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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.

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_2 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.

Bruson 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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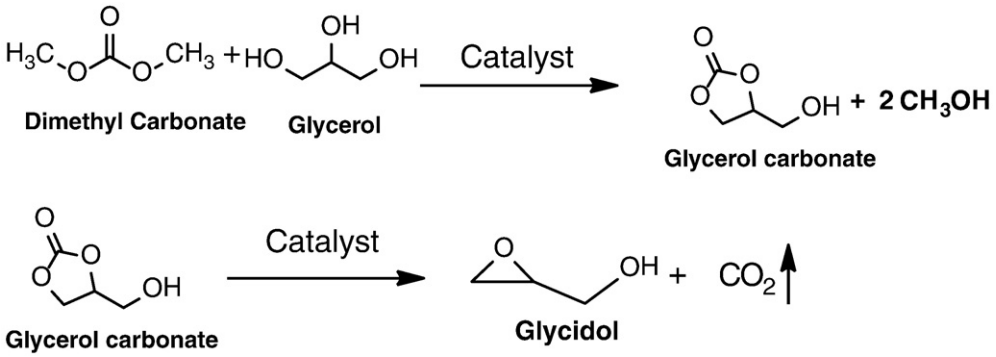

Scheme 1. Synthesis of glycerol carbonate from glycerol and synthesis of glycidol from glycerol carbonate.

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_3]) and tetrabutylammonium bicarbonate ([TBA][HCO_3]) 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^- 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_2 was bubbled through the solution for 2 h under constant stirring to obtain aqueous solution of [TMA][HCO_3]. [TBA][HCO_3] was prepared by following the similar procedure. ^{13}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 ^{13}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_3]:
^1H NMR: 3.08, 12H (s)
^{13}C NMR: 55.17, 160.38
[TBA][HCO_3]:
^1H NMR: 0.89, 12H (t), 1.25–1.36, 8H (m), 1.56–1.64, 8H (m), 3.15, 8H (t)
^{13}C NMR: 12.93, 19.1, 23.05, 57.94, 160.07
[Me-DABCO][OH]:
^1H NMR: 3.01, 3H 9 (s), 3.14, 6H (t), 3.35, 6H (t)
FT-IR (cm^{-1}): 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_2 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