



## Short Communication

# Synthesis of glycidol from glycerol and dimethyl carbonate using ionic liquid as a catalyst

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## ABSTRACT

Transesterification of dimethyl carbonate with glycerol has been investigated using various ionic liquids as catalysts. Synthesis of glycidol with high selectivity (78%) has been achieved using tetramethylammonium hydroxide ([TMA][OH]) as a catalyst at 80 °C. Effect of various reaction conditions on the activity and selectivity was investigated and catalyst concentration had a significant influence on conversion as well as selectivity to glycidol. Activity as well as selectivity of the catalyst decreased significantly with increase in moisture content. Recycle experiment indicated slight drop in glycerol conversion and selectivity to glycidol because of dilution of reaction mixture and also the presence of products from the initial experiment.

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## 1. Introduction

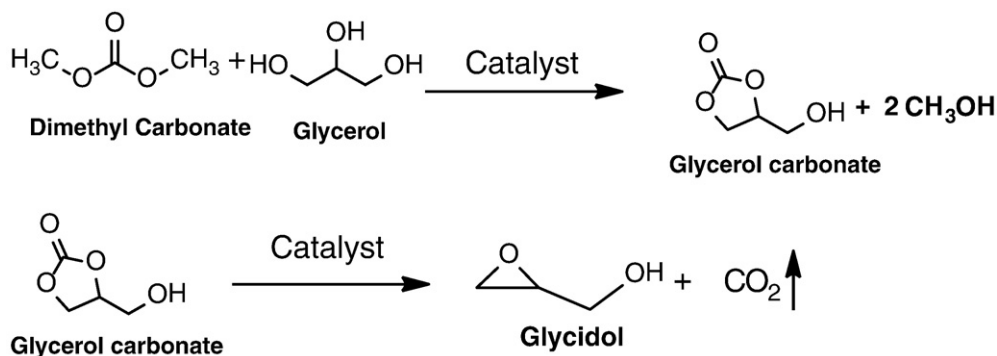
Glycerol is a non-toxic biodegradable compound, which can be obtained from glucose fermentation, sorbitol hydrogenolysis, or in huge amounts during the production of biodiesel from the transesterification of plant oils and animal fats [1]. The effective utilization of the glycerol that is formed during the production of biodiesel is a key factor to promote biodiesel commercialization and future developments. This has led to the development in the synthesis of value added chemicals from glycerol as can be seen from number of review articles on this subject [1–3]. Among various products proposed, glycerol carbonate and glycidol are important products with many applications. Glycerol carbonate has applications in the synthesis of polymers such as polyesters, polycarbonates, polyurethanes, polyamides, surfactants, and lubricating oils [3–6], while glycidol is used as a chemical intermediate in the synthesis of glycidyl ethers, esters, amines and as a high-value component in the production of glycidyl carbamate resins and polyurethanes [7–9].

Several methods have been described for the synthesis of glycerol carbonate from glycerol, including reaction of glycerol with hazardous phosgene, or carbon monoxide and oxygen at high pressure in the presence of copper based catalyst [10], carboxylation with carbon dioxide [11], reaction with urea [12] or transesterification with dialkyl carbonate such as dimethyl carbonate or cyclic carbonate [13]. Routes based on phosgene and oxidative carbonylation are hazardous because of toxicity

or explosion hazards associated with the reactants and are not attractive. Similarly direct carboxylation of glycerol with CO<sub>2</sub> is moisture sensitive and is an equilibrium controlled reaction [11]. Reaction of glycerol with urea or transesterification of dialkyl or cyclic carbonates with glycerol are interesting and significant amount of work is being carried out on the development of new catalysts for these reactions. Glycidol is commercially produced by epoxidation of allyl alcohol using tungsten based catalyst [14]. Drawback of this process is the number of steps involved and decomposition of the catalyst. There are few patents on the synthesis of glycidol from glycerol carbonate using basic catalysts [15,17]. The schematic of the reactions is shown below in Scheme 1.

Brunson et al. [16] have synthesized glycidol from glycerol and cyclic carbonates like ethylene carbonate under reduced pressure in a two step process. The reaction is carried out under reduced pressure in a temperature range of 140–240 °C to give ~63% yield of glycidol. Malkemus and Currier [15] have disclosed a process for the preparation of glycidol from glycerol using alkali and alkaline earth metal phosphates, chlorides, bromides, acetates, carbonates or bicarbonates as catalyst under reduced pressure at a temperature of 125–275 °C to obtain glycidol yield of ~72%. Yoo et al. [17] have reported synthesis of glycidol using zeolite exchanged with alkali or alkaline earth metals as catalyst. The reaction was carried out under reduced pressure and temperature in a range of 170–210 °C to obtain glycidol yield of 66–83%. Thus there are reports on the synthesis of glycerol carbonate from glycerol and dialkyl carbonate as reactants using basic catalysts and synthesis of glycidol from glycerol carbonate using basic catalysts. To the best of our knowledge there are no publications on the single pot synthesis of glycidol directly from glycerol. Herein we report our results on the synthesis of glycidol with high selectivity under mild operating conditions using ionic liquid catalyst.

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Scheme 1. Synthesis of glycerol carbonate from glycerol and synthesis of glycidol from glycerol carbonate.

## 2. Experimental

### 2.1. Chemicals

Glycerol (GL), glycidol (GD), glycerol carbonate (GC), methyl iodide (MeI) and the aqueous solutions of Bronsted basic ionic liquids tetramethylammonium hydroxide (25% [TMA][OH]), tetraethylammonium hydroxide (35% [TEA][OH]), tetrabutylammonium hydroxide (40% [TBA][OH]), tetramethylammonium bromide ([TMA][Br]), and tetrabutylammonium bromide ([TBA][Br]) were purchased from Aldrich chemicals. 20% aqueous solution of tetrapropylammonium hydroxide (TPAOH), dimethyl carbonate (DMC), tetramethylammonium hydroxide (25% [TMA][OH] in methanol), and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased from Spectrochem. All the chemicals were used as received from suppliers. Aqueous solutions of tetramethylammonium bicarbonate ([TMA][HCO<sub>3</sub>]) and tetrabutylammonium bicarbonate ([TBA][HCO<sub>3</sub>]) were prepared from aqueous solutions of [TMA][OH] and [TBA][OH] respectively according to the literature procedure [18]. Similarly [Me-DABCO][I] [19] was prepared by literature procedure. [Me-DABCO][OH] was prepared using an anion exchange resin in the OH<sup>-</sup> form by halide exchange. Water was removed to obtain [Me-DABCO][OH] as the product. Iodine present in the ionic liquid was estimated by addition of silver nitrate to known quantity of ionic liquid. Purity of ionic liquid prepared was 93.5% in the present case.

### 2.2. Experimental procedure for the synthesis of bicarbonate ionic liquid

Bicarbonate ionic liquids were prepared using the literature procedure [18] and typical experimental procedure followed is as below. Aqueous [TMA][OH] (25 wt.%) solution (10 ml) was taken in a 25 ml round bottom flask. CO<sub>2</sub> was bubbled through the solution for 2 h under constant stirring to obtain aqueous solution of [TMA][HCO<sub>3</sub>]. [TBA][HCO<sub>3</sub>] was prepared by following the similar procedure. <sup>13</sup>C NMR of the solutions for both the ionic liquids showed the appearance of a peak at δ value of 160, which is characteristic of carbonyl carbon of the bicarbonate group [20]. This indicated the formation of bicarbonate ionic liquids.

### 2.3. Experimental procedure for transesterification of DMC with glycerol

The transesterification of GL was carried out in a 50 ml round bottom flask equipped with a reflux condenser under vigorous stirring. In a typical run, 0.217 mmol of catalyst with respect to GL was charged to the 50 ml round bottom flask containing GL 2 g, (21.73 mmol) and DMC 5.87 g, (65.21 mmol). The reaction was carried out at 80 °C for the selected reaction time. Standard reaction was carried out for 90 min. The reaction mixture was cooled, a sample was taken out for analysis and it was diluted with N,N-dimethylformamide. The products were analyzed by gas chromatography on an Agilent 6890 gas chromatograph with HP-Innowax capillary column (30.0 m × 0.53 mm × 1.00 μm film

thickness). Identification of products was done using gas chromatography–mass spectrometry (GC–MS) on an Agilent 6890N gas chromatograph coupled to an Agilent 5973 MSD mass spectrometer using HP-5 MS capillary column of 30 m × 0.32 mm × 0.25 μm dimension. Activity of catalyst was based on conversion of limiting reagent measured under standard conditions of reaction.

### 2.4. Catalyst characterization

All the catalysts were characterized by IR and NMR analyses. NMR experiments were carried out on a Bruker Avance 400 wide bore spectrometer equipped with a superconducting magnet with a field of 9.4 T. The operating frequency for <sup>13</sup>C was 75.4 MHz electron microscope. IR spectrum was recorded on Agilent Technologies, Cary 600 series FT-IR Spectrometer.

The details of catalyst characterization for ionic liquids prepared are as follows:

[TMA][HCO<sub>3</sub>]:

<sup>1</sup>H NMR: 3.08, 12H (s)

<sup>13</sup>C NMR: 55.17, 160.38

[TBA][HCO<sub>3</sub>]:

<sup>1</sup>H NMR: 0.89, 12H (t), 1.25–1.36, 8H (m), 1.56–1.64, 8H (m), 3.15, 8H (t)

<sup>13</sup>C NMR: 12.93, 19.1, 23.05, 57.94, 160.07

[Me-DABCO][OH]:

<sup>1</sup>H NMR: 3.01, 3H (s), 3.14, 6H (t), 3.35, 6H (t)

FT-IR (cm<sup>-1</sup>): 796, 1123, 2894, 3424.

## 3. Results and discussion

Various basic ionic liquids were screened for the transesterification of glycerol with dimethyl carbonate and the results obtained are presented in Table 1. Halide based ionic liquids were not active for the reaction and only trace amount of product was formed in these reactions (Table 1, Sr. nos. 1, 2). All other ionic liquids screened were active for the reaction. Thus moderate to high glycerol conversions (77–95%) were obtained with all hydroxide and bicarbonate types of ionic liquids investigated with selectivity to GC in a range of 33–56% and GD selectivity in a range of 43–67% (Table 1, Sr. nos. 3–9). The higher activity observed with hydroxide and bicarbonate based ionic liquids could be because of the higher basicity of hydroxide and bicarbonate counter ions compared to bromide counter ions. All the hydroxide and bicarbonate types of ionic liquids (Table 1, Sr. nos. 3–9) showed formation of GD as a product with good selectivity. Thus, decarboxylation of GC formed as a product leads to the formation of GD. Formation of CO<sub>2</sub> in these experiments was confirmed by passing the gas phase through saturated barium hydroxide solution to obtain white precipitate of barium carbonate. Decarboxylation of the GC to GD is well known in presence of strong bases [15,17]. The probable reason for higher selectivity to GD could

**Table 1**  
Screening of ionic liquids for transesterification of glycerol.

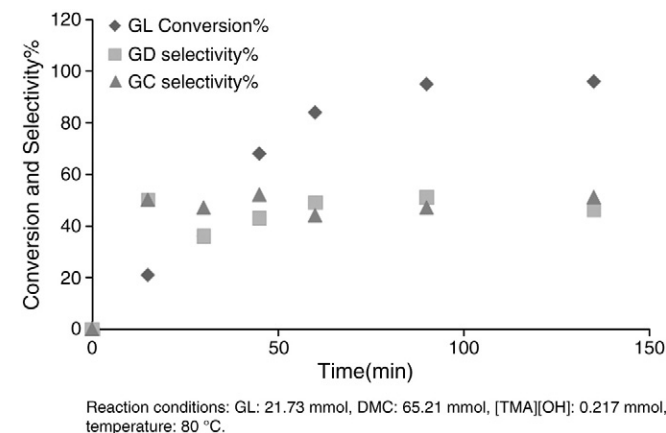
Sr. no.	Catalyst	GL conversion (%)	Selectivity (%)	
			GD	GC
1	[TMA][Br]	Very low	Trace	Trace
2	[TBA][Br]	Very low	Trace	Trace
3	[TPA][OH]	77	58	42
5	[Me-DABCO][OH]	87	54	46
5	[TMA][HCO <sub>3</sub> ]	83	67	33
6	[TBA][HCO <sub>3</sub> ]	86	58	42
8	[TEA][OH]	89	43	56
8	[TBA][OH]	90	53	47
9	[TMA][OH]	95	51	47

Reaction conditions: GL: 21.73 mmol, DMC: 65.21 mmol, catalyst: 0.217 mmol, temperature: 80 °C, time: 90 min.

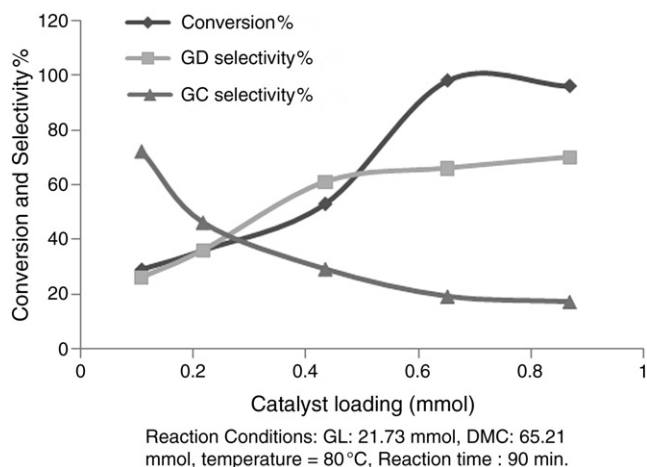
be higher basicity of the ionic liquids with hydroxide and bicarbonate counter ions used in the present work. From the results it was observed that the activity of the [TMA][OH] ionic liquid was good (95% conversion of GL) and also the selectivity to GD was 51% after 90 min and hence it was taken up for further investigations with the aim of improving the selectivity to GD.

Typical concentration–time profile is presented in Fig. 1. From the C–T profile it can be seen that at lower conversion GD selectivity is slightly lower (till 45 min reaction time). With progress of the reaction GD selectivity increases marginally from 36 to 51. At lower conversion material balance was lower (~90%), however, GC analysis did not show any extra peak. It is likely that the intermediate product wherein one primary OH of GL reacts with DMC to form the aliphatic carbonate is formed as reported by Herseczki et al. [21]. Material balance of the reaction was >95% at higher conversions. Conversion did not increase beyond 90 min reaction time, hence further experiments were carried out for 90 min.

The effect of catalyst concentration on activity and selectivity was investigated in a range of 0.108 to 0.868 mmol catalyst loading keeping other parameters constant. With aqueous solution of [TMA][OH] the quantity of water in the reaction would be high and may not give correct result. In order to avoid this, stock solution of 10 mol% [TMA][OH] in GL was prepared from 25 wt.% [TMA][OH] solution in methanol. Methanol from the solution was removed on rotary evaporator. The concentration of [TMA][OH] in GL was estimated by titration with HCl. This stock solution was used to study the catalyst loading effect (Figs. 2 and 3). Activity of the catalyst was very high and 98% conversion was observed in 30 min reaction time at a catalyst loading of 0.651 mmol. Hence, in order to see the effect of catalyst loading on activity the data has been presented at 30 min reaction time in Fig. 2 for catalyst loading in a range of 0.108 to 0.868 mmol. To see the effect of catalyst loading on GD selectivity the data has been presented for



**Fig. 1.** Typical concentration–time profile for transesterification of DMC with glycerol using [TMA][OH] as catalyst.

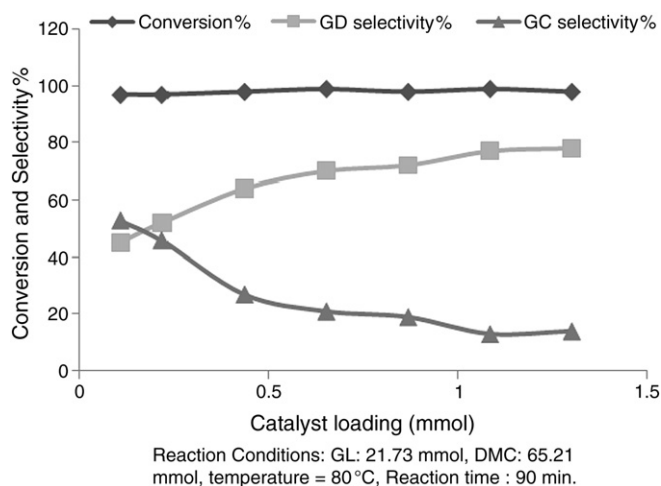


**Fig. 2.** Effect of catalyst loading on conversion and selectivity at 30 min reaction time.

90 min reaction time for catalyst loading in a range of 0.108–1.302 mmol (Fig. 3). Conversion of glycerol increased with increase in catalyst loading at the intermediate stage of the reaction (30 min reaction time) (Fig. 2) and also selectivity to GD increased significantly from 26 to 70%. This increase in the selectivity of GD could be due to increase in the concentration of catalyst in the reaction mixture leading to increase in GC decarboxylation.

The data on the effect of catalyst loading on GL conversion and selectivity at 90 min reaction time is presented in Fig. 3. Conversion of GL was very high (>90%) at all catalyst concentration investigated at 90 min reaction time, while GD selectivity increased significantly with increase in catalyst concentration (Fig. 3). Thus GD selectivity of 78% was observed at a catalyst loading of 1.302 mmol. Observed results also suggest that GC decarboxylation increases with increase in concentration of catalyst in the solution.

The effect of GL to DMC mole ratio on the catalyst activity was studied by varying GL: DMC molar ratio in the range of 1:3, 1:2, 1:1, 2:1, and 3:1 respectively keeping other conditions constant and the results are presented in Table 2. GL and DMC quantity of 21.7 mmol was used in the experiment carried out with GL:DMC ratio of 1:1. In other experiments, the quantity of one of the reactant was varied keeping the quantity of other reactant constant at 21.7 mmol, depending on the GL:DMC ratio investigated. From the results it was observed that conversion of GL was very low at GL:DMC ratio of 1:1. Only 45% conversion of GL was observed at GL:DMC ratio of 1:1. This is expected since the reaction is equilibrium controlled and excess DMC is used to achieve high conversions [22,23]. With increase in either GL or DMC concentration, conversion increased



**Fig. 3.** Effect of catalyst loading on conversion and selectivity at 90 min reaction time.

**Table 2**  
Effect of GL:DMC molar ratio on activity and selectivity.

Run	GL:DMC	Conversion (%)	Selectivity (%)	
			GD	GC
1	1:1 <sup>a</sup>	45	51	39
2	1:2 <sup>a</sup>	74	55	40
3	1:3 <sup>a</sup>	97	52	46
4	2:1 <sup>b</sup>	66	43	30
5	3:1 <sup>b</sup>	55	45	51

Reaction conditions: [TMA][OH]: 0.217 mmol, temperature: 80 °C, time: 90 min.

<sup>a</sup> Conversion with respect to GL.

<sup>b</sup> Conversion with respect to DMC.

significantly. High conversion (97%) was observed at GL:DMC ratio of 1:3, compared to only 55% at GL:DMC molar ratio of 3:1. GD selectivity was not affected significantly by a change in GL:DMC ratio. Observed results may be due to increase in viscosity of reaction mixture at high GL concentrations leading to mass transfer issues.

The effect of water content on the activity and selectivity of the reaction was studied and the results are presented in Table 3. From the results obtained it can be clearly seen that conversion of GL as well as selectivities to both GC and GD decreased significantly with increase in water content. This clearly shows negative effect of water on the reaction. Previously Rokicki et al. [4] have used GL with <2% water in K<sub>2</sub>CO<sub>3</sub> catalyzed transesterification with DMC. Similarly for reaction of GL and urea with solid base catalysts, water has negative effect on the reaction [24].

Effect of temperature on the conversion of glycerol was studied at three different temperatures (70 °C, 80 °C and 90 °C) (Fig. 4) using standard reaction conditions. The conversion was found to increase significantly with increase in temperature from 70 to 80 °C. Activity was not affected with further increase in temperature to 90 °C. Selectivity pattern was not significantly affected by a change in the reaction temperature. Cho et al. [25] have observed a similar trend in the transesterification of GL to GC using tetraalkylammonium salts immobilized on MCM-41 as the catalyst.

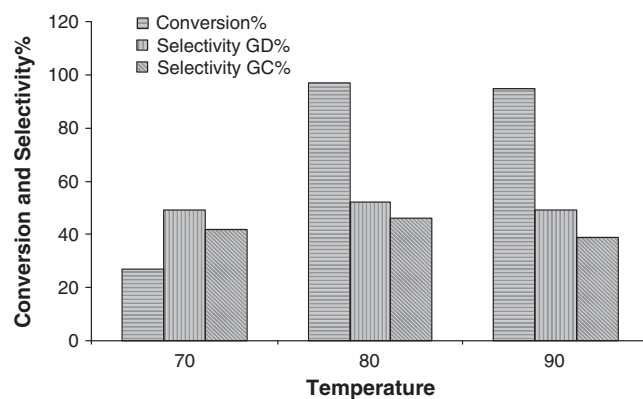
Finally recycle experiment was carried out to check stability of the catalyst. Initial experiment was carried out using standard reaction conditions. Sample was analyzed on GC to check conversion and selectivity. Fresh GL (21.7 mmol) and DMC (21.7 mmol) were added to the reaction mixture to maintain GL:DMC ratio of 1:3 and reaction was carried out again. The results are presented in Table 4. Conversion of GL as well as selectivity to GD has gone down slightly (78% conversion and 45% selectivity to GD) during recycle of the catalyst. In this experiment significant dilution of reaction mixture is taking place and also products of the initial experiment are present in the reaction mixture. Hence activity and selectivity cannot be compared with the initial experiment carried out. However, significant conversion of GL (78%) observed shows that the catalyst is active in recycle experiment.

There is a report on the synthesis of GC by transesterification of GL with ethylene carbonate with small amount of GD as a by-product [12]. In the present work GD formation with very high selectivity is observed at lower temperatures like 70–90 °C. From the literature it is observed that syntheses of GC from GL [26] and GD from GC [15] have been investigated separately at high temperatures and in some cases

**Table 3**  
Effect of water on activity and selectivity.

Amount of water (g)	GL conversion (%)	Selectivity (%)	
		GD	GC
0.059	95	51	46
0.118	66	47	40
0.177	41	44	37
0.238	35	41	34

Reaction conditions: GL: 21.73 mmol, DMC: 65.21 mmol; [TMA][OH]: 0.217 mmol; temperature: 80 °C, Reaction time: 90 min.



Reaction conditions: GL: 21.73 mmol, DMC: 65.21 mmol, [TMA][OH]: 0.217 mmol, Reaction time: 90 min.

**Fig. 4.** Effect of temperature on activity and selectivity.

the type of catalysts used are similar. Synthesis of GD is carried out at higher reaction temperatures (170–200 °C) [15] and reduced pressure to remove GD as it forms. There is a need to develop catalyst active at lower temperatures for the synthesis of GD, since GD is reactive and can polymerize at high temperatures [27].

Tundo et al. [28] have investigated the reaction of aliphatic alcohols with DMC using basic catalysts at 200 °C yielding unsymmetric carbonates with K<sub>2</sub>CO<sub>3</sub>. However, with basic alumina and Mg–Al hydrotalcite (KW2000) as catalysts, decarboxylation was observed forming the corresponding ethers in a single pot. They emphasize the significance of both the acidic and basic properties of the catalyst for decarboxylation reaction. Kricheldorf et al. [29] also have observed decarboxylation of cyclic carbonates during polymerization with methyl triflate (cationic initiator). They observed that the initiator alkylates the exocyclic oxygen forming a trioxocarbenium ion, which on rearrangement leads to the formation of an oxonium ion. Oxonium ion is attacked by the anion (triflate) leading to decarboxylation. Thus both cation and anion of the catalyst are involved in the decarboxylation of carbonates. It is quite likely that in the present work also GC formed in the first step is decarboxylated to GD because of the presence of basic (anionic) center and acidic (cationic) center in the ionic liquid catalyst used. Quaternary ammonium center can interact with oxygen of the carbonyl group of GC making the bond weaker. Further interaction with the anion can lead to decarboxylation and formation of GD as the product. Detailed work on this reaction is in progress in our laboratory.

#### 4. Conclusions

Transesterification of DMC with glycerol was studied using various ionic liquids as catalysts. Ionic liquids containing hydroxide and bicarbonate counterions were active for the reaction and gave high conversions of GL (77–95%) at 90 min reaction time with high selectivity to GD (43–67%). Effect of various reaction conditions on the activity and selectivity was investigated using [TMA][OH] as a catalyst. Highest selectivity of 78% to GD was obtained using [TMA][OH] loading of 1.302 mmol at 80 °C in 90 min reaction time. Activity as well as selectivity of the catalyst decreased significantly with increase in moisture

**Table 4**  
Recycle of [TMA][OH] catalyst.

Sr. no.	GL conversion (%)	Selectivity %	
		GD	GC
RE-0	89	53	46
RE-1	78	45	54

Reaction conditions: GL: 21.73 mmol, DMC: 65.21 mmol; [TMA][OH]: 0.217 mmol; temperature: 80 °C, Reaction time: 90 min.



content. Recycle experiment indicated slight drop in GL conversion and selectivity to GD because of dilution of reaction mixture and also the presence of products from the initial experiment.

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