_BC_AC_BCt^2}{\left(1 + \sum K_iC_i\right)^2} \tag{11}$$

$$= \frac{k_rwC_AC_B}{\left(1 + \sum K_iC_i\right)^2} \tag{12}$$

where $k_rw = k_{\mathrm{SR}}K_AK_BCt$; w is catalyst concentration. Analysis of initial rate data showed that all species were weakly adsorbed and the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model reduced to the power law model. It would mean reactants DMC and glycerol were weekly adsorbed on the catalyst.

Then the above equation reduces to,

$$-\frac{dC_A}{dt} = k_rC_AC_Bw \tag{13}$$

Let $C_{B0}/C_{A0} = M$, the molar ratio of glycerol to DMC at time $t = 0$. Then, Eq. (13) can be written in terms of fractional conversion as,

$$\frac{dX_A}{dt} = k_rC_{A0}^2w(1 - X_A)(M - X_A) \tag{14}$$

This upon integration leads to:

$$\mathrm{Ln}\left\{\frac{M - X_A}{M(1 - X_A)}\right\} = k_1C_{A0}(M - 1)t \tag{15}$$

A plot of $\ln[(M - X_A)/M \times (1 - X_A)]$ against time gave an excellent fit, thereby supporting the model (Fig. 8). The initial reaction

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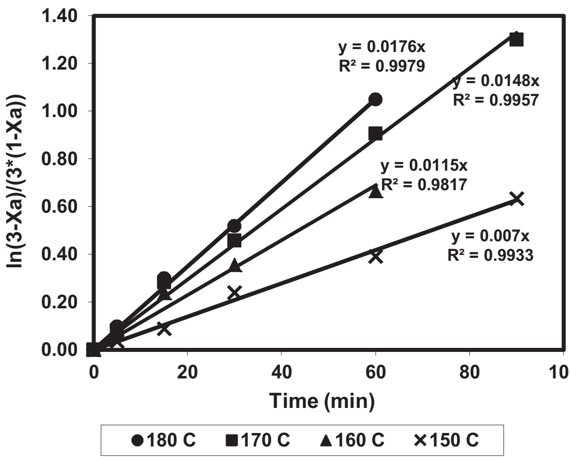

Fig. 8. Plot of $\mathrm{Ln}[(M - X_A)/M(1 - X_A)]$ against time.

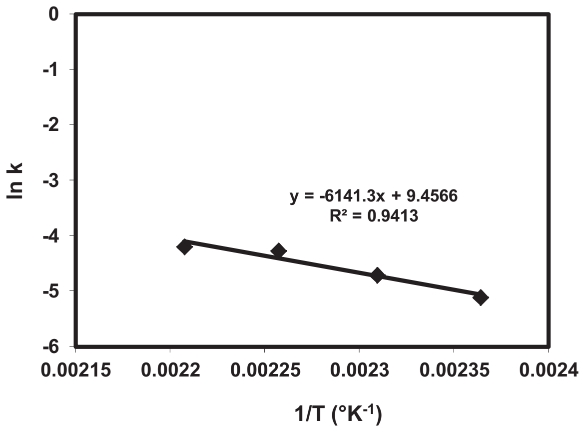

Fig. 9. Arrhenius plot.

Table 3
Catalyst reusability.

Sr. no.	Catalyst reusability	Reaction time (h)	Conversion of glycerol (%)	Selectivity to glycerol carbonate (%)
1	Fresh	2.5	84.7	84.3
2	1st Reuse	2.5	77.8	94.6
3	2nd Reuse	2.5	76.6	92.9
4	3rd Reuse	2.5	76.2	93.4
5	4th Reuse	2.5	75.7	92.8
6	5th Reuse	2.5	75.6	92.3

rates were calculated and the Arrhenius plot gave activation energy 12.56 kcal/mol (Fig. 9) which indicated an intrinsically kinetically controlled reaction with overall second order.

3.7. Catalyst reusability

The reaction mixture was filtered under vacuum; the catalyst was washed with methanol and dried. The dried catalyst was refluxed in methanol to remove the adsorbed species, again filtered and dried in oven at 120 °C. The residual catalyst was reused for same the reaction up to 5 cycles (Table 3). From the results it was clearly seen that, the catalyst was reusable with minimum loss in its activity and stability. The conversion of glycerol and the selectivity towards desired glycerol carbonate remained high. The initial drop in the catalyst activity could be due to loosely bound active component which could have been leached during the first run; however, thereafter a steady activity was observed for the next cycles with maintained high selectivity.

4. Conclusions

This work dealt with conversion of glycerol and dimethyl carbonate into glycerol carbonate using CHT-HMS as the solid base catalyst. A new catalytic method was developed. A reusable CHT-HMS (Al:Mg:: 1:2; 15% w/w on HMS), calcined hydrotalcite catalyst for the conversion of glycerol to glycerol carbonate was found to the best. It was fully characterized to understand its superior activity. All the reaction parameters were optimized to get high conversion of glycerol. The reaction was free from any external mass transfer resistance and intra-particle diffusion resistance and was intrinsically kinetically controlled. A kinetic model for the reaction was developed and validated. The reaction was found to be overall second order with activation energy of 12.56 kcal/mol. The catalyst activity was tested upto 5 cycles with intact activity after the first run.

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References

[1] http://www.eia.gov/biofuels/biodiesel/production/ (accessed 12.01.14).
[2] R. Medina, L.E. Cerdan, A. Gimenez, B.C. Paez, J. Biotechnol. 70 (1999) 379–391.
[3] J.M. Clacens, Y. Pouilloux, J. Barrault, Appl. Catal., A 227 (2002) 181–190.
[4] M. Roice, K.P. Subhashchandran, A.V. Gean, J. Franklin, V.N. Rajasekharan Pillai, Polymer 44 (2003) 911–922.
[5] G. Olga, R. Juana, B. Jorge, R. Jose, C. Tomas, Recent Patents Chem. Eng. 2 (2009) 11–21.
[6] F. Xiaohu, B. Rachel, Z. Yongchang, Open Fuels Energy Sci. J. 3 (2010) 17–22.
[7] G.D. Yadav, P.A. Chandan, N. Gopalaswami, Clean Technol. Environ. Policy 14 (2012) 85–95.
[8] G.D. Yadav, P.A. Chandan, D.P. Tekale, Ind. Eng. Chem. Res. 51 (2012) 1549–1562.
[9] G.D. Yadav, R.V. Sharma, S.O. Katole, Ind. Eng. Chem. Res. 52 (2013) 10133–10144.
[10] M.O. Sonnati, S. Amigoni, E.P. Taffin de Givenchy, T. Darmanin, O. Choulet, F. Guittard, Green Chem. 15 (2013) 283–306.
[11] M. Tudorache, L. Protesescu, S. Coman, V.I. Parvulescu, Green Chem. 14 (2012) 478–482.
[12] T. Mizuno, T. Nakai, M. Mihara, Heteroat. Chem. 21 (2010) 99–102.
[13] C. Hammond, J.A. Lopez-Sanchez, M.H. Ab Rahim, N. Dimitratos, R.L. Jenkins, A.F. Carley, Q. He, C.J. Kiely, D.W. Knight, G.J. Hutchings, Dalton Trans. 40 (2011) 3927–3937.
[14] W. Liguo, M. Yubo, W. Ying, L. Shimin, D. Youquan, Catal. Commun. 12 (2011) 1458–1462.
[15] M.J. Climent, A. Corma, P. De Frutos, S. Iborra, M. Noy, A. Velty, P. Concepcion, J. Catal. 269 (2010) 140–149.
[16] L. Wang, Y. Ma, Y. Wang, S. Liu, Y. Deng, Catal. Commun. 12 (2011) 1458–1462.
[17] S. Fujita, Y. Yamanishi, M. Arai, J. Catal. 297 (2013) 137–141.
[18] R.A. Grey, US5091543, Arco Chemical Tech. Inc., USA, 1992.
[19] J.R. Ochoa-Gomez, O.G. Jimenez-Aberasturi, B.M. Madurga, A.P. Rodrıguez, C.R. Lopez, L.L. Ibarreta, J.T. Soria, M.C. Villara Velasco, Appl. Catal., A 366 (2009) 315–324.
[20] M.G. Alvareza, A.M. Segarra, S. Contreras, J.E. Sueiras, F. Medina, F. Figueras, Chem. Eng. J. 161 (2010) 340–345.
[21] C. Chiappe, S. Rajamani, Pure Appl. Chem. 84 (2012) 755–762.
[22] G. Rokicki, P. Rakoczy, P. Parzuchowski, M. Sobiecki, Green Chem. 7 (2005) 529–539.
[23] A. Kumar, K. Iwatani, S. Nishimura, A. Takagaki, K. Ebitani, Catal. Today 185 (2012) 241–246.
[24] A. Takagaki, K. Iwatani, S. Nishimura, K. Ebitani, Green Chem. 12 (2010) 578–581.
[25] G.D. Yadav, P. Aduri, J. Mol. Catal. A: Chem. 355 (2012) 142–154.
[26] G.D. Yadav, G.P. Fernandes, Catal. Today 207 (2013) 162–169.
[27] G.D. Yadav, M.S. Krishnan, Org. Process Res. Dev. 2 (1998) 86–95.
[28] G.D. Yadav, S. Sengupta, Org. Process Res. Dev. 6 (2002) 256–262.
[29] G.D. Yadav, M.S. Krishnan, Chem. Eng. Sci. 54 (1999) 4189–4197.
[30] G.D. Yadav, P.H. Mehta, Ind. Eng. Chem. Res. 33 (1994) 2198–2208.

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