Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

The efficient synthesis of diethyl carbonate via coupling reaction from propylene oxide, CO_2 and ethanol over binary PVEImBr/MgO catalyst

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ARTICLE INFO

Article history:
Received 7 November 2015
Received in revised form 28 January 2016
Accepted 25 February 2016
Available online xxx

Keywords:
Carbon dioxide
Diethyl carbonate
Coupling reaction
Binary
Mechanism

ABSTRACT

Direct synthesis of diethyl carbonate (DEC) from propylene oxide, CO_2 and ethanol via coupling reaction over a heterogeneous catalyst was demonstrated. In this work, a cross linked poly(ionic liquid) containing poly(1-vinyl-3-ethylimidazolium bromide)(PVEImBr) moiety was prepared via a free radical polymerization. Meanwhile, the MgO nanoplatelet with abundant basic sites was prepared, which was combined with PVEImBr to form a composite catalyst of PVEImBr/MgO. N_2 physisorption, TG, XRD, SEM, CO_2-TPD and FT-IR were conducted to thoroughly characterize the structure and texture of the catalysts. The as-prepared heterogeneous catalyst, which simultaneously possessed the dual function of nucleophilicity and basicity, was used in the coupling reaction of propylene oxide, CO_2 and ethanol to synthesize diethyl carbonate and propylene glycol. The composite catalyst could promote the reaction with high efficiency, and a good catalytic performance of 54.4% diethyl carbonate yield and 59.8% propylene glycol yield could be achieved. The ^{1}H NMR and DFT calculation disclosed that greatly faster reaction rate was ascribed to the synergistic effect between the $Br^{\ominus}$ anion of PVEImBr and hydroxyl group of ethanol. Accordingly, a mechanism of the sequential reaction consisting of cycloaddition and transesterification steps was proposed.

1. Introduction

The excessive consumption of fossil fuel resources in human activities inevitably results in massive release of CO_2, which has adverse influence on the global climate and environmental changes [1,2]. Numerous approaches were developed for efficient conversion of CO_2 into industrially interesting chemicals, e.g. methanol, esters or polymer materials, which have attracted wide concerns in recent years [3,4]. It should be noted that the syntheses of dialkyl carbonates from CO_2 could realize the cooperative utilization of carbon and oxygen source [5]. As an important member of dialkyl carbonate, diethyl carbonate (DEC) has wide applications in the fields of organic synthesis, solvent and fuel additives [5–7]. It can be used as carbonylation or ethylation reagent, for example, DEC could be used as a substitute for toxic phosgene to react with phenol to synthesize diphenyl carbonate, which is an important raw material for the manufacture of polycarbonate in industry. In a potential application field, DEC has also been considered as superior fuel oxygenate additive compared to methyl *tert*-butyl ether (MTBE). It has been found that DEC possesses lower volatility due to the higher boiling point, better fuel/water partitioning coefficient. Meanwhile, when released into the environment, DEC could be converted into more eco-friendly hydrolysis products (CO_2 and ethanol) than its homologue of dimethyl carbonate (CO_2 and methanol), demonstrating a promising application as green solvent for organic synthesis and catalysis.

Until now, various phosgene-free synthetic routes for diethyl carbonate synthesis have been reported, including the oxidative carbonylation of ethanol with CO and O_2 [8], ethanolysis of urea or ethyl carbamate [9–11], transesterification of dimethyl carbonate with ethanol [12,13]. In our recent study, a new methodology for the synthesis of DEC was developed from ethylene oxide, ethanol and CO_2 over a homogeneous KI/NaOEt catalyst [14]. Although a good synthetic performance was obtained, the involvement of low-boiling ethylene oxide is very dangerous in terms of safety because it is flammable and explosive. Meanwhile, the homogeneous catalyst system will impose difficulty in the catalyst separation of the

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http://dx.doi.org/10.1016/j.cattod.2016.02.052
0920-5861/

continuous manufacture process [15,16]. Unfortunately, there are few reports on the efficient synthesis of DEC from CO_2 in a safe manner over a heterogeneous catalyst.

To address the issues above-mentioned, the exploration of efficient heterogeneous catalyst system for the activation and chemical utilization of CO_2 to synthesize high-valued chemical of DEC via the coupling reaction is highly attractive and desirable. As proposed in our previous study, this process was considered to be consisted of the sequential cycles of cycloaddition and transesterification. In recent years, a variety of ionic liquids were found to effectively catalyze the cycloaddition reaction [17]. Alternatively, the cross-linked poly(ionic liquid)s, which originated from the polymerization of ionic liquid monomer and a cross-linker, could retain the high catalytic activity of quasi-homogeneous ionic liquid moiety with good recyclability [18,19]. In this regard, the imidazolium-based poly(ionic liquid), which possessed a typical polymeric backbone with a highly delocalized anion charge, has attracted growing attention in the cycloaddition reaction. For the transesterification reaction, appropriate basic catalyst was efficient for achieving a good catalytic performance. As a typical and versatile basic catalyst, magnesium oxide (MgO) possessed abundant basic sites and applied in many base-catalyzed reactions [20,21]. Generally, the surface area is very important influencing factor for achieving high catalytic activity by providing more active sites. Importantly, the development of MgO catalyst with large amount of accessible active sites has attracted great attention. Compared to the bulk MgO, the construction of MgO in nanoscale has demonstrated a useful tool to enhance the catalytic activity because of the larger surface to volume ratio. The strength and distribution of basicity could be finely tuned by tuning preparation method [22], which could result in distinct catalytic performance.

Herein, we describe an effective method for the synthesis of DEC through coupling reaction from commodity chemicals of propylene oxide (PO), carbon dioxide and ethanol, as shown in Scheme 1. In this route, propylene glycol (PG) was simultaneously co-produced, which is also an important raw material in the manufacture of polyester fibers and pharmaceutical industry [23]. The structure of the composite catalyst was characterized in details to disclose the structure-performance relationship. The varied catalyst species and reaction variables, e.g. catalyst composition, reaction temperature, and reaction time, were evaluated. Moreover, the catalytic mechanism was studied by means of ^{1}H NMR and theoretical calculation. On the basis of these results, a possible reaction mechanism was also proposed. Additionally, the recyclability of the composite catalyst was also investigated. In comparison with the reported processes, this route has provided an effective way to realize the synthesis of DEC directly from abundant CO_2 via the coupling reaction over a heterogeneous catalyst.

2. Experimental

2.1. Materials

Propylene oxide (PO, 99.5% purity), divinyl benzene (DVB, 80% purity, mixture of isomers, stab. with 1000 ppm 4-*tert*-butylcatechol), and 2,2-azobisisobuytronitrile (AIBN, >99.8% purity), were purchased from Sinopharm Chemical Reagent Co., Ltd. 1-Vinyl-3-ethylimidazolium bromide(VEImBr, 99% purity) and 1-vinyl-3-ethylimidazolium iodine (VEImI, 99% purity) were purchased from Shanghai Cheng Jie Chemical Co. Ltd. Ethanol, $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ were purchased from Xilong Chemical Industry Incorporated Co., Ltd. CO_2 (>99.9% purity) and Ar (99.999% purity) were purchased from Beijing Qianxi Company. All the chemicals were of analytical grade and used without further purification unless noted otherwise.

PVEImBr containing poly(1-vinyl-3-ethylimidazolium bromide) moiety was synthesized by a free radical copolymerization with DVB cross linker [24], as shown in Scheme 2. In a typical process, a 250 mL flask bottle with a condenser pipe was charged under argon with a mixture of 9.0 g 1-butyl-3-methylimidazolium bromide (41.1 mmol), 0.3 g AIBN (0.546 mmol), 3.0 mL divinyl benzene (DVB) and 180 mL acetonitrile. The mixture was maintained at 80 °C under reflux for 4 h under vigorous magnetic stirring. After the polymerization, white solids were collected by simple centrifugation and washed repeatedly with acetonitrile and ethanol, respectively. Finally, the obtained white solids were dried at 120 °C in air oven overnight, and the obtained white powder was denoted as PVEImBr. Similarly, PVEImI was synthesized according to the same procedure as that of PVEImBr except using the 1-vinyl-3-ethylimidazolium iodine (VEImI) as the monomer instead of VEImBr.

MgO catalyst was prepared by a precipitation method: $Mg(NO_3)_3{\cdot}6H_2O$ was dissolved in distilled water to form 1.5 mol/L Mg^{2+} solution. 2 mol/L Na_2CO_3 solution was used as precipitant, and dropped into a beaker containing 100 mL Mg^{2+} solution aforementioned. The pH value during the precipitation process was maintained constant at 10. Subsequently, the resulting precipitate was aged in mother solution at 80 °C overnight, filtered and washed with distilled water until the filtrate was as neutral as possible. The precipitate was then dried in an oven at 120 °C. After grinding, the obtained powder was calcined at 450 °C, 550 °C, 650 °C for 3 h in air atmosphere, respectively, and denoted as MgO-T, where T represents the calcination temperature. ZnO, $ZnMg_2O_x$ and $ZnMgO_x$ (n(Zn)/n(Mg) = 0.5, 1) were obtained by similar precipitation method as that of MgO-450 catalyst, respectively.

Mg_3AlO_x derived from Mg-Al hydrotalcite was prepared by the following procedure: 100 mL of an aqueous mixture of $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ with Mg:Al molar ratio of 3 was pre-made in a beaker, and then was added slowly with an aqueous solution of 2 mol/L NaOH. The pH of the mixture was continuously monitored by a pH meter and remained at 10. The resulting mixture was filtered and the precipitate was washed with distilled water until the filtrate was approximately neutral. The precipitate was dried in an oven at 120 °C, calcined at 450 °C for 3 h, and denoted as Mg_3AlO_x.

2.2. Catalytic activity test

In a typical reaction, diethyl carbonate was synthesized from PO, CO_2 and ethanol in the presence of the composite catalysts composed of PVEImBr and basic MgO. A mixture of ethanol and PO with molar ratio of 15:1 was fed into a stainless steel reactor with the desired amount of catalyst added in advance. 3 MPa carbon dioxide (CO_2) was injected to the reactor. The reaction mixture was gradually heated to 160 °C and retainded for 3 h under continuous stirring. Subsequently, reaction mixture was cooled down to room temperature and residual CO_2 inside of the reactor was released completely. Then the reactor was sealed and the reaction mixture was again heated to 160 °C and retainded 160 °C for 1.5 h–3 h under continuous stirring. After the completion of the reaction, the catalyst was recovered from the reaction mixture by centrifugation, washed with ethanol and reused directly in the next run. Finally, the product was analyzed on a Shimadzu GC 2010 Plus equipped with a capillary column (Rtx-Wax, 30 m × 0.25 mm × 0.25 μm) using a flame ionization detector (FID). The conversion of reactant and yield of products were defined and calculated as follows:

$$\text{Conversion of PO}(\%) = 1 - \frac{\text{residual mole of PO}}{\text{mole of epoxide charged}} \times 100\%$$

Please cite this article in press as: L. Wang, et al., The efficient synthesis of diethyl carbonate via coupling reaction from propylene oxide, CO_2 and ethanol over binary PVEImBr/MgO catalyst, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.02.052