Journal of Molecular Catalysis A: Chemical 386 (2014) 42–48

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Halide aided synergistic ring opening mechanism of epoxides and their cycloaddition to CO_2 using MCM-41-imidazolium bromide catalyst

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ARTICLE INFO

Article history:
Received 25 September 2013
Received in revised form 10 January 2014
Accepted 9 February 2014
Available online 18 February 2014

Keywords:
Cycloaddition
Carbon dioxide
Ring opening of Epoxide
Imidazole
Synergistic effect

ABSTRACT

Imidazole was immobilized on MCM-41 using 3-chloropropyltriethoxysilane (CPTES) as the anchoring agent followed by alkylation with 1,2-dibromoethane at 110 °C. The resulting catalyst was designated as MCM-41-Imi/Br. The catalyst was used for the synthesis of cyclic carbonates via cycloaddition of CO_2 with several epoxides under solvent free condition. The use of MCM-41-Imi (without bromide ion) to catalyze the reaction led to the elucidation of the reaction mechanism involved in the synergistic catalysis. The catalyst was used in the cycloaddition of styrene oxide, epichlorohydrine, glycidol, allyl glycidyl ether and phenyl glycidyl ether. A high yield and excellent selectivity of cyclic carbonates were obtained under optimized conditions. The yields of the respective cyclic carbonates were 98.8% for styrene oxide, 97.0% for epichlorohydrin, 98.3% for glycidol, 97.5% for allyl glycidyl ether, 96.7% for phenyl glycidyl ether and 100% for 1,2-epoxyhexane.

1. Introduction

Cyclic carbonates have been produced conventionally by reacting phosgene ($COCl_2$) with ethane-1,2-diol in the presence of an excess amount of dichloromethane as solvent. Hydrochloric acid and chlorinated solvents are produced as byproducts that are harmful to human and the environment [1]. Due to the extreme toxicity attributed to phosgene, CO_2 seems to be the most appropriate substitute. Carbon dioxide is a greenhouse gas found to be present in the atmosphere at a concentration of 398.58 ppm [2]. The rising demand of cyclic carbonates has also resulted in the need to look for safer and greener techniques for its synthesis. Scheme 1 shows the reactions used to synthesize cyclic carbonates using the traditional route and the new green route. The use of carbon dioxide will also help to reduce the amount of carbon dioxide in the atmosphere. Although this will not be enough to reduce global warming, it will at least help to reduce the amount of carbon dioxide in the environment. It has been known that CO_2 can be incorporated into epoxides without the formation of byproducts [3]. However, due to the inert nature of CO_2, its activation and incorporation into epoxides remains inadequately explained and are actively being investigated.

One of the main factors that can accelerate the reaction between CO_2 and epoxide are the catalysts that are used in the reaction. A wide range of homogeneous and heterogeneous catalysts has been developed to catalyze the reaction between CO_2 and epoxides to form cyclic carbonates. Homogeneous catalysts, such as $CoCl_2$/onium salt [4], diimine Ru(II) complex [5], Al-salen-PEA [6], betaine-based quaternary ammonium ion and carboxylic acid [7], DMF [8,9], $Au/Fe(OH)_3–ZnBr_2/Bu_4NBr$ [10], ionic liquid with highly cross linked polymer [11], $BrBu_3PPEG_{600}PBU_3Br$ [12], cellulose/KI [13], and Au/R201 [14] have been studied. Several heterogeneous catalysts, such as metal oxides; MgO [15,16], Nb_2O_5 [1], Mg–Al oxide [17], guanidine-MCM-41 [18], Adeine-Pr-Al-SBA-15 [19], Cr-salen-SiO_2 [20], Mn-salen-SiO_2 [21], ClAlPC-MCM-41 [22], as-synthesized MCM-41 [23], Ti-SBA-15-Pre-Ade [24], 3-(2-hydroxyl-ethyl)-1-propyl imidazolium bromide-SBA-15 [25] and zeolite based organic-inorganic hybrid catalyst [26] have also been investigated. Both homogeneous and heterogeneous catalysts have their own advantages and disadvantages. The major problem associated with most homogeneous catalyst is the difficulty in the separation of the catalyst from the reaction mixture and recycling of the catalyst. These drawbacks has been overcome in heterogeneous catalyst system.

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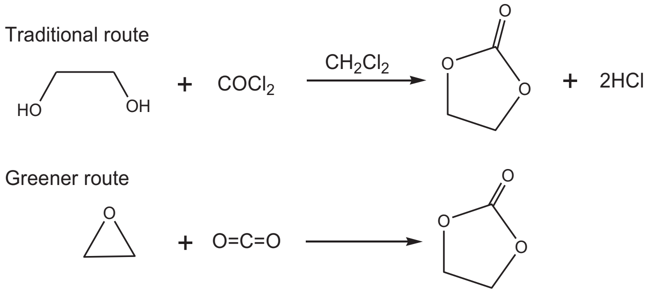
http://dx.doi.org/10.1016/j.molcata.2014.02.008
1381-1169/



Scheme 1. The synthesis of cyclic carbonates via traditional route and greener route.

The catalyst is crucial to activate the CO_2 in the chemical reaction. Lu et al. [22] had used MCM-41 supported aluminium phthalocyanine (AlPc) complex for the reaction of CO_2 and epoxides. It required a co-catalyst, n-Bu_4NBr which enhanced the reaction as well as gave high catalytic activity. The activation of CO_2 was initiated by nucleophilic attack of the alcoholate ($-OCH_2CH_2Br$) on the carbon atom of CO_2 which was aided by the weak interaction between the central metal ion of (ClAlPc) and the lone pair electron of one of the oxygen of CO_2. The catalyst showed a synergistic effect during the reaction that resulted in the insertion of CO_2 to the Al—O bond of $Pc(Cl)Al-OCH_2CH_2Br$. This formed a linear carbonate, which converted into cyclic carbonates by the intramolecular substitution of the halides. Nevertheless, the mechanism for the formation of cyclic carbonates by this binary catalyst has not been reported. Qiao et al. [27] had reported that imidazolium-styrene copolymer supported zinc catalyst which was denoted as Zn/PS-IL[X] ($X = Br^-, Cl^-, BF_4^-, PF_6^-$) was a suitable catalyst for the cycloaddition of CO_2 to styrene oxide (SO). Among the catalyst investigated, Zn/PS-IL[Br] was the most efficient, which gave 97.5% yield with a TOF of 3800 h^{-1}.

In 1992, researchers at the Mobil Oil Cooperation successfully synthesized MCM-41 (hexagonal) [28] and MCM-48 (cubic) materials from silica [29]. These materials had amorphous silica wall with long range ordered framework with uniform mesopores. These materials have been used in catalysis, as adsorbents and recently in drug delivery systems. Due to the tremendous interest in the area of catalysis, MCM-41 has been utilized for various chemical reactions and has shown remarkable catalytic activity. These materials are of particular interest due to the well-ordered mesopores with high accessibility for reactants as well as products. Moreover, this materials can be used to synthesize hybrid organic-inorganic materials with an ionic liquid functionality unit as part of the solid network. The ionic liquid being connected to the surface of MCM-41 through an appropriate linker.

In this study, the silica from RHA [30–34] was converted to MCM-41 and used as support for heterogeneous catalyst to synthesize cyclic carbonates. The production of cyclic carbonates in high yield not only depends on the catalyst, but also on other reaction parameters such as temperature, pressure, catalyst amount and reaction time. The optimized conditions vary depending on the type of epoxide and the active site of the catalyst. In the past 10 years, there has been much research using a wide range of homogeneous and heterogeneous catalysts with different epoxides. However, none of them studied the detailed reaction parameters for various epoxides with the same catalyst.

Recently, the synthesis and catalytic activity of MCM-41-Imi/Br [35] was reported. It was found that MCM-41-Imi/Br catalyzed the cycloaddition reaction between CO_2 and styrene oxide effectively under solvent free condition. As an extension to this work, herein we describe the systematic investigation leading to the mechanism of the cycloaddition reaction. This paper describes the role of the quaternary imidazolium center and bromide ion which is shown to play a synergistic role in the activation of the CO_2 and the subsequent ring opening of the epoxide. To the best of our knowledge, this is the first report that also show the important role of water molecules in the formation of intermediates and byproducts under CO_2 free condition. Based on the data obtained, a most likely reaction mechanism has been proposed.

2. Experimental

2.1. Material

The rice husk (RH), for the preparation of MCM-41 was obtained from a rice mill in Penang. Other materials used were nitric acid (Qrec, 65.0%), sodium hydroxide pellets (R&M Chemicals, 99.0%), acetone (Qrec, 99.5%), cetyltrimethylammonium bromide (CTAB) (Riedel-de Haen, 98.0%), 3-chloropropyltriethoxysilane (CPTES) (Sigma-Aldrich, 95.0%), toluene (Qrec, 99.5%), acetonitrile (Qrec, 99.5%), 1,2-dibromoethane (Merck, >99.0%), imidazole (Scharlau, 99.0%), styrene oxide (SAFC, >97.0%), epichlorohydrin (FlukaChemika,99%), glycidol (Aldrich, 96%), allylglycidyl ether (Aldrich, >99%), phenyl glycidyl ether (Aldrich, 99%) and 1,2-epoxyhexane (Aldrich, 97%). The carbon dioxide was purchased from CAMBREX-HENKEL, Penang and used as received. All other reagents used were of analytical grade and used without further purification.

2.2. Synthesis of MCM-41-Imi/Br

The preparation of MCM-41-Imi/Br was carried out according to published method [35]. 2.0 g of MCM-41-Imi and 1.4 mL of 1,2-dibromoethane was refluxed at 110 °C for 24 h. The excess alkyl halide was filtered off, followed by repeated washing with dichloromethane. The resulting solid was dried in an oven at 100 °C. The yield of MCM-41-Imi/Br was 2.1 g with a BET surface area of 130 $m^2\,g^{-1}$ [35].

2.3. Cycloaddition reaction and the analysis

In a typical catalytic reaction, epoxide (30 mmol) and 300 mg of the catalyst (MCM-41-Imi or MCM-41-Imi/Br) were charged into a high pressure laboratory autoclave, equipped with a magnetic stirrer and a heating mantle system. The reactor was carefully flushed once with CO_2. About 30 bar of CO_2 was dosed into the reactor, and heating and stirring started. Once the temperature reached 100 °C, the reaction was allowed to proceed for 4 h.

After the reaction was complete, the autoclave was allowed to cool down to room temperature, and the excess CO_2 was released by opening the outlet valve. After depressurization, the autoclave was opened slowly, and the reaction mixture was separated by filtration. To a 0.5 mL of the reaction product, 20 μL of cyclohexanol or acetophenone as internal standard was added. The resulting mixture was analyzed with gas chromatography (Clarus 500 Perkin Elmer) equipped with Elite Wax or Elite 1 capillary column (Perkin Elmer) and flame ionization detector. The reaction mixture was also analyzed by GC–MS (Clarus 600 Perkin Elmer) with a mass selective detector and helium as the carrier gas to identify the formation of products.