Eu$^{3+}$ and lysine co-intercalated $\alpha$-zirconium phosphate and its catalytic activity for copolymerization of propylene oxide and CO$_2$

Wen-Zhuo Li, Cheng-Gang Qin, Chun-Sheng Lv, Lian-Sheng Li, and Jie-Sheng Chen*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130023, PR China

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A novel composite material, $\alpha$-Zr(HPO$_4$)$_2\cdot$1.5Lysine:0.06Eu$^{3+}$ (designated ZLE), has been prepared through intercalation of L-lysine (Lys) molecules and Eu$^{3+}$ ions into between the layers of $\alpha$-Zr(HPO$_4$)$_2$ ($\alpha$-ZrP). It is proposed that the ZLE material contains Eu complexes lying between adjacent layers of Lys molecules which are attached on the inner surface of $\alpha$-ZrP, and the Eu$^{3+}$ ions are coordinated by carboxyl groups of Lys molecules. The ZLE composite in combination with Al(1-Bu)$_3$ and glycerin has been used as a catalyst for the copolymerization of propylene oxide (PO) and CO$_2$, and the catalytic system exhibits performance superior to the previously reported Y(P$_{204}$)$_3$-Al(1-Bu)$_3$-glycerin system.

KEY WORDS: layered composite compound; zirconium phosphate; rare earth complex; propylene oxide; CO$_2$; copolymerization.

1. Introduction

Layered inorganic materials such as clays, dichalcogenides and metal phosphates have been extensively studied due to growing interest in their catalytic activity, ion-exchange capacity and physical-chemical stability [1]. The important feature of these materials is their ability to incorporate guest molecules which form highly ordered arrays between adjacent layers. On the basis of this feature, many novel assembly structures can be tailored at the molecular level through the design of the host and the guest species [2]. These assembly structures have been utilized widely in the preparation of functional materials such as catalysts [3], conducting polymers [4], energy storage devices [5], and receptors [6].

It is known that $\alpha$-zirconium phosphate with a layered structure is very similar to that of smectite clays [7]. Crystallographic studies [8] reveal that each layer of $\alpha$-ZrP consists of zirconium atoms lying nearly in a plane and bridged through tetrahedral PO$_3$-OH groups located alternately above and below the plane of zirconium atoms. The interlayer spacing of $\alpha$-ZrP is about 7.58 Å. Each phosphate group in $\alpha$-ZrP carries one ionizable hydroxyl group that can be readily deprotonated and the resulting ionic sites serve to bind cations. Studies on $\alpha$-ZrP have been mainly focused on synthesis, ion exchange, thermal stability, adsorption and catalysis [9], whereas intercalation into $\alpha$-ZrP was mainly concentrated on transition metal compounds and porphyrins [10]. There are very few reports on rare earth (RE) metal complexes intercalated into layered $\alpha$-ZrP [11].

Some RE elements and their ions have been widely used in the preparation of materials with useful optical, magnetic properties and catalytic activities [12]. Recent progress has shown that the molecular environment influences the photophysical and photochemical process of the RE ion to a great extent [13]. For many RE complexes, light is absorbed by the ligands as an antenna and energy is transferred to the emitting metal ion. Especially if these complexes are modified by interaction with a host compound, their chemical and photophysical properties will have unexpected changes [12].

Carbon dioxide (CO$_2$) is an ideal synthetic feedstock since it is abundant, inexpensive, nontoxic, and nonflammable. It is estimated that nature uses CO$_2$ to make over 200 billion tons of glucose by photosynthesis each year, but human beings have had little success in exploiting this attractive raw material [14–16]. Recent research suggests that copolymerization of carbon dioxide with epoxides to produce polycarbonates may become a very useful and practical route to take advantage of CO$_2$ effectively [17,18]. The search of new, efficient catalysts for this polymerization process is a significant scientific goal because of the low cost, accessibility of the monomers, and the attractive properties of polycarbonates [19–22]. But due to the inert characteristic of CO$_2$, it is difficult to develop a highly effective catalyst for this type of polymerization to proceed. As yet catalytic systems concerning this reaction include: (a) zinc-based catalysts, such as Zn(C$_2$H$_5$)$_2$–H$_2$O, Zn(C$_2$H$_5$)$_2$–di- or tri-hydric phenol, and multiprotonic compounds [19,23–25]; (b) (ttp)AlCl$_3$ (H$_2$ttp = tetraphenylporphyrin) and its derivatives [26–28]; (c) zinc salts [29]. However, the catalytic activity of most known systems is still not high enough so that copolymerization is yield-low and long reaction time is needed. Many attempts to improve the catalytic activity have been made. For example, for the zinc-based catalysts, the use of diethyl zinc/polyhydric phenol...
[30], zinc glutarate and its derivatives [31,32], and cadmium(II) carboxylates [33] as the catalysts were found to enhance the reactivity of CO2 with propylene oxide (PO) to some extent. At present, zinc glutarate is regarded as the most promising catalyst used in the industrial production of the polycarbonate. In recent publications, RE metal coordination catalysts exhibiting reasonable activity in the copolymerization of PO and CO2 have also been reported [20,34–37]. The typical catalytic system among these is RE(P2O4)3–Al(i-Bu)3–glycerin [20] (RE= La, Nd, Eu, Gd, Dy, Ho, Er, Yb, Lu, Sc, and Y) with the Y(P2O4)3–Al(i-Bu)3–glycerin system showing the highest catalytic activity, where P2O4 stands for CH3(CH2)3CH(C2H5)CH2O)2P(O)O–. The RE metal is the catalytic center for these systems. In this paper, we describe a novel composite that has been obtained by addition of water, washed with distilled water until the filtrate contained no C for 24 h and 0.05 g EuCl3 Æ 6H2O. The mixture was ground in a mechanical grinding of a mixture of 1 g ZL solid powder and 0.05 g EuCl3 Æ 6H2O. The mixture was ground in a 1,4-dioxane solution under the protection of N2. Copolymerization of carbon dioxide with PO was conducted at 60 °C and at a pressure of CO2 ranging from 3 to 4 MPa. After proceeding for 12 h, the CO2 in the autoclave was driven out until the pressure of CO2 in the autoclave decreased to 1 atm. The autoclave was opened and a methanol solution containing 5% hydrochloric acid was added into the autoclave to terminate the reaction. A white solid product was obtained by addition of water, washed with distiller water, and then dried in vacuum at room temperature. The relevant molar ratios and concentrations for the reaction are as follows: [Eu]= 1.0 × 10−2 mol/L; Al/Eu = 8.0; glycerin/Al = 0.5; [PO] = 2.5 mol/L, 1,4-dioxane was used as the solvent. The weight of the copolymer was that of the white solid product minus the weight of the catalyst. For comparison, the catalytic performance of EuCl3 · 6H2O was also tested under similar conditions.

2.4. Characterization

The powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with CuKα (λ = 1.5418 Å) radiation. The X-ray photoelectron spectroscopy (XPS) of the powders was performed on a VG Escalab MK II spectrometer with MgKα radiation. The UV–vis absorption spectra were measured using a Perkin-Elmer Lambda 20 spectrometer, whereas the infrared (IR) spectra were recorded on a Nicolet Impact-410 FTIR spectrophotometer using KBr pellets. Thermogravimetric and differential thermal analyses (TG-DTA) of the samples were conducted on a Netsch STA-449C thermal analyzer. The photoluminescent spectra were obtained on a Spex Fluorolog-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source (the slits of the excitation state and the emission state were 5.0 and 1.5 nm, respectively). All the samples were measured under the same conditions. The luminescence lifetime measurements were performed on a Spex 1934D phosphorimeter. The distance between the sample and the center of the lamp was 14 cm. The contents of metal ions in the compounds were analyzed on a Perkin-Elmer Optima 3300 DV inductively coupled plasma (ICP) spectrometer, whereas the C, H and N elemental analysis was performed on a Perkin-Elmer Lambda 20 spectrometer, whereas the UV–vis absorption spectra were measured using a Perkin-Elmer Lambda 20 spectrometer. The contents of metal ions in the compounds were analyzed on a Perkin-Elmer Optima 3300 DV inductively coupled plasma (ICP) spectrometer, whereas the C, H and N elemental analysis was performed on a Perkin-Elmer Lambda 20 spectrometer. The contents of metal ions in the compounds were analyzed on a Perkin-Elmer Optima 3300 DV inductively coupled plasma (ICP) spectrometer, whereas the C, H and N elemental analysis was performed on a Perkin-Elmer Lambda 20 spectrometer.

2.2. Preparation of x-ZrP-Lys-Eu (ZLE) composite

The preparation procedure for the precursor materials, Zr(HPO4)2 and Zr(HPO4)2 · 1.85 Lys (ZL), was the same as that referred to in the literature [39,40]. While the x-ZrP-Lys-Eu (ZLE) composite was prepared through mechanical grinding of a mixture of 1 g ZL solid powder and 0.05 g EuCl3 · 6H2O. The mixture was ground in a mortar for about 3 h. The final mixture obtained was washed with distilled water until the filtrate contained no Eu3+ ions and then dried at room temperature.

2.3. Copolymerization

The ZLE sample was dried in vacuum at 60 °C for 24 h before copolymerization. It was then mixed with Al(i-Bu)3 for 10 h in a 1,4-dioxane solution under the protection of N2 and finally a white slurry was obtained. The slurry, PO and glycerin were mixed in an 80 ml stainless steel autoclave, again under the protection of N2. CO2 gas was loaded from a gas cylinder into the autoclave followed by venting from the autoclave. This process was repeated for three times in order to get rid of the previously loaded N2. Copolymerization of carbon dioxide with PO was conducted at 60 °C and at a pressure of CO2 ranging from 3 to 4 MPa. After proceeding for 12 h, the CO2 in the autoclave was driven out until the pressure of CO2 in the autoclave decreased to 1 atm. The autoclave was opened and a methanol solution containing 5% hydrochloric acid was added into the autoclave to terminate the reaction. A white solid product was obtained by addition of water, washed with distiller water, and then dried in vacuum at room temperature. The relevant molar ratios and concentrations for the reaction are as follows: [Eu] = 1.0 × 10−2 mol/L; Al/Eu = 8.0; glycerin/Al = 0.5; [PO] = 2.5 mol/L, 1,4-dioxane was used as the solvent. The weight of the copolymer was that of the white solid product minus the weight of the catalyst. For comparison, the catalytic performance of EuCl3 · 6H2O was also tested under similar conditions.