



Synthesis of high-molecular-weight aliphatic polycarbonates from diphenyl carbonate and aliphatic diols by solid base

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ABSTRACT

Various solid bases were synthesized and used as catalyst for direct transesterification of diphenyl carbonate (DPC) with aliphatic diols to synthesize high-molecular-weight aliphatic polycarbonates (APCs). Physical-chemical properties of these catalysts were characterized by means of different techniques to show the relationship between catalyst structure and catalytic performance. MgO prepared *via* simple coprecipitation method was found to be the most active catalyst among all the solid bases and magnesium compounds tested in the present study. The high-molecular-weight poly(1,4-butylene carbonate) (PBC) could be easily obtained over this MgO with M_w up to 182 200 g/mol under its optimization condition. Additionally, the amplification experiment in a 5.0 L stainless steel reactor also verified the reliability of this transesterification process with MgO as catalyst, giving maximum M_w value for PBC as high as 208 600 g/mol. It was found that medium and strong basic sites were responsible for this transesterification process. Simultaneously, strong basic sites also could favor the decomposition and depolymerization of the resultant PBC, leading to the decrease for M_w and yield at higher temperature. In addition, based on the experimental results and relevant literature, a plausible reaction mechanism involving the activation of diols *via* the abstraction of proton with basic site over MgO was proposed for this process.

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1. Introduction

Aliphatic polycarbonates (APCs) have been used for a variety of applications in the field of biological medicine owing to their outstanding biocompatibility and biological reactivity [1]. They can also be used as raw material for waterborne polyurethane industry because of their good hydrolysis and oxidation resistance properties [2]. More importantly, APCs with number-average molecular weight (M_w) greater than 70000 g/mol have also been thought to be promising alternatives to petrochemical monomers as biodegradable plastic [3,4]. Traditionally, these APCs can be synthesized *via* copolymerization of CO₂ with epoxides and ring-opening polymerization of cyclic carbonates. Unfortunately, these routes are still suffering from various drawbacks, such as poor structure for resultant polymer, low effective for current catalysts as well as high cost

for raw feedstocks, which all restrict the production and application of these APCs on a large scale [5,6].

The melt transesterification of dimethyl carbonate (DMC) with aliphatic diols *via* a two-step condensation polymerization route has been regarded as a clean and sustainable synthetic route for the production of APCs with diverse structures, since this route is a high efficiency solvent-free process [7–10]. Recently, a simpler one-pot method was also developed in our previous work by replacing DMC with high boiling-point diphenyl carbonate (DPC), in which the by-product, phenol, can be easily separated and reused [11]. No matter which process we selected, highly effective catalyst is a key factor for the preparation of APCs with satisfactory M_w value. Therefore, a wide range of compounds, including metal salts [8,11–13], BMIM-2-CO₂ [10], TiO₂/SiO₂(PVP) (TSP-44) [4,7], organic base [14] and even enzyme [15], have shown great promise for this reaction. Up to now, the most efficient catalysts proposed for this process have been confined to homogeneous basic catalysts [8,12]. However, the thorny issue associated with such strong bases is the presence of undesirable side reactions, and the residual of these catalysts also could decrease the thermal stability of polymer. Moreover, the structure-activity correlation of these basic catalysts for this process has not been well elucidated. In this con-

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text, it is highly desired to develop a new catalyst that can allow an excellent activity and well understand its action mechanism for this transesterification reaction.

Most recently, magnesium compounds have been widely used as catalysts for the synthesis of sustainable polymers from renewable resources [16]. Particularly, MgO as a typical solid base catalyst has been extensively used in many transesterification processes. Using a triblock copolymer as soft template, Lee et al. have prepared a series of MgO through a surfactant-assisted route, which showed excellent catalytic performance in the transesterification of DMC with glycerol for the synthesis of glycerol carbonate (GLC) [17]. Wherein, the catalytically active sites were attributed to the higher basic site concentration on their surface. A K-doped MgO catalyst was also reported by Lago et al. for biodiesel synthesis through transesterification of soybean oil with methanol [18]. Also, magnesium-based mixed oxides (e.g. Mg-Al mixed oxides) have been found to be able to catalyze this reaction, in which the concentration of basic sites, specific surface area and crystallite size of MgO were thought to responsible for their excellent activity [19]. Di Serio and co-workers found that MgO was also the best single catalyst for the transesterification of dimethyl terephthalate with ethylene glycol for the production of poly(ethylene terephthalate) (PET)[20]. And the obtained PET polymer has chemical and physical properties very close to that of commercial sample. Additionally, MgO-catalyzed transesterification reaction is often used as a valuable tool for polymer modification due to its nontoxic and low cost [21]. Moreover, MgO itself is also outstanding inorganic filler for many polymers. The addition of MgO not only can improve their mechanical properties but also can provide them with new application performance [22,23].

In the present work, we also found that MgO exhibited remarkably higher activity than other solid bases and magnesium compounds for direct transesterification of DPC with aliphatic diols to synthesize APCs. Combining a variety of characterization results, the relationship between catalyst structure and catalytic performance was investigated by comparing MgO with other solid bases. Additionally, a plausible reaction mechanism involved the promotion effect of basic sites was also proposed.

2. Experimental

2.1. Materials and preparation of catalyst

Commercial DPC was purified by recrystallization in absolute ethyl alcohol before use. All aliphatic diols were dehydrated by distillation over calcium hydride under dry nitrogen gas. Other reagents were all purchased from Chengdu Kelong Chemical Reagent Co., Ltd. (in China) and used as received without further treatment.

In this study, two kinds of MgO were synthesized: direct thermal decomposition of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (MgO-T) and coprecipitation of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with Na_2CO_3 (MgO-P). In direct calcination method, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was calcined at 500°C in air atmosphere for 4.0 h. In coprecipitation method, Na_2CO_3 (0.1 mol) in 50 g distilled water was dropwise added into the solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ until the pH reach 10.0 and stirred for 4.0 h at room temperature. The obtained white precipitate was filtered and washed with hot water until the pH value to 7.0, dried at 100°C overnight, and subsequently calcined at given temperature for 4.0 h. ZnO and ZrO_2 were also obtained by thermal decomposition of $\text{Zn}(\text{OH})_2$ and $\text{Zr}(\text{OH})_4$ at 500°C for 4.0 h according to the same procedure as MgO-P, while CaO was prepared by calcination of calcium carbonate at 900°C in N_2 for 4.0 h. The commercial source MgO (AR) labeled as MgO-C was also supplied by Chengdu Kelong Chemical Reagent Co., Ltd. To obtain MgO surface with dif-

ferent basic site amount, a series of $\text{Mg}(\text{Al})\text{O}$ samples with different content of Al were prepared by incipient impregnation route as described in literature [24]. Typically, a certain amount of aluminum isopropoxide was dissolved in 30 mL of benzene at 50°C . Then the solution was quickly added into $\text{Mg}(\text{OH})_2$, dried at 100°C overnight and thermally decomposed in N_2 at 500°C to get the impregnated catalyst.

2.2. Transesterification reaction

The reaction was conducted in a 150 mL round-bottomed flask, equipped with a mechanical stirrer, reflux condenser and thermometer. In a typical process, DPC (100 mmol, 21.41 g), BD (100 mmol, 9.01 g) and a catalyst were successively charged into the reactor under N_2 atmosphere. The reaction mixture was heated at 120°C and stirred continually for 30 min until it became homogeneous. Before starting the polymerization process, the reaction pressure was slowly reduced to 200 Pa. Then the temperature was further increased to a given value and maintained for a certain time to carry out the polymerization reaction. After reaction, the reaction mixture was cooled to room temperature and the residue was purified by dissolving in CH_2Cl_2 and precipitating with ethanol. The PBC polymer was isolated by centrifugation and dried under vacuum at 65°C for 4.0 h.

2.3. Characterization of obtained polymers and catalyst

M_w and PDI of polymers were determined by gel permeation chromatography (GPC). The GPC measurement was carried out at 30°C on a Waters 515 HPLC system equipped with a 2690D separation module and a 2410 refractive index det. Tetrahydrofuran (THF) was used as eluent at a flow rate of 0.5 mL/min. Polystyrene with a narrow molecular weight distribution was used as standard for calibration.

XRD analysis was carried out on a PANalytical X'pert Pro diffractometer system, using CoKa radiation (0.1789 nm). N_2 physisorption was measured on the gas adsorption instrument Nova Win2, then the surface area was obtained by BET equation. The basicity of the catalysts was evaluated by temperature-programmed desorption of carbon dioxide (CO_2 -TPD) using an AutoChem 2910 instrument (Micromeritics) and the detector was MSC-200 quadruple mass analyzer from Balzer Company, Ltd. The sample was treated at 500°C for 2.0 h under a flow of He atmosphere (flow rate of 30 mL/min). After being cooled down to room temperature, pure CO_2 was adsorbed at room temperature for 1.5 h. Then the physisorbed CO_2 was removed by a flushing with He at room temperature for 1.5 h. TPD was carried out in the stream of He (20 mL/min) at a heating rate of 10°C up to 500°C (all the samples were 100 mg).

3. Results and discussion

3.1. Screening of catalyst

The typical performances of different solid base catalysts in the transesterification of DPC with BD at given conditions are summarized in Table 1. One can see that ZrO_2 , MgO-T and CaO were all active to this reaction at the same condition, giving PBC with M_w of 21 300, 36 600 and 47 800 g/mol, respectively. However, the polymerization rate of ZnO was so low that the M_w of its PBC polymer could not be detected under the given condition. Additionally, the catalytic performance and preparation method appeared to be significantly related for MgO, and M_w of PBC over MgO-P (115 200 g/mol) is much higher than those of MgO-C and MgO-T. Moreover, one also can find that the catalytic activity of MgO-P in this process is also evidently comparable to those of other magnesium

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