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ZnO/SiO_2-modified rare-earth-metal ternary catalyst bearing quaternary ammonium salts for synthesis of high molecular weight poly(propylene carbonate)

Ruihua Cheng *, Yujie Zhou, Qiaoli Hou, Boping Liu

State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

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A modified rare-earth-metal catalyst system combined with quaternary ammonium salts (QASs) as cocatalysts was investigated in the alternating copolymerization of CO_2/propylene oxide (PO) to produce poly(propylene carbonate) (PPC). In the presence of ZnO/SiO_2, the $ZnEt_2$-glycerine-$Y(CCl_3OO)_3$ catalyst presented higher activity for CO_2/PO copolymerization, as well as a higher molecular weight of polycarbonate, while maintaining the high carbonate content originating from the neat $ZnEt_2$-glycerine-$Y(CCl_3OO)_3$ catalyst. In the presence of QASs bearing different halide anions (F^-, Cl^-, and Br^-), the type of the halide anion had a strong influence on the activity of the catalyst for CO_2/PO alternating copolymerization. Only tetramethylammonium fluoride (TMAF) could promote the alternating copolymerization without increasing the by-product. Combined the ZnO/SiO_2 catalyst and TMAF, the catalytic activity for CO_2/PO polymerization increased dramatically compared to the basic ternary catalyst system. The improved catalyst system produced a polymer with a high carbonate unit level equivalent to that of the polycarbonate produced by the basic $ZnEt_2$-glycerine-$Y(CCl_3OO)_3$ catalyst system.

1. Introduction

The catalytic fixation of CO_2 into a series of valuable chemical products has gained widespread interest in recent years due to environmental and economic concerns [1–3]. In this context, the conversion of CO_2 and aliphatic epoxides into aliphatic polycarbonates and/or cyclic carbonates is a well-investigated reaction with high efficiency of CO_2 transformation, and research on this topic is still ongoing [4–7]. The aliphatic polycarbonate polymer has a good combination of biodegradable and mechanical properties, while the cyclic carbonate product could be used as raw material for engineering plastics, cosmetics, and polar solvents. Thus, the search for high activity and ecological catalysts is in progress, though a variety of catalyst complexes have already been applied in the reaction of CO_2/PO, including $ZnEt_2$-base catalyst, double metal cyanide (DMC), zinc β-diiminate, metal-Salen complexes, and QASs [4].

Following the pioneering work on high molecular weight poly(propylene carbonate) synthesized by the alternating copolymerization of CO_2 and epoxide using a catalyst derived from diethyl zinc and water by Inoue *et al.* [8], catalyst systems consisting of $ZnEt_2$ and an active hydrogen compound have been developed. The di- or tri-hydric sources of active hydrogen compounds, such as water, primary amines, di- or trihydroxybenzenes, and aromatic dicarboxylic acids, have been explored. Meanwhile, rare earth compounds have also been introduced in this reaction [9–11]. Our theoretical study showed that a rare earth compound decreased the Gibbs free

* Corresponding author. Tel: +86-21-64253364; Fax: +86-21-64253627; E-mail: rhcheng@ecust.edu.cn
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energy barrier of the rate-determining step and improved the catalytic activity [12]. Compared with other CO_2/epoxide catalyst systems, rare-earth-metal ternary catalysts offer highly alternating polymers. The synthesis of PPC is characterized by a high molecular weight product, small amounts of side products, such as cyclic carbonate and polyester, as well as high atom economy and high carbonate content (up to 90%), which is directly associated with a high tensile modulus. A typical rare-earth-metal ternary catalyst system, $ZnEt_2$-glycerine-$Y(CCl_3OO)_3$, seems to be a promising alternative and has been applied on a pilot plant scale to produce poly(propylene carbonate) in China. Furthermore, Wang and coworkers explored this catalyst in the production of cross-linkable PPC by the copolymerization of CO_2 and furfuryl glycidyl ether from renewable hemicellulose and cellulose materials [13], in the one-pot terpolymerization of CO_2, propylene oxide (PO), and L-lactide (L-LA) [14]. However, since the catalyst suffers from low activity and high cost, its improvement still remains a major challenge.

To improve catalytic activity, several methods have been adopted. Recently, a strategy involving the dispersion of metal active complexes on the surface of a support with a high surface area was reported. Actually, supported catalyst is dominant in the petrochemical and industrial chemical fields, especially for noble metal catalysts. The supports, usually inorganic and polymeric materials, might offer interesting properties for immobilization. For heterogeneous catalysts, one of the key features is the influence of mass transport, in particular the issues relating to diffusion into, within, and out of the pores of the material. The surface chemistry, porosity, surface area of the supports, as well as the catalyst preparation method, show a significant influence on the catalytic activity and the selectivity. Furthermore, in the polymerization process, the physical and chemical properties of the support impart some unique reactivities in controlling the performance of the catalyst, as well as the properties of the polymer product. Supported catalyst polymerization processes are remarkable in that thousands of kilograms of polymer might be accumulated per gram of active site without significant catalyst deactivation, making the role of the support more important. Thus, the supports for olefin polymerization catalysts, such as $MgCl_2$ for the Ti-based Ziegler-Natta catalyst, and amorphous silica gel for the Phillips Cr/silica polyethylene catalyst, are all thoroughly researched as a principal, inseparable, and vital component of the catalyst system, and are selected to meet the practical demands. For example, the spherical silica gel support provides adequate morphology and moderate surface area to disperse the active site, high thermal stability to endure the anchoring of the active site during calcination, as well as a unique pore structure, which should be sturdy enough to handle during the process and fragile enough to fragment into smaller particles during polymerization. Furthermore, the modification of silica by titania or fluoride tunes the PE microstructure to the desired performance [15]. Regarding the copolymerization of CO_2/PO, Wang and coworkers [16] reported an increase in the activity by 16%–36% for the $ZnEt_2$-glycerine-$Y(CCl_3OO)_3$ catalyst supported over a series of inorganic oxide supports. The γ-Al_2O_3-supported catalyst system prepared by an *in situ* method presented the highest activity. More recently, we selected a special silica gel, Grace Davison 955, which is a commercial support for the Phillips Cr/silica ethylene polymerization catalyst, in the process of copolymerization of CO_2/PO over $ZnEt_2$-glycerine-$Y(CCl_3OO)_3$ catalyst [12]. Through modification of the silica gel, the activity increased by 69% at optimal conditions over Al_2O_3/SiO_2 support prepared by an impregnation method with moderate Lewis acid active sites.

Another promising approach to increase the catalyst activity is the combination of two dual catalysts in the CO_2/PO copolymerization process, which may lead to a synergistic hybrid effect. Wang and coworkers [17] found that the $ZnEt_2$-glycerine-$Y(CCl_3OO)_3$ ternary catalyst and DMC catalyst system yielded a copolymer with the balanced properties of the individual catalysts. The DMC and Salen-cobalt(III) complex bearing three QASs significantly increased the amount of carbonate fractions by shuttling the growing polymer chains between the two catalyst sites [18].

Combined the two strategies, we report herein a simple but very effective way to tune polymerization activity as well as polymer properties through the dispersion of $ZnEt_2$-glycerine-$Y(CCl_3OO)_3$ catalyst on ZnO-modified silica gel, and using various quaternary ammonium halides as cocatalysts.

2. Experimental

2.1. Materials

Propylene oxide, purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd., was refluxed over CaH_2 for 48 h before use. CO_2 (purity 99.999%), supplied by Shanghai Wetry Standard Reference Gas Co. Ltd., was used without further purification. Glycerol ($C_3H_8O_3$, ≥ 99.5%) was purchased from Alfa Aesar and distilled under reduced pressure prior to use. Diethylzinc ($ZnEt_2$, ≥ 97%) was purchased from Shanghai Ziegler Trade Development Co. Ltd. Yttrium oxide (Y_2O_3, 99.9%) and trichloroacetic acid (CCl_3COOH, ≥ 99%) were purchased from Alfa Aesar and used without further purification. Silica gel (Davison 955, surface area 270.4 m^2/g, pore volume 1.65 cm^3/g, and average pore size 24.5 nm) was from Grace Co., US. $Zn(NO_3)_2\cdot 6H_2O$ (AR) was purchased from Sinopharm Chemical Reagent Co. Ltd. A series of quaternary ammonium halides, namely tetramethylammonium fluoride (TAMF, Me_4NF), tetramethylammonium chloride (TMAC, Me_4NCl), and tetrapropylammonium bromide (TPAB, n-Pr_4NBr), were purchased from Shanghai Darui Fine Chemical Co. Ltd.

2.2. Catalyst preparation

Yttrium trichloroacetate ($Y(CCl_3COO)_3$) was prepared by reaction of yttrium oxide and trichloroacetic acid at 50 °C for 5 h, then dried at 100 °C under vacuum for 6 h. $ZnEt_2$-glycerol-$Y(CCl_3COO)_3$ ternary catalyst was prepared as follows. Glycerol was first added to a pretreated three-necked flask bottle prefilled with yttrium trichloroacetate and propylene oxide under a nitrogen atmosphere to form a clear solution. Then $ZnEt_2$ was