available at www.sciencedirect.com

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

Article (Special Column on the 15th International Conference on Carbon Dioxide Utilization (ICCDU XV))

ZnO/SiO₂-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

ARTICLE INFO

Article history:

Received 12 January 2018

Accepted 27 February 2018

Published 5 August 2018

Keywords:

CO₂/epoxide copolymerization

Rare-earth-metal catalyst

ZnO-modified silica gel

Quaternary ammonium salt

Molecular weight

ABSTRACT

A modified rare-earth-metal catalyst system combined with quaternary ammonium salts (QASs) as cocatalysts was investigated in the alternating copolymerization of CO₂/propylene oxide (PO) to produce poly(propylene carbonate) (PPC). In the presence of ZnO/SiO₂, the ZnEt₂-glycerine-Y(CCl₃OO)₃ catalyst presented higher activity for CO₂/PO copolymerization, as well as a higher molecular weight of polycarbonate, while maintaining the high carbonate content originating from the neat ZnEt₂-glycerine-Y(CCl₃OO)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 CO₂/PO alternating copolymerization. Only tetramethylammonium fluoride (TMAF) could promote the alternating copolymerization without increasing the by-product. Combined the ZnO/SiO₂ catalyst and TMAF, the catalytic activity for CO₂/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 ZnEt₂-glycerine-Y(CCl₃OO)₃ catalyst system.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

The catalytic fixation of CO₂ 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 CO₂ and aliphatic epoxides into aliphatic polycarbonates and/or cyclic carbonates is a well-investigated reaction with high efficiency of CO₂ 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 CO₂/PO, including ZnEt₂-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 CO₂ and epoxide using a catalyst derived from diethyl zinc and water by Inoue *et al.* [8], catalyst systems consisting of ZnEt₂ 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

This work was supported by the Pujiang Talent Projects (16PJD016).

DOI: 10.1016/S1872-2067(18)63012-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 8, August 2018

energy barrier of the rate-determining step and improved the catalytic activity [12]. Compared with other CO₂/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, ZnEt₂-glycerine-Y(CCl₃OO)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 CO₂ and furfuryl glycidyl ether from renewable hemicellulose and cellulose materials [13], in the one-pot terpolymerization of CO₂, 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 MgCl₂ 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 CO₂/PO, Wang and coworkers [16] reported an increase in the activity by 16%–36% for the ZnEt₂-glycerine-Y(CCl₃OO)₃ catalyst supported over a series of inorganic oxide supports. The

γ-Al₂O₃-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 CO₂/PO over ZnEt₂-glycerine-Y(CCl₃OO)₃ catalyst [12]. Through modification of the silica gel, the activity increased by 69% at optimal conditions over Al₂O₃/SiO₂ 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 CO₂/PO copolymerization process, which may lead to a synergistic hybrid effect. Wang and coworkers [17] found that the ZnEt₂-glycerine-Y(CCl₃OO)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 ZnEt₂-glycerine-Y(CCl₃OO)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 CaH₂ for 48 h before use. CO₂ (purity 99.999%), supplied by Shanghai Wetry Standard Reference Gas Co. Ltd., was used without further purification. Glycerol (C₃H₈O₃, ≥ 99.5%) was purchased from Alfa Aesar and distilled under reduced pressure prior to use. Diethylzinc (ZnEt₂, ≥ 97%) was purchased from Shanghai Ziegler Trade Development Co. Ltd. Yttrium oxide (Y₂O₃, 99.9%) and trichloroacetic acid (CCl₃COOH, ≥ 99%) were purchased from Alfa Aesar and used without further purification. Silica gel (Davison 955, surface area 270.4 m²/g, pore volume 1.65 cm³/g, and average pore size 24.5 nm) was from Grace Co., US. Zn(NO₃)₂·6H₂O (AR) was purchased from Sinopharm Chemical Reagent Co. Ltd. A series of quaternary ammonium halides, namely tetramethylammonium fluoride (TAMF, Me₄NF), tetramethylammonium chloride (TMAC, Me₄NCl), and tetrapropylammonium bromide (TPAB, *n*-Pr₄NBr), were purchased from Shanghai Darui Fine Chemical Co. Ltd.

2.2. Catalyst preparation

Yttrium trichloroacetate (Y(CCl₃COO)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. ZnEt₂-glycerol-Y(CCl₃COO)₃ ternary catalyst was prepared as follows. Glycerol was first added to a pretreated three-necked flask bottle pre-filled with yttrium trichloroacetate and propylene oxide under a nitrogen atmosphere to form a clear solution. Then ZnEt₂ was

dropped into the stirring solution at 0 °C to obtain a white suspension, followed by stirring for 0.5 h. The pure SiO₂ support, previously dried at 120 °C to remove the physisorbed water for 12 h, was added into a fluidized-bed quartz reactor followed by calcination at 200 °C for 1 h, and at 600 °C for 4 h in dried air (600 mL/min). The ZnO/SiO₂ supports with ZnO loadings of 1, 3, and 5 wt%, respectively, were prepared by wet impregnation of Zn(NO₃)₂ aqueous solutions of zinc nitrate hexahydrate on silica gel, and then dried at 120 °C for 12 h. The ZnO/SiO₂ precursors were calcined at 200 °C for 1 h, and at 600 °C for 4 h in dried air (600 mL/min) in the fluidized-bed quartz reactor. The supported rare-earth-metal ternary catalyst was prepared by adding the support into the prepared ternary catalyst, and was kept stirring for 0.5 h. The mixture was used in the copolymerization reaction.

2.3. Polymerization experiments

Copolymerization of CO₂/PO was carried out in a 1 L stainless steel autoclave according to a procedure analogous to that described previously [12]. After charging the catalyst into the autoclave by PO, CO₂ was introduced up to a pressure of 3.5 MPa. Then the reactor was heated to 70 °C and kept at this temperature for 8 h with vigorous stirring (350 r/min). The reactor was cooled to room temperature and the pressure was slowly released. Finally, the reaction was terminated by addition of methanol aqueous solution. The obtained copolymer was dissolved in chloroform and precipitated with methanol solution. Finally, the methanol-insoluble copolymer was collected and dried at 50 °C under vacuum until a constant weight was obtained.

2.4. Characterization of products

¹H NMR spectra of the copolymers were recorded at room temperature on a Bruker AVANCE 500 spectrometer with tetramethylsilane as the internal reference. The carbonate unit content of the copolymer (CU%) was calculated from the area ratio of peaks at 5.0, 4.2, and 3.5 ppm in the ¹H NMR spectrum according to the following equation [19]:

$$\text{CU}\% = \frac{A_{5.0} + A_{4.2}}{A_{5.0} + A_{4.2} + A_{3.5}}$$

The molecular weight and polydispersity of the copolymer were obtained on a Waters-1515 gel permeation chromatography (GPC) system using polystyrene as the standard and tetrahydrofuran as the eluent. The glass transition temperature was determined from TA-Q200 differential scanning calorimetry (DSC) at a heating rate of 10 °C/min, from 10 to 80 °C, and under nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out in an SDT Q600 series thermal analysis system (TA Instruments Co., USA) under a protective nitrogen atmosphere from 50 to 500 °C, at a rate of 10 °C/min, and under a nitrogen flow of 20 mL/min. The Zn content was measured by the Thermo Elemental IRIS 1000 inductively coupled plasma (ICP) after the sample was purified by chloroform solution, then washed with methanol solution.

3. Results and discussion

3.1. Effect of ZnO/SiO₂

Anchoring the organometallic species on the solid support has been achieved by a variety of routes involving the functional group of the support. Due to the air sensitivity of ZnEt₂, the immobilization of the active center on the inorganic support was performed in propylene oxide reactant during the progress of the mixture of the reaction system under an inert atmosphere. ZnEt₂ can react with hydroxyl groups on the silica surface, which has been confirmed to be easily anchored [20], and a -Zn-O-Zn-Et structure might be formed as the γ-Al₂O₃-supported analog [21]. Table 1 shows the results of CO₂/PO copolymerization over the ZnO/SiO₂-supported rare-earth-metal ternary catalyst. The activities for the ZnO/SiO₂-supported catalysts (Table 1, entries 3–5) increased compared to the silica-supported one (Table 1, entry 2). The yield was at the level of 4009.2 g/mol_{Zn} (based on the amount of ZnEt₂ involved) with 3.0 g of 3 wt% ZnO/SiO₂ support. As a typical amphoteric oxide, the ZnO-modified silica catalyst showed higher activity than that of the acidic Al₂O₃-modified one [12]. Better dispersion of the active sites on ZnO/SiO₂ might be obtained. The

Table 1

CO₂/propylene oxide copolymerization over various rare-earth-metal ternary catalysts ^a.

Entry	Modifier	Modifier amount (g)	Activities ^b (g/mol _{Zn})	T _g (°C)	CU% ^c (%)	Mn×10 ⁻⁴ ^d	PDI ^d
1	None	—	2140.6	40.9	97.4	12.9	3.58
2	Pure SiO ₂	3.0	2898.6	41.9	98.0	4.8	5.31
3	1 wt% ZnO/SiO ₂	3.0	3588.6	41.2	95.0	34.8	1.75
4	3 wt% ZnO/SiO ₂	3.0	4009.2	40.6	95.7	19.1	2.34
5	5 wt% ZnO/SiO ₂	3.0	3465.2	40.3	94.0	22.6	2.43
6	TMAF	0.38	3087.5	40.6	95.0	22.4	2.78
7	TMAC	0.45	2541.0	40.8	96.0	20.2	2.49
8	TPAB	1.09	712.7	38.5	95.8	12.4	2.83
9	3 wt% ZnO/SiO ₂ + TMAF	3.0 + 0.38	4888.0	40.5	96.6	22.6	2.43
10	3 wt% ZnO/SiO ₂ + TMAC	4.0 + 0.38	5016.5	40.7	94.0	26.3	2.78
11	3 wt% ZnO/SiO ₂ + TPAB	5.0 + 0.38	5223.0	40.4	95.6	20.0	2.81

^a Polymerization conditions: PO 1 L, CO₂ 3.5 MPa, ZnEt₂ 4 mL, glycerol 1.4 mL, Y(CCl₃COO)₃ 1.14 g, 70 °C, 8 h.

^b Calculated based on ZnEt₂ involved.

^c Selectivity of polycarbonate over cyclic carbonate in units of % as determined by ¹H NMR spectroscopy of the crude product.

^d Determined on GPC using a polystyrene standard.

adsorption of CO₂ on ZnO [22] would also benefit the ring-opening of PO and promote increased activity, though the Gibbs free energy of the adsorption and the insertion of CO₂ into the ZnEt₂ active site are relatively low, according to our calculation [12].

The properties of the copolymers obtained over a series of rare-earth-metal ternary catalysts are shown in Table 1 and Fig. 1. Based on the ¹H NMR spectra, the CU% slightly decreased from 97.3% for the polymer by the ternary catalyst to around 95% for the polymer by the ZnO/SiO₂-supported ternary catalysts. The molecular weight of the polymer obtained over the virginal silica-supported ternary catalyst greatly decreased from 12.9×10⁴ to 4.8×10⁴ by virtue of the amount of surface hydroxyl on the silica, which could act as a chain transfer in the polymerization process. In the presence of 1.0 wt% ZnO/SiO₂, the molecular weight of the polymer produced increased dramatically to 34.8×10⁴, while the molecular weight distribution became narrower. Increasing the ZnO loading on the silica support led to the decrease of the MW of the polymer. The MW of the catalyst of 3.0 wt% ZnO/SiO₂ was 19.1×10⁴.

The glass transition temperature (*T*_g) of the resultant copolymers measured by DSC are presented in Table 1. The *T*_g values for the PPC products obtained by the support catalysts were in the range of 40–41 °C, which is similar to that of the unsupported one; that is, the microstructure and the regioregularity of the copolymer were maintained, and were not influenced by the various supports involved or the increased activity. The thermal decomposition of PPC was carried out by TGA, and the initial decomposition temperature, *T*_{-5%}, which is the onset of degradation with respect to 5 wt% loss for the PPC, and the maximum weight loss rate temperature (*T*_{max}) are shown in Table 2. The *T*_{-5%} values of the polymers produced by the unsupported and silica-supported ternary earth catalyst were similar (around 233 °C), and their *T*_{max} occurred at 247 and 249 °C, respectively. However, *T*_{-5%} and *T*_{max} decreased dramatically with increasing ZnO loadings on silica, and those over 5 wt% ZnO/SiO₂-modified ternary catalyst were even shifted to 96 and 220 °C, respectively. As this point, the amount of residual Zn species in the polymer tested by elemental analysis was 33 ppm, which might be attributed to the high degra-

Fig. 1. GPC curves of the copolymers from the ZnO/SiO₂-supported rare-earth-metal ternary catalysts. (1) Blank; (2) SiO₂; (3) 1 wt% ZnO/SiO₂; (4) 3 wt% ZnO/SiO₂; (5) 5 wt% ZnO/SiO₂.

Table 2

Thermal properties of the copolymer produced over rare-earth-metal ternary catalyst with various ZnO/SiO₂ loadings.

Entry	Modifier	<i>T</i> _{-5%} ^a (°C)	<i>T</i> _{max} ^b (°C)
1	None	233	247
2	Pure SiO ₂	232	249
3	1 wt% ZnO/SiO ₂	183	221
4	3 wt% ZnO/SiO ₂	209	222
5	5 wt% ZnO/SiO ₂	96	220

^a Onset of degradation with respect to 5 wt% loss.

^b The maximum weight loss rate temperature for the PPC.

dation of the PPC product. It is known that the back-biting reaction could lead to depolymerization of polycarbonate to thermodynamically favored cyclic carbonates. Furthermore, PPC was purified by a dissolution/precipitation procedure with acetone as the solvent and ethanol as the precipitate for several cycles. After a single purification cycle, the *T*_{-5%} of the treated polymer increased to 207 °C. Four purification cycles caused the *T*_{-5%} and *T*_{max} of the polymer to increase to 220 and 246 °C, respectively, reaching the levels of the polymer produced by the unsupported catalytic system. From elemental analysis of the amount of residual Zn species in the polymer, it was found that the amount of Zn in the polymer decreased from 33 to 25 ppm after purification. A decreased degradation of PPC also suggested that the residual catalyst was important in PPC degradation [23].

The effect of ZnO/SiO₂ in the reaction was further investigated in terms of the charged amount. In Fig. 2, keeping the amount of the rare-earth-metal ternary catalyst constant, the activities of CO₂/PO copolymerization showed dependence on the amount of 3.0 wt% ZnO/SiO₂. When the amount of ZnO/SiO₂ increased from 2.0 to 7.0 g, the activities reached the highest value at 4845.2 g/mol_{Zn} on 5.0 g support, then decreased dramatically. In the blank experiment over 3.0 wt% ZnO/SiO₂, the activity of CO₂/PO copolymerization was negligible. Apparently, the silica gel does not act as an inert substrate, but is actually involved during copolymerization. With increasing amounts of 3.0 wt% ZnO/SiO₂, more ZnEt₂ might immigrate on the solid support. Additionally, the increased residual Si-OH groups on the silica surface might act as a weak acid to activate the propylene oxide. Similar results were also found in the cy-

Fig. 2. Effect of the amount of 3 wt% ZnO/SiO₂ on the copolymerization of CO₂/PO.

clic carbonates synthesized over the modified silica-supported tetrabutylammonium bromide catalyst [24].

3.2. Effect of quaternary ammonium halides

It is well known that a Lewis base could be a good co-catalyst for the coupling reaction of CO₂ with PO. Thus, quaternary ammonium halides were introduced in the reaction. Table 1 shows the CO₂/PO copolymerization results over the ZnEt₂-glycerine-Y(CCl₃OO)₃ and quaternary ammonium halide catalyst systems. The polymerization activities, as well as the polymer properties dramatically depended on the type of halide, while the effect of the high CU% was minor. The counter anion of the halide significantly affected the catalytic activity. The activities of the corresponding catalysts showed the following trend: Me₄NF > Me₄NCl > *n*-Pr₄NBr, which is in the order of the nucleophilicity of the anion [25]. Only Me₄NF could act as a promoter to increase the activity dramatically, while the presence of Me₄NCl and *n*-Pr₄NBr had a negative effect on the reaction, resulting in decreased activity. The presence of Me₄NF could increase the activity level to 3087.5 g/mol_{Zn}, which was higher than that of the pure ZnEt₂-glycerine-Y(CCl₃OO)₃ catalyst with a value of 2140.6 g/mol_{Zn}. Moreover, the polymer properties greatly depended of the type of anion in the quaternary ammonium halide modifier. Under these conditions, the typical Mn ranged from 12.4×10⁴ to 22.4×10⁴ with PDI values of 2.78 to 2.83, as shown in Table 1. The Mn of the copolymer was enhanced for the catalyst system with Me₄NF species to 22.4×10⁴, while that for the ternary rare-earth-metal catalyst was 12.9×10⁴. Thus, a high polymer strength could be achieved. It was found in the literature that simple metal salts, such as KI alone, had low activity for the cycloaddition reaction, while the KI/hydroxyl (OH) substance system was effective for the cycloaddition of CO₂/propylene oxide [26]. In our study, the test of KF showed no effect on the activity and selectivity of the ZnEt₂-glycerine-Y(CCl₃COO)₃ ternary catalyst under the same reaction conditions.

3.3. Effect of combination of ZnO/SiO₂ and QASs

Subsequently, the ZnEt₂-glycerine-Y(CCl₃COO)₃ combined with ZnO/SiO₂ and Me₄NF under optimal conditions was applied to CO₂/PO copolymerization. As expected, the activity over the catalyst system (in Table 1) was dramatically enhanced. The activity over ZnEt₂-glycerine-Y(CCl₃COO)₃ with 5.0 g ZnO/SiO₂ and Me₄NF could reach 5223.0 g/mol_{Zn}. The molecular weight reached 26.3×10⁴ with 4.0 g ZnO/SiO₂ and Me₄NF; that is, the involved components present a synergetic effect on the promotion of catalytic activity, as well as the molecular weight. At the same time, the carbonate level was maintained at a high level of 95%.

3.4. Discussion

The role of quaternary ammonium halides in conjunction with the ZnEt₂-glycerine-Y(CCl₃OO)₃ catalyst system in the reaction of CO₂/PO to form PPC is interesting to be investigated.

The quaternary ammonium halide alone was effective and stable for the reaction of CO₂/PO to cyclic carbonates at high temperature. The molten tetraalkylammonium halides can serve as the solvent as well as the catalyst in the production of cyclic carbonate [27].

Quaternary ammonium halides were also typically reported as cocatalysts in combination with several catalyst systems in the synthesis of cyclic carbonate [7]. For the Schiff base/QAS system catalysts, North *et al.* [28] found that in the bimetallic Al(Salen)/*n*-Bu₄NBr system, the second-order kinetics of CO₂/styrene oxide cyclic addition depended on the concentration of *n*-Bu₄NBr. Jiang and coworkers [29] reported the Ni(Salphen)-based metal-organic framework catalytic system, which strongly depended on the QAS used. The reaction could present an 80% yield of cyclic carbonate in the presence of *n*-Pr₄NBr, while no reaction occurred in the absence of QAS. It was well established that one role of QAS catalysts in cyclic carbonate synthesis was nucleophilic attack by the halogen ion to help PO monomers coordinate the metal active sites with the leading ring opening followed by CO₂ insertion [25,27,30]. Furthermore, in some cases, the anion of the QAS could dramatically alter the selectivity of cyclic and polymeric products. Lu and coworkers [7,31–33] found that in the reaction of CO₂/PO over a chiral Co(Salen)X/QAS system, both the axial X group of Co(Salen)X and the anion Y of *n*-Bu₄NY drastically affected the PPC/PC selectivity. In general, a cobalt complex with an electron-withdrawing axial group X and a QAS with poor leaving ability was beneficial for polycarbonate formation, while the anion of the QAS with high nucleophilicity and good leaving ability increased the selectivity for cyclic carbonate. In these reports, quaternary ammonium bromide showed the best the performance, while the fluoride salt gave the lowest yield [25,34].

For other hybrid catalyst systems involving QASs, Dharman *et al.* [35] and Wei *et al.* [36] reported that the Zn₃[Co(CN)₆]₂-based double metal cyanide complex/QAS system was effective to produce several cyclic carbonates under mild conditions. As we known, Zn₃[Co(CN)₆]₂ is a typical epoxide-ring opening/CO₂ copolymerization catalyst to produce high molecular weight polycarbonate with polyester as the by-product. The authors claimed that the double metal cyanide complex promoted the ring opening of epoxide [32]. The subsequent addition of CO₂ to the ring-opened epoxide may be preferred by the presence of QAS, which stabilized the polarized intermediate. The presence of quaternary salt, especially bearing the Br[−] anion, may not only accelerate the diffusion of CO₂ into the reaction mixture, but also favor the backbiting mechanism to exclusively produce the cyclic carbonate. In this combined catalyst system, it seemed that the QAS component strengthened the CO₂/PO coupling reaction followed the route of cyclic carbonate formation.

Despite also being a hybrid catalyst system, ZnEt₂-glycerine-Y(CCl₃OO)₃/QAS shows a totally different phenomenon from the above QAS-involved system. The CO₂/epoxides copolymerization routine still dominated in the presence of QASs and led to successive chain propagation to produce polycarbonate with high Mn. In our case, Me₄NF seemed to activate the epoxide

Scheme 1. Possible CO₂/PO copolymerization mechanism using the ZnO/SiO₂-supported ZnEt₂-glycerine-Y(CCl₃COO)₃/Me₄NF catalyst system.

ring rather than restrict the extension of the polymer chain to form the cyclic carbonate, as Lu and coworkers [7,31–33] described for the reaction of CO₂/PO over a chiral Co(Salen)X/QAS system. The QAS of F[−] presented stronger nucleophilicity, which could attack more easily and led PO to ring-opening.

In view of the above experimental results and our previous theoretical studies [12], we proposed a plausible reaction mechanism for CO₂/PO copolymerization over the rare-earth-metal ternary catalyst supported on ZnO/SiO₂ with a tetraalkylammonium halide as the cocatalyst, as demonstrated in Scheme 1. As indicated by DFT studies [12], the rate-determining step for the alternating copolymerization of CO₂ and PO is the insertion of PO into the Zn-carbonate bond, and the corresponding activation barrier could be decreased by increasing the natural bond order (NBO) charge of the zinc species. Moreover, the critical step of the copolymerization of CO₂/PO is the cleavage of the epoxide; that is, a way to increase the reaction rate is to design catalysts capable of activating the epoxide. In this complex catalyst system, the coordination ability, leaving ability, and nucleophilicity of the quaternary ammonium halides have a great effect on the performance of the polymerization. The enhancement of catalytic performance might presumably be attributed to the activation of the epoxide ring by nucleophilic activation of the carbon atom by the Lewis-basic F[−] center. During the stirring, the ZnEt₂ in ternary catalysts might be well supported on the ZnO/SiO₂ surface. In the initiation stage of the copolymerization process, PO is adsorbed on the Lewis acidic ZnEt₂ site, followed by PO activation through coordination between the oxygen atom of propylene oxide with the ZnEt₂ active site. F[−] in Me₄NF attacks the less sterically hindered carbon atom of propylene oxide. Therefore, the epoxy ring opens easily. The oxygen anion interacts with CO₂ to form an alkylcarbonate anion. The F[−] might be on the end of the carbonate, then the second PO and CO₂ monomers insert. Repetition of this step resulted in the formation of long chains consisting of carbonate groups as monomer units.

4. Conclusions

In this work, the modification of the ZnEt₂-glycerine-Y(CCl₃COO)₃ ternary catalyst was studied. By the immobilization of ZnO-modified silica gel support, the catalytic activity, as well as the molecular weight of the product increase significantly. It was found that the influence of immobilization of the catalyst on a support was very small on the content of car-

bonate units and the glass transition temperature. The optimal conditions were 3 wt% ZnO/SiO₂ with 5.0 g amount. Additionally, the purification treatment to remove ZnO from the polymer can effectively improve its thermal properties. With the immobilization, the QAS cocatalyst, especially the fluoride, showed positive effects on the performances. TMAF could also significantly increase the activities. ZnO/SiO₂ and Me₄NF were combined with ZnEt₂-glycerine-Y(CCl₃COO)₃ as an excellent catalyst system for CO₂/PO copolymerization. The catalyst system could maintain a high carbonate level.

Acknowledgments

The authors thank for the financial support by China Blue Chemical Ltd., CNOOC and Wanhua Chemical Group Co., Ltd.

References

- [1] T. Sakakura, J. C. Choi, H. Yasuda, *Chem. Rev.*, **2007**, 107, 2365–2387.
- [2] M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem. Int. Ed.*, **2011**, 50, 8510–8537.
- [3] M. Mikkelsen, M. Jorgensen, F. C. Krebs, *Energy Environ. Sci.*, **2010**, 3, 43–81.
- [4] D. J. Darensbourg, M. W. Holtcamp, *Coord. Chem. Rev.*, **1996**, 153, 155–174.
- [5] M. North, R. Pasquale, C. Young, *Green Chem.*, **2010**, 12, 1514–1539.
- [6] S. Klaus, M. W. Lehenmeier, C. E. Anderson, B. Rieger, *Coord. Chem. Rev.*, **2011**, 255, 1460–1479.
- [7] X. B. Lu, W. M. Ren, G. P. Wu, *Acc. Chem. Res.*, **2012**, 45, 1721–1735.
- [8] S. Inoue, H. Koinuma, T. Tsuruta, *J. Polym. Sci. Polym. Lett.*, **1969**, 7, 287–292.
- [9] C. S. Tan, T. J. Hsu, *Macromolecules*, **1997**, 30, 3147–3150.
- [10] B. Y. Liu, X. J. Zhao, X. H. Wang, F. S. Wang, *J. Polym. Sci. Part A*, **2001**, 39, 2751–2754.
- [11] Z. L. Quan, X. H. Wang, X. J. Zhao, F. S. Wang, *Polymer*, **2003**, 44, 5605–5610.
- [12] X. Pan, Z. Liu, R. H. Cheng, D. L. Jin, X. L. He, B. P. Liu, *J. Organomet. Chem.*, **2014**, 753, 63–71.
- [13] Y. X. Hu, L. J. Qiao, Y. S. Qin, X. H. Zhao, X. H. Chen, X. H. Wang, F. S. Wang, *Macromolecules*, **2009**, 42, 9251–9254.
- [14] L. Gu, Y. S. Qin, Y. G. Gao, X. H. Wang, F. S. Wang, *Chin. J. Chem.*, **2012**, 30, 2121–2125.
- [15] M. P. McDaniel, *Adv. Catal.*, **1985**, 33, 47–98.
- [16] H. W. Lu, Y. S. Qin, X. H. Wang, X. G. Yang, S. B. Zhang, F. S. Wang, *J. Polym. Sci. Part A*, **2011**, 49, 3797–3804.

Graphical Abstract

Chin. J. Catal., 2018, 39: 1303–1310 doi: 10.1016/S1872-2067(18)63012-8

ZnO/SiO₂-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
East China University of Science and Technology

A modified rare-earth-metal catalyst system combined with quaternary ammonium salts as cocatalyst was investigated in the alternating copolymerization of CO₂/propylene oxide to produce poly(propylene carbonate) with high molecular weight.

- [17] Y. L. Dong, X. H. Wang, X. J. Zhao, F. S. Wang, *J. Polym. Sci. Part A*, **2012**, 50, 362–370.
- [18] J. K. Varghese, A. Cyriac, B. Y. Lee, *Polyhedron*, **2012**, 32, 90–95.
- [19] X. H. Chen, Z. Q. Shen, Y. F. Zhang, *Macromolecules*, **1991**, 24, 5305–5308.
- [20] R. Duchateau, W. J. van Meerendonk, S. Huijser, B. B. P. Staal, M. A. van Schilt, G. Gerritsen, A. Meetsma, C. E. Koning, M. F. Kemmere, J. T. F. Keurentjes, *Organometallics*, **2007**, 26, 4204–4211.
- [21] K. Soga, K. Hyakkaku, K. Izumi, S. Ikeda, *J. Polym. Sci. Part A*, **1978**, 16, 2383–2392.
- [22] T. Hikov, A. Rittermeier, M. B. Luedemann, C. Herrmann, M. Muhler, R. A. Fischer, *J. Mater. Chem.*, **2008**, 18, 3325–3331.
- [23] W. Kuran, P. Górecki, *Die Makromol. Chem.*, **1983**, 184, 907–912.
- [24] T. Cao, L. T. Sun, Y. Shi, L. Hua, R. Zhang, L. Guo, W. W. Zhu, Z. S. Hou, *Chin. J. Catal.*, **2012**, 33, 416–424.
- [25] N. Kihara, N. Hara, T. Endo, *J. Org. Chem.*, **1993**, 58, 6198–6202.
- [26] J. Ma, J. L. Liu, Z. F. Zhang, B. X. Han, *Green Chem.*, **2012**, 14, 2410–2420.
- [27] V. Caló, A. Nacci, A. Monopoli, A. Fanizzi, *Org. Lett.*, **2002**, 4, 2561–2563.
- [28] M. North, R. Pasquale, *Angew. Chem. Int. Ed.*, **2009**, 48, 2946–2948.
- [29] Y. W. Ren, Y. C. Shi, J. X. Chen, S. R. Yang, C. R. Qi, H. F. Jiang, *RSC Adv.*, **2013**, 3, 2167–2170.
- [30] J. Q. Wang, K. Dong, W. G. Cheng, J. Sun, S. J. Zhang, *Catal. Sci. Technol.*, **2012**, 2, 1480–1484.
- [31] X. B. Lu, B. Liang, Y. J. Zhang, Y. Z. Tian, Y. M. Wang, C. X. Bai, H. Wang, R. Zhang, *J. Am. Chem. Soc.*, **2004**, 126, 3732–3733.
- [32] X. B. Lu, Y. Wang, *Angew. Chem. Int. Ed.*, **2004**, 43, 3574–3577.
- [33] X. B. Lu, L. Shi, Y. M. Wang, R. Zhang, Y. J. Zhang, X. J. Peng, Z. C. Zhang, B. Li, *J. Am. Chem. Soc.*, **2006**, 128, 1664–1674.
- [34] J. Q. Wang, D. L. Kong, J. Y. Chen, F. Cai, L. N. He, *J. Mol. Catal. A*, **2006**, 249, 143–148.
- [35] M. M. Dharman, J. I. Yu, J. Y. Ahn, D. W. Park, *Green Chem.*, **2009**, 11, 1754–1757.
- [36] R. J. Wei, X. H. Zhang, B. Y. Du, Z. Q. Fan, G. R. Qi, *J. Mol. Catal. A*, **2013**, 379, 38–45.

稀土三元催化体系ZnO/SiO₂负载化及季铵盐催化CO₂与环氧丙烷合成高分子量聚碳酸酯

程瑞华*, 周宇杰, 侯侨丽, 刘柏平

华东理工大学化学工程国家重点实验室, 上海200237

摘要: 由环氧丙烷(PO)和CO₂交替共聚成脂肪族聚碳酸亚丙酯, CO₂利用率高, 所得产物具有一定的力学性能和生物降解性能, 具有广泛应用前景。目前, 用于CO₂和环氧化合物共聚的催化体系主要包含锌、钴、镍、铬、铝和稀土等金属活性中心, 结构、活性各异的催化剂体系, 其催化性能和产物性能也各具特色。其中, 稀土三元催化剂(ZnEt₂-甘油-三氯乙酸钇)因合成聚碳酸酯产物的分子量高、碳酸酯单元含量高、聚醚及环碳酸酯副产物少的特点而受到关注。但是由于催化剂催化效率低, 聚合时间长, 产品成本高, 使得工业化规模生产受到限制。

本文基于稀土三元催化体系, 将催化剂负载于硅胶及锌改性硅胶, 优化了其制备条件, 同时考察了添加季铵盐对催化CO₂/环氧丙烷共聚成聚碳酸酯性能的影响。结果表明, 在1 L聚合釜中, 于3.5 MPa和70 °C反应条件下, ZnO负载量及ZnO/SiO₂添加量对反应性能均有影响。当3 wt% ZnO/SiO₂的添加量为5 g时, 稀土三元催化体系的活性为4845.2 g/mol_{Zn}。所得聚合物经过多次纯化处理后, 能够有效提高材料的热学性能, 即有效除去产物中的ZnO对聚合物的热稳定性有重要作用。添加含有不同阴离子(F⁻, Cl⁻和Br⁻)的季铵盐可显著影响稀土三元催化剂的活性。其中, 仅四甲基氟化铵可以明显提高反应活性乃至聚合物分子量。在3 wt% ZnO/SiO₂载体和四甲基氟化铵的协同作用下, 稀土三元催化体系的共聚性能明显提

升, 活性最高可达 $5223.0 \text{ g/mol}_{\text{Zn}}$. 聚合物结构分析表明, 在载体和四甲基氟化铵存在下, 聚合物分子量明显提高, 可达到20万以上, 分子量分布明显变窄, 且聚合物结构如碳酸酯的单元含量、副产物含量以及聚合物产品玻璃化温度基本不变, 后者均保持在 $40\text{--}41^\circ\text{C}$. 基于此, 我们提出了在ZnO改性硅胶载体及四甲基氟化铵存在下稀土三元催化体系催化 CO_2 /环氧丙烷共聚的反应机理: ZnO/ SiO_2 载体有利于稀土三元催化体系的分散, 而四甲基氟化铵则有利于吸附在 ZnEt_2 上的环氧丙烷开环.

关键词: CO_2 /环氧烷烃共聚; 稀土金属催化剂; ZnO改性硅胶; 季铵盐; 分子量

收稿日期: 2018-01-12. 接受日期: 2018-02-27. 出版日期: 2018-08-05.

*通讯联系人. 电话: (021)64253364; 传真: (021)64253627; 电子信箱: rhcheng@ecust.edu.cn

基金来源: 浦江人才计划(16PJD016).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).