Catalysis Communications 66 (2015) 25–29

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Facile one-pot synthesis of glycidol from glycerol and dimethyl carbonate catalyzed by tetraethylammonium amino acid ionic liquids

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ARTICLE INFO

Article history:
Received 31 January 2015
Received in revised form 11 March 2015
Accepted 12 March 2015
Available online 13 March 2015

Keywords:
Ionic liquids
Glycidol
Glycerol
Dimethyl carbonate
One-pot synthesis

ABSTRACT

Four tetraethylammonium amino acid ionic liquids (TAAILs) were prepared and used as catalysts for facile one-pot synthesis of glycidol from glycerol and dimethyl carbonate. The results indicate that tetraethylammonium pipecolinate ($[N_{2222}]$[Pipe]) exhibits the best catalytic activity compared with other three TAAILs, and catalyzes the reaction to reach a glycerol conversion of 96% and a glycidol yield of 79% under optimum conditions. Moreover, DFT calculated results further manifest that such excellent performance originates from the carboxyl group in $[N_{2222}]$[Pipe], which enables $[N_{2222}]$[Pipe] to activate the substrates effectively.

1. Introduction

Concerning about fossil fuel consumption and exhaustion, the demand for the biomass-derived biodiesel is increasing globally in the last decades, which makes by-product glycerol available in huge amounts at decreasing prices. Therefore, the conversion of glycerol to various commodity chemicals, such as dehydration to acrolein, hydrogenolysis to 1,2-propanediol, and gasification to syngas has attracted considerable attention recently [1–4]. Among various derivatives of glycerol, glycidol is one of the most attractive and valuable chemical intermediates. Indeed, glycidol can be widely used in the fields of pharmaceuticals, cosmetics, detergents, demulsifiers, dye leveling agents, etc. [5,6].

Generally, the industrial production of glycidol involves two environmentally unfriendly routes (Scheme 1a) [7]. One is the epoxidation of allyl alcohol using hydrogen peroxide in the presence of tungsten or vanadium homogeneous catalyst. Another method is through the reaction of epichlorohydrin under alkaline conditions. However, both these two processes have several inherent drawbacks, including high production cost, a large amount of waste liquid and chloride salt, and serious equipment corrosion. In order to overcome the above issues, using dimethyl carbonate (DMC) as a raw material to produce glycidol has recently attracted significant attention. As well known, DMC is an environmentally friendly chemical intermediate because of its low toxicity, low bioaccumulation and high biodegradability [8]. Thus, the synthesis of glycidol through glycerol and DMC is considered to be an attractive green and sustainable chemical process.

As shown in Scheme 1b, the two-step protocol for the preparation of glycidol includes the formation of glycerol carbonate followed by its decarboxylation. So far, there are a few research groups concentrating on glycerol carbonate and glycidol [9–16]. Malkemus et al. [9] were the first to patent the synthesis of glycidol through decarboxylation of glycerol carbonate using metal salts as catalysts. Later, Choi et al. [12] and Bolívar-Diaz [13] obtained glycidol through glycerol carbonate using [BMIm]-based ionic liquids and metallic oxide modified ZSM-5 zeolite as catalysts, respectively. Despite the excellent yields and selectivities, there has been little attention paid to the one-pot synthesis of glycidol directly from glycerol and DMC [17–20]. Kelkar et al. [17] reported their pioneering work on the one-pot synthesis of glycidol using tetramethylammonium hydroxide as catalyst. However, this catalyst has some inherent drawbacks such as poor thermal ability and difficult reusability. Li et al. [18] investigated that $NaAlO_2$ induced a glycidol yield of 76% in the one-pot synthesis of glycidol. Unfortunately, an inevitable disadvantage is that the utilization of $NaAlO_2$ must be performed under rigorously anhydrous conditions due to its nature of easy hydrolysis. Therefore, there is still an urgent need to develop excellently stable, highly efficient, and easily reusable catalysts for the facile one-pot synthesis of glycidol.

In recent years, amino acid ionic liquids have attracted much attention owing to their cheap cost and environment-friendly characteristics [21,22]. Because of their certain basicities, they could provide a potential application in the one-pot synthesis of glycidol. Herein, we prepared a series of tetraethylammonium amino acid ionic liquids (TAAILs). Their

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http://dx.doi.org/10.1016/j.catcom.2015.03.011
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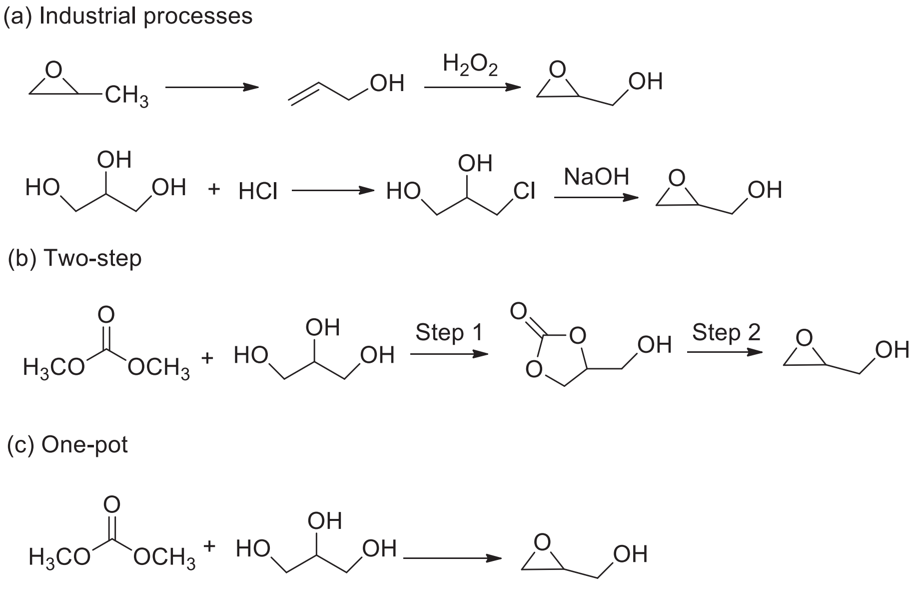


Scheme 1. Various routes for the synthesis of glycidol.

catalytic behavior in the one-pot synthesis of glycidol from glycerol and DMC was investigated systematically.

2. Experimental

2.1. Materials

Tetraethylammonium hydroxide (25 wt.% aqueous solution) was purchased from Aldrich Chemical Reagent Co. Ltd. Other reagents such as amino acid, glycerol, and DMC were of analytical grade and used without any further purification.

2.2. Preparation and characterization of TAAILs

Four TAAILs composed of different anions, $[N_{2222}]$[Pipe], $[N_{2222}]$[Pro], $[N_{2222}]$[H-pyr], and $[N_{2222}]$[Thio] (Fig. 1) were synthesized via the simple neutralization reaction. The detailed preparation methods and characterization results of these TAAILs were then listed in the Supplementary data.

2.3. Catalytic test

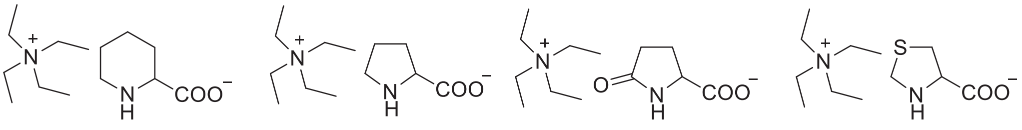
In a typical procedure, glycerol (20 mmol), DMC (40 mmol) and 3 wt.% of catalyst (0.16 g) were added into a round-bottomed flask (25 ml) equipped with a magnetic stirrer and condenser. Then, the reaction mixture was stirred at 130 °C for 2 h. Samples were taken from the reactor at regular intervals. Qualitative analyses of products were examined by a Thermo Trace 1300 GC-ISQ, and quantitative analyses were carried out by a GC-FID (Agilent 7890B). A capillary column HP-5 (30 m × 0.32 mm × 1 μm) was used to determine the composition of the samples using tetraethylene glycol as an internal standard with nitrogen as the carrier gas at a flow rate of 1.5 mL/min. The temperature of the column, the inlet and the detector were kept at 250, 270, and 300 °C, respectively. The calculation methods of glycerol conversion, glycidol selectivity and glycidol yield were then given in the Supplementary data. After the reaction was completed, the mixture was extracted with deionized water, and the aqueous phase containing TAAILs could be separated by simple decantation. The catalyst TAAILs was thus recovered and reused in the next run.

3. Results and discussion

3.1. Catalytic performance

The one-pot synthesis of glycidol from glycerol and DMC was studied in the presence of various TAAILs and other base catalysts. As seen from Table 1, the catalyst TAAILs display various catalytic performances, and the sequence is $[N_{2222}]$[Pipe] > $[N_{2222}]$[Pro] > $[N_{2222}]$[Thio] > $[N_{2222}]$[H-Pyr] (Entries 1–4). Among these four TAAIL catalysts, $[N_{2222}]$[Pipe] catalyzes the reaction to lead to the highest conversion of glycerol (96%) and selectivity in glycidol (82%). To gain insight into this catalytic process, we calculated the natural bond orbital (NBO) charges of the oxygen atoms of the carboxylate group in the four TAAILs (Computational methods was shown in the Supplementary data). The results are summarized in Fig. 2 and reveal that the sequence of the quantity of negative charges on oxygen atom in these TAAILs matches well with the order of their catalytic performance. In another word, TAAIL possessing more negative charges on oxygen atom shows a relatively high catalytic activity. Compared with $[N_{2222}]$[Pro], the poor catalytic performance of $[N_{2222}]$[Thio] and $[N_{2222}]$[H-Pyr] is ascribed to the less negative charges on oxygen atom with the result of the electron withdrawing effect of sulfur atom and carbonyl group, respectively. This implies that more negative charges concentrated on oxygen atom in TAAIL could activate glycerol and glycerol carbonate easily, and catalyze this one-pot reaction to obtain higher glycidol yield.

For comparison, the use of Amberlite-IR A400 resin leads to a low selectivity in glycidol (Entry 5). A low yield of glycidol is also obtained



$[N_{2222}]$[Pipe] **$[N_{2222}]$[Pro]** **$[N_{2222}]$[H-pyr]** **$[N_{2222}]$[Thio]**

Fig. 1. Structures of four TAAILs.