



Rapid copolymerization of carbon dioxide and propylene oxide catalyzed by double metal cyanide complexes in an ultrasonic field



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ARTICLE INFO

Article history:

Received 13 April 2016

Received in revised form

17 May 2016

Accepted 25 May 2016

Available online 26 May 2016

Keywords:

Poly (propylene carbonate)

Polymers

Sonochemistry

Rapid copolymerization

Double metal cyanides

Nanosize

ABSTRACT

Sonochemistry as a clean, efficient and environmentally friendly synthetic method has shown great potential in the chemical synthesis. In this work, poly (propylene carbonate) (PPC) was successfully obtained from carbon dioxide (CO₂) and propylene oxide (PO) by using Zn-Co and Zn-Fe double metal cyanides (DMCs) as catalyst with the sonochemistry method. With FTIR, ¹H NMR and GPC analysis, PPCs prepared in the ultrasonic field have high yield, high molecular weight and wide polydispersity index (PDI). It is proven to be effective for the copolymerization of CO₂ and PO with the sonochemistry method.

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1. Introduction

The fixation of CO₂ to polymeric materials for the application in industrial fields is one of the most valuable researches. In past decades, many researchers focused on finding a highly active catalyst for the copolymerization of CO₂ and PO [1–5]. Homogeneous catalysts such as zinc phenoxide [6] and zinc (β-diiminates) [7] complexes have high catalytic activity and selectivity for CO₂/epoxides copolymerization. However, such homogeneous catalysts require a complex synthesis procedure and strict conditions for polymerization. As heterogeneous catalysts, ZnEt₂/protonic compounds [8], rare earth-based catalysts [9], and zinc dicarboxylate [10] can catalyze CO₂-PO copolymerization with high M_n and M_w, while they often suffer from low productivities of 10–200 g polymer/g catalyst. Sonochemistry is the application of ultrasound to activate or modify the rate of chemical reactions in liquid media [11]. The ultrasound irradiation is used in a great number of chemical reactions, such as acetylation of alcohols [12], synthesis of stilbenes by Suzuki cross-coupling [13] and Michael addition [14]. In order to improve low productivities and decrease copolymerization time, we focused on the copolymerization of CO₂ and PO catalyzed by Zn-Co and Zn-Fe DMCs in the ultrasonic

field. And the effect of ultrasound on the synthesis of PPC was investigated in detail.

2. Experimental

Materials and characterization: ZnCl₂, K₃Fe(CN)₆, K₃Co(CN)₆ and *t*-BuOH, were of analytical purity. PO (≥ 98%) and CO₂ (purity more than 99.9%) were used without further purification.

The DMC catalysts were characterized by a scanning electron microscope (SEM) (Model: JEM-7100F), X-ray diffraction (XRD) (BrukerAXS/D8), thermo gravimetric analysis (TGA) (Netzsch-STA 449F3), and fouriertrans form infrared spectroscopy (FT-IR) (6700/Thermo Fisher Scientific). Analyses of PPCs were performed using FTIR, a Bruker NMR spectrometer (Model: Bruker AV 400 MHz) and a gel permeation chromatography (GPC) (PLGPC220, Polymer Laboratories).

A typical DMC catalyst was synthesized as follows: an amount of ZnCl₂ (8.0 g) was dissolved in the solution of de-ionized water (10 ml) and *t*-BuOH (10 ml). K₃Co(CN)₆ (or K₃Fe(CN)₆) (6.6 g) dissolved in 10 ml de-ionized water was added into ZnCl₂ solution under vigorous stirring. Then the precipitation reaction was heated to 75 °C and agitated greatly for 3 h. The resulting white precipitate was separated by filtration and reslurried in a mixture of *t*-BuOH and water (v/v=1/1) with vigorous stirring. The precipitation was isolated by filtration to remove potassium ion.

The copolymerization was carried out in a 100-ml steel

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autoclave equipped with a magnetic stirrer and an ultrasonic generator. DMC was added into the autoclave, followed by adding a desired amount of PO under vacuum conditions. The autoclave was pressurized to 4.0 MPa with CO₂. Then the autoclave was heated at 60 °C with stirring in the ultrasound environment. After the reaction, the autoclave was cooled down to the room temperature and slowly depressurized. The obtained products were dissolved in acetone, stirred for 30 min, then poured into water, isolated, and dried at 50 °C.

3. Results and discussion

3.1. Characterization of DMC catalysts

Zn-Co and Zn-Fe DMC catalysts were prepared as described in experimental section. Fig. 1(a, b) shows SEM images of Zn-Co catalyst. It shows lamellar structures with an edge length of approximately 100–600 nm and a thickness of 20–60 nm. The lamellae overlap in a layer-by-layer and loose fashion. Fig. 1(c, d) shows SEM images of Zn-Fe catalyst, which is irregular granule with a size of 20–400 nm. The nano-structure of Zn-Co and Zn-Fe DMC catalysts ensures a better dispersion in the monomers and better exposure of active sites to the reactants, thus yields high catalytic activity.

The FTIR spectra of Zn-Co DMC catalyst exhibit characteristic peaks including the CN stretching absorption in the Zn²⁺-CN-Co³⁺ unit at 2189 cm⁻¹, and Co-CN flexural vibration absorption at 492 cm⁻¹ (shown in Fig. 2(a)). And because of existing complexing agent t-BuOH in the DMC catalyst, the -OH in DMC shows

a broad band assigned to stretching vibration absorption at 3577 cm⁻¹, CH stretching vibration absorption peak appeared at 2983 cm⁻¹. Because of the similar chemical structure, the FTIR spectra of Zn-Co DMC and Zn-Fe DMC have the similar characteristic peaks. The FTIR spectra of Zn-Fe DMC in Fig. 2(a) exhibit characteristic peaks of CN stretching absorption at 2108 cm⁻¹, Fe-CN flexural vibration absorption at 697 cm⁻¹, -OH stretching vibration absorption at 3550 cm⁻¹, CH stretching vibration absorption at 2923 cm⁻¹.

The essence of DMC with high activity is amorphous, this means the lower crystallinity of DMC is, the higher its catalytic activity is. Crystallization of the DMC was determined by an X-ray diffractometer. As shown in Fig. 2(b), Zn-Co DMC only shows reflections at 16.40°, 17.15° and 24.45° 2θ, a typical cubic lattice structure. Compared with Zn-Co DMC, Zn-Fe DMC, exhibiting two peaks at 2θ=17.4°, 24.5°, shows the important role of K₃Fe(CN)₆ in crystallinity decreasing. As shown in Fig. 2(b), it could infer that all the catalysts are the lower crystallinity.

The catalysts were further characterized by TGA with a heating rate of 10 °C/min under N₂ atmosphere in a high throughput mode. The weight loss is shown in Fig. 2(c). TGA analysis shows that physisorbed water is removed at first (< 100 °C), then followed by t-BuOH. And the Zn-Fe (or Zn-Co) cyanide salt is converted to Fe₂O₃ (or Co₂O₃) and ZnO. From Fig. 2(c), it is found that two DMCs are relatively stable at temperature up to 100 °C. And the temperature of CO₂-PO copolymerization is 60 °C. Thus, it implies that catalyst is stable during the copolymerization of CO₂-PO.

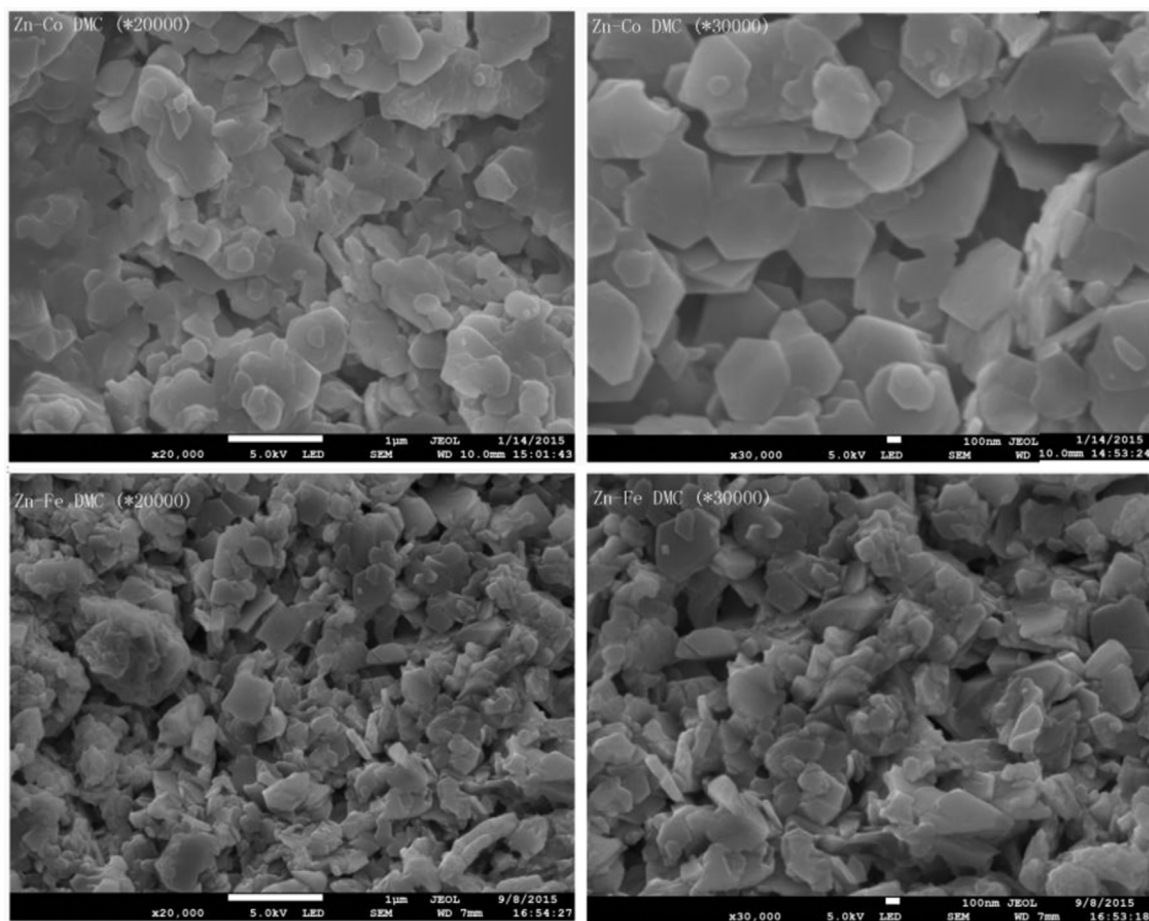


Fig. 1. SEM images of Zn-Co and Zn-Fe DMCs.

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