



ELSEVIER

Contents lists available at ScienceDirect

Molecular Catalysis

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

MCAT



Research Paper

Multifunctional alkanolamine as a catalyst for CO₂ and propylene oxide cycloadditionHyeon-Gook Kim^{a,b}, Chung-Sun Lim^b, Dong-Woo Kim^b, Deug-Hee Cho^b, Dong-Koo Lee^b, Jin Suk Chung^{a,*}^a School of Chemical Engineering and Bioengineering, University of Ulsan, 93 Daehakro, Nam-gu, Ulsan 44610, Republic of Korea^b Chemical Industry Development Center, Korea Research Institute of Chemical Technology, 45 Jongga-ro, Jung-gu, Ulsan 44412, Republic of Korea

ARTICLE INFO

Article history:

Received 11 March 2017

Received in revised form 25 May 2017

Accepted 26 May 2017

Available online 3 June 2017

Keywords:

Alkanolamine

Carbon dioxide fixation

Cycloaddition

Organocatalysis

Propylene carbonate

ABSTRACT

Multifunctional alkanolamines without metals or halides were designed as catalysts for the synthesis of propylene carbonate (PC) by the cycloaddition of CO₂ and propylene oxide (PO). New catalysts were synthesized in a one-step, low-temperature reaction. Among the multifunctional alkanolamine catalysts, bis(methylpiperazinyl)triol (Catalyst 1) showed the best performance, with a 96% yield of PO in 3 h at 120 °C and 10 bar using 1 mol% catalyst. A 90% yield of PO could be obtained using 5.60 mol% of Catalyst 1 under mild conditions (100 °C and 5 bar). A reaction mechanism was proposed based on the synergistic effects between the hydroxyl and amine groups in one multifunctional molecule. The effects of the reaction parameters (temperature, CO₂ pressure, and catalyst loading) on the yield of PC were interpreted using response surface methodology. The metal- and halide-free catalysts will facilitate an environmentally friendly process for the application of other carbonates.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Substantial CO₂ emissions from the massive consumption of fossil fuels have brought about global warming and climate change [1–3]. Extensive research has been undertaken toward reducing CO₂ emissions to identify three possible strategies to diminish CO₂ buildup in the atmosphere: (i) reducing the amount of CO₂ produced, (ii) utilizing the emitted CO₂, or (iii) storing the emitted CO₂ [4,5]. Among the alternatives, using CO₂ as a feedstock in chemical production is an interesting route for commercial production of valuable materials. CO₂ can be converted to useful chemicals, such as urea, salicylic acid, inorganic carbonates, pigments, cyclic organic carbonates, and additives for the synthesis of methanol [6]. Of all the possible conversions of CO₂ to C1 or higher-carbon chemicals using molecular catalysts, the most promising reactions in terms of market needs, catalyst performance, and reusability are the formation of cyclic carbonates (e.g., propylene carbonate (PC)) by reacting CO₂ with epoxides (e.g., propylene oxide (PO)); Scheme 1 [7–14].

Moreover, the cycloaddition of CO₂ to epoxides is atom-efficient, and it is one of the most successful examples of CO₂ fixation, producing cyclic carbonates that can be used as excellent

aprotic polar solvents, intermediates in the pharmaceutical and fine chemical industries, and precursors for polycarbonate materials [15–17]. Numerous catalyst systems have been successfully deployed to materialize CO₂-epoxide coupling [18,19], including ionic liquids, metal oxides [20,21], modified molecular sieves [22,23], supported catalysts [24–28], metal-organic frameworks with lodged metallic centers and/or halide anions [29–32], and metal-free catalysts [33–35]. An environmentally friendly organic catalyst that does not contain metals or halogens could be favorable for developing inexpensive and green processes. In essence, organocatalysts act as nucleophiles in the synthesis of cyclic carbonates by opening the epoxide ring prior to the addition of CO₂ and subsequent cyclization [36,37]. Several types of metal-free catalysts for this reaction have been presented, including halides containing weakly interacting cations (e.g., ammonium and imidazolium) [38–40], nitrogen donor bases [41–43], and bifunctional organocatalysts that show synergistic effects of nucleophilic halide salts and a hydroxyl-containing electrophile [44–49].

Bifunctional organocatalysts for the production of cyclic carbonates have undergone remarkable developments in the past decade because of the ingenious design of catalysts, resulting in excellent yields and selectivities because of the synergy effect [44–48]. Hydrogen bonding-inspired organocatalysts and carboxyl-containing organocatalysts, including EDTA (ethylenediaminetetraacetic acid) and polyphenol for CO₂ fixation with

* Corresponding author.

E-mail address: jschung@mail.ulsan.ac.kr (J.S. Chung).