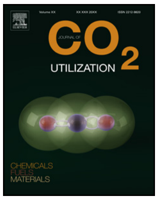
Journal of CO_2 Utilization 2 (2013) 39–48

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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



Mechanism for alternating copolymerization of CO_2 and propylene oxide in diethylzinc–water catalytic system: A DFT study

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ARTICLE INFO

Article history:
Received 29 May 2013
Received in revised form 12 July 2013
Accepted 19 July 2013
Available online 27 August 2013

Keywords:
CO_2 utilization
Propylene oxide
Alternating copolymerization mechanism
Density functional theory calculations

ABSTRACT

The mechanism of alternating copolymerization of CO_2 with propylene oxide (PO) catalyzed by the diethylzinc–water system has been studied by means of density functional theory (DFT) calculations. Six most plausible molecular models for the active species of the diethylzinc–water systems (C_2H_5ZnOH, $C_2H_5(ZnO)_2H$, $C_2H_5(ZnO)_3H$, $C_2H_5(ZnO)_4H$, HOZnOH, $C_2H_5ZnOC_2H_5$) have been constructed. Possible reaction pathways and their corresponding reaction energy barriers have been investigated. It is found that the reaction follows monometallic mechanism and is initiated by PO insertion into the Zn–OR bond of the catalyst. The ring-opening of PO is inclined to occur via the methine–oxygen bond (C_{CH}–O) cleavage. The rate-determining step is the second molecular PO insertion into Zn–carbonate group. CO_2 insertion proceeds easily and the reverse reaction of CO_2 insertion is also easy to occur. It is likely that the most possible active species is the condensed species with repeated Zn–O group, which shows high Gibbs free energy barrier to the formation of cyclic propylene carbonate. The consecutive PO insertion to give polyether and consecutive CO_2 insertion to give dicarbonate linkages have been found to be disfavored. The non-condensed species could be excluded due to its easy formation of cyclic propylene carbonate.

1. Introduction

Carbon dioxide, a final product of fossil fuel combustion and biological metabolism, is renewable and extremely rich in capacity, while the industrial application of carbon dioxide as a raw material is a great challenge due to its high thermodynamic stability, which is still limited to the production of urea, salicylic acid and some carbonates, etc. Due to the growing concern about the greenhouse effect and the economical benefits arising from the utilization of renewable sources, catalytic transformation of CO_2 into useful compounds is attracting more and more attention [1]. Within the last decades, a significant amount of research has been made toward the synthesis of methanol, synthetic gas, dimethyl carbonate (DMC), cyclic carbonates, and aliphatic polycarbonates, etc. [2,3]. Aliphatic polycarbonate, prepared by the alternating copolymerization of CO_2 and epoxides, is one of the catalytic transformations of carbon dioxide into polymer materials [4]. The alternating copolymerization of epoxides (propylene oxide (PO)) and carbon dioxide to generate polycarbonate was firstly reported by Inoue in 1969 using the diethylzinc–water catalyst system [5,6]. The product poly(propylene carbonate) (PPC) is biodegradable with good mechanical property showing potential applications as additives, pore formers, and mid-segment of polyurethanes, etc. Thereafter, this milestone discovery has promoted significant amount of research directing toward the development of new catalysts with improved activity and selectivity for the synthesis of various aliphatic polycarbonates depending on the epoxide used [7–11].

In the past four decades, many new catalysts have been developed, including heterogeneous catalysts like $ZnEt_2$ and di- or tri-hydric sources catalyst systems [12,13], dicarboxylic zinc complexes [14,15], double metal cyanide complexes (DMCC) [16,17], rare earth metal ternary catalysts [18–20], and also homogeneous catalysts, such as metal porphyrins complexes [21], discrete zinc bis-phenoxide complexes [22], zinc β-diiminate complexes [23], metal salen complexes [24,25], etc. However, only a few studies have mainly focused on the alternating copolymerization mechanism of CO_2 and epoxides for homogeneous catalyst systems. Coates et al. firstly proposed the binuclear mechanism (sometimes also called bimetallic mechanism) for the zinc β-diiminate complexes, involving two zinc complexes active species in the transition state of epoxide ring-opening step [26]. Other investigations have indicated a bimetallic initiation or binary initiation, followed by a monometallic propagation step [27,28]. Chisholm et al. studied metal porphyrin complexes and proposed a monometallic mechanism according to kinetic studies [29,30]. However, no direct detection of the intermediates has been

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http://dx.doi.org/10.1016/j.jcou.2013.07.004

provided for alternating copolymerization mechanism of CO_2 and epoxides.

Much fewer researches referred to the alternating copolymerization mechanisms for CO_2 and epoxides on heterogeneous catalysts due to the complexity of catalysts. Wang et al. investigated the catalytic mechanism of heterogeneous rare-earth-metal ternary catalyst in the copolymerization of PO and CO_2 using X-ray photoelectron spectroscopy technique [31]. The results showed that the rare-earth-metal compound in the ternary catalyst decreased the electron density of zinc and increased the Lewis acidity around catalytic center. Rieger et al. studied the mechanism of copolymerization of CO_2 and epoxide with heterogeneous zinc dicarboxylates with experimental and theoretical methods [32]. The theoretical calculations identified that an "ideal" Zn–Zn distance was in the range of 4.3–5.0 Å for the copolymerization of CO_2 and ethylene oxide (EO), which gave a balanced optimum between activation energy and selectivity toward copolymerization. Zhang et al. investigated the copolymerization mechanism of CO_2 and cyclohexene oxide (CHO) catalyzed by Zn–Co (III) DMCC catalyst with combining the kinetic study and electrospray ionization-mass spectrometry analyses [33]. It was found that CO_2/CHO copolymerization was initiated by Zn–OH bond. The early diethylzinc and multi-protic catalyst systems are also heterogeneous catalysts. Copolymerization mechanisms on these catalysts have not been reported so far, and only few proposals concerning about the nature of active species, the chain initiation and by-products formation were made in the literatures. According to Inoue [5,6], the catalyst activity of diethylzinc and water catalyst system was highly dependent on the $H_2O/ZnEt_2$ molar ratio with a clear optimum point at 1:1. Inoue pointed out the possible nature of active species for diethylzinc and multi-protic catalyst systems was condensed zinc species with repeated Zn–OR units [34,35]. Inoue also inferred that the reaction of $ZnEt_2$ and diprotic sources (such as resorcinol, hydroquinone) (molar ratio: 1:1) finally produced the species of $Et(Zn–OR)_nH$ with $n \approx 3$ after 19 h reaction time by measuring the amount of ethane evolved [12]. Kuran proposed that the reaction was initiated by CO_2 incorporation into the Zn–OR bond of the catalyst according to the ^{13}C NMR spectrum of diethylzinc/oxygen compounds produced by the reaction of CO_2 with $ZnEt_2–Ar(OH)_2–PhOPrOH$ catalyst [36]. The PPC was subjected to react with separately prepared $ZnEt_2$–trihydric phenol catalysts to study the degradation process by Gorecki and Kuran [37]. The polymer intrinsic viscosity decreased and cyclic propylene carbonate (CPC) formed during reaction. It was shown that the formation of cyclic species resulted from degradation of the growing polycarbonate chain by depolymerization or backbiting process, a putative intramolecular reaction in which a metal-bound alkoxy chain end was presumed to attack the nearest carbonyl carbon atom in the chain. Thus, the alternating copolymerization mechanism for CO_2 and PO over those earliest catalytic systems was still unclear. As the first generation and simple catalyst, diethylzinc–water catalyst system, which showed a high selectivity for alternative copolymerization of CO_2 and PO, is an ideal model catalyst system and most suitable for the study on this catalytic copolymerization mechanism.

Recently, with theoretical simulation methods becoming more and more important, a growing number of theoretical simulation methods are used for the mechanistic study. Morokuma et al. studied the mechanism of copolymerization of CO_2 with CHO catalyzed by the zinc β-diiminate compound with the hybrid molecular orbital method ONIOM [38]. The calculation results showed that the insertion of CO_2 into a zinc-alkoxyl initiated the reaction with kinetically favored over the insertion of epoxide, the rate-determining step was found to correspond to epoxide insertion. In 2005, Rieger investigated the mechanism of the copolymerization reaction of CO_2 and EO catalyzed by (salen)CrCl in the presence of anionic and 4-dimethylamiopryidine activators using density functional theory (DFT) [39]. The results indicated that the most likely propagation reaction was a binuclear process in which the metal-bound nucleophile attacked a metal-bound epoxide. Williams et al. studied the mechanism of CO_2/CHO copolymerization using dinuclear dizinc complexes with experimental and computational methods [40]. The DFT calculations showed that the rate-determining step for the copolymerization of CO_2 and CHO was the nucleophilic attack of the coordinated epoxide molecule by the zinc-bound carbonate group with the binuclear mechanism. Wu et al. researched the coupling reaction of CO_2 with epoxides (such as EO, PO) affording the cyclic carbonates using different catalysts using DFT [41,42]. The results showed that the preferred mechanism for the catalytic production of cyclic carbonate depended on different catalysts. These results further reinforce the potential for theoretical simulation methods as a tool to study both the catalytic mechanism and to design new catalysts. However, until now, the mechanism of alternating copolymerization of CO_2 with PO with theoretical simulation method has not been reported yet.

In this work, we investigated the mechanism of alternating copolymerization of CO_2 and PO over diethylzinc–water system using the DFT method. The most possible reaction pathways associated with the nature of active species, the chain initiation and by-products formation were explored by theoretical method in order to shed some light on the underlying catalytic reaction mechanism in detail.

2. Computational details

All geometry optimizations and transition state searches were performed with the program GAUSSIAN 09 [43] using the non-local method B3LYP. The LANL2TZ (Los Alamos National Laboratory second triple – zeta) basis set [44] was used for Zn atoms, and the 6-311G(d, p) basis set was used for C, H, and O atoms. All transition states were verified using intrinsic reaction coordinate (IRC) calculations [45]. All energies reported referred to Gibbs free energy corrections to the total electronic energies at 298.15 K. NBO [46] analysis were carried out on some structures for interpretation purposes.

To take the solvent effect into account, single-point self-consistent reaction field (SCRF) calculations based on the polarizable continuum model (CPCM) [47,48] were performed on the optimized gas-phase geometries for all intermediates and transition states at the B3LYP/6-311G(d,p) level. The solvent effects almost did not change the Gibbs free energy differences of crucial steps and the general trend for the reaction potential energy surfaces for all models. Therefore, the results of solvent effects are only showed in Supporting Information (see Figs. S7, S9, S12, S16 and S19).

To support our choice for the functional and basis set, further single-point BPW91/6-311G(d,p), and M06/6-311G(d,p) calculations were performed on model **C** or **1C** ($C_2H_5(ZnO)_3H$). The results are presented in Supporting Information (see Figs. S13 and S14). It was found that the single-point energy differences were small between B3LYP/6-311G(d,p) and BPW91/6-311G(d,p) and M06/6-311G(d,p) levels.

3. Results and discussion

3.1. Catalyst models and reaction pathways

The catalytic system we adopted in the present study was the $ZnEt_2$–water system studied by Inoue experimentally. According to Inoue [5,34,35], the catalyst reached the highest activity when