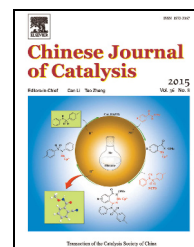


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Article

Preparation of crown ether complexing highly active double metal cyanide catalysts and copolymerization of CO₂ and propylene oxide

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ABSTRACT

Double metal cyanide (DMC) catalysts are generally prepared by coprecipitation of potassium hexacyanocobaltate(III) with zinc chloride followed by complexation with *tert*-butanol, and these materials have been used for several decades in the copolymerization of CO₂ and epoxides. However, the catalytic efficiency of DMC catalysts can be adversely affected by the presence of excess K⁺, and the preparation of these catalysts can therefore become complicated and time-consuming because of the multiple washing and centrifugation stages required for the removal of the excess K⁺. In this study, 18-crown-6 ether was used as an effective co-complexing agent for the removal of K⁺. A series of DMCs containing 18-crown-6 were prepared with different quantities of the crown ether and different washing times. The resulting crown ether-complexing catalysts (CDMCs) and DMC catalysts without crown ether were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric analysis-IR and X-ray diffraction. These characterization results showed that the inclusion of 18-crown-6 allowed for the formation of uniform and highly dispersed CDMC catalysts. In contrast, the DMC catalysts prepared in the absence of 18-crown-6 became uneven and delaminated during the purification by centrifugation, with high- and low-density portions of the material forming on the bottom and top of the catalyst cakes, respectively. The inclusion of 18-crown-6 not only trapped K⁺ but also participated in the complexation process. The complexation of *tert*-BuOH and 18-crown-6 led to a less crystalline form of the CDMC catalyst. Elemental analysis revealed that CDMC1 contained 1.2% K⁺. The copolymer was obtained by the copolymerization of CO₂ with propylene oxide using CDMC3 catalyst, which was superior to the copolymer prepared using DMC1. CDMC3 was as active as DMC2 prepared without the crown ether but with seven washing steps. A hypothetical two-stage catalytic mechanism was proposed.

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1. Introduction

CO₂, which is widely known as one of the main greenhouse gases, could potentially be used as building block for the con-

struction of useful aliphatic polycarbonates. Aliphatic polycarbonates are becoming increasingly important because of their extensive range of applications in the production of polyurethanes, coating materials, biodegradable surfactants and bio-

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medical materials [1,2]. Aliphatic polycarbonates are mainly prepared by transesterification [3] and CO₂ coupling [4] reactions. A wide variety of catalytic systems have been developed during the last three decades for the efficient copolymerization of CO₂ with epoxides, including ZnEt₂-protic compounds [5,6], zinc glutarate or adipate [7–9], rare-earth catalysts [10–12], metal-porphyrins [13–15], zinc bis(β-diiminates) [16–18], salen-metal systems, metal microporous polymers [19–25] and double metal cyanide (DMC) catalysts [26–37]. DMC catalysts in particular have promising industrial prospects because of their high activity, cost-effectiveness and insensitivity to moisture.

DMC catalysts were initially used in the production of polyether and later utilized in the copolymerization of propylene oxide with CO₂ [24–30]. DMC catalysts are typically prepared via a precipitation process with a heavy organic complexing agent such as *tert*-butyl alcohol (*t*-BuOH), followed by multiple washing and centrifugation stages to allow for the removal of the excess potassium ions [26–29], which can have an adverse impact on the copolymerization of CO₂ and propylene oxide [29]. A new process was recently developed to avoid the production of K⁺ where H₃Co(CN)₆ was prepared according to an ion exchange method using K₃Co(CN)₆, followed by precipitation with ZnCl₂ in methanol to give [ZnCl]₂[HCo(CN)₆]²⁻ without any K⁺ [29]. This material was subsequently used in the copolymerization of CO₂ with propylene oxide to give a copolymer product with a high molar fraction of CO₂ (about 60%). Sebastian et al. [30] prepared a series of Zn–Co DMC catalysts with K⁺ contents in the range of 0.41%–2.0% without the inclusion of an additional washing step. However, the highest catalytic efficiency achieved with these Zn–Co DMC catalysts for the copolymerization of CO₂ and cyclohexene oxide was only 52.8 g polymer/g catalyst. In light of the problems posed by the presence of K⁺ in these catalysts, significant research efforts have been directed towards the development of new techniques for the removal of free potassium ions from heterogeneous DMC catalysts. However, the traditional methods for the preparation of DMC catalysts require multiple washing and centrifugation (up to seven times), making these processes time consuming, inefficient and poorly reproducible [26–28,31,32].

It is noteworthy that 18-crown-6 ether has an appropriate hole size (0.26–0.32 nm) for the binding of K⁺ (0.266 nm). Herein, we describe the results of our study towards the preparation of DMC catalysts in the presence of 18-crown-6 with the aim of simplifying the washing and centrifugation steps. The resulting crown ether complexing Zn–Co DMC catalysts were subsequently evaluated as catalysts for the copolymerization of CO₂ with propylene oxide.

2. Experimental

2.1. Materials

Potassium hexacyanocobaltate(III), 18-crown-6, zinc chloride and *tert*-butyl alcohol were purchased as the analytical grade from Aladdin Reagent (Shanghai, China) and used without further purification. Propylene oxide was refluxed over

calcium hydride and then stored over 3Å molecular sieves prior to being used in the copolymerization reactions. CO₂ (>99.9%) was purchased from Kedi Air Chemical (Foshan, China) and used without further purification.

2.2. Preparation of the catalysts

The methods used for the preparation of the catalysts are summarized in Table 1. CDMC1 was prepared according to Ref. [28,32] with minor modifications. Briefly, a solution of K₃[Co(CN)₆] (1.66 g, 5 mmol) in distilled H₂O (25 mL) was added in a dropwise manner to a vigorously stirred suspension of ZnCl₂ (2.5 g, 18.4 mmol) in a mixture of distilled H₂O (75 mL) and *t*-BuOH (40 mL) at 45 °C over 30 min, and the resulting mixture was stirred for 2 h. 18-Crown-6 (8 g, 30.3 mmol) was then added to the reaction in a single portion, and the resulting mixture was stirred for 3 h to allow for the complete complexation of the K⁺ ions. The resulting white precipitate was isolated by centrifugation (25 °C, 15 min), suspended in *t*-BuOH (140 ml) and stirred for 2 h at 45 °C. The mixture was then purified by centrifugation (25 °C, 15 min) to give the catalyst, which was dried under vacuum at 50 °C to constant weight, resulting in a cake. The top and bottom portions of the CDMC1 cake were labeled as CDMC1-T and CDMC1-B, respectively. All of the other catalysts prepared were defined in a similar manner. Elemental analysis of CDMC1 revealed 21.6% Zn, 8.1% Co and 1.2% K.

CDMC2 and CDMC3 were prepared according to a procedure similar to CDMC1 but with different crown ethers and washing times with a 1:1 (*v/v*) mixture of *t*-BuOH and water.

DMC1 and DMC2 were synthesized according to a similar procedure to that used for CDMC 1 but without addition of the crown ether [28,32]. In the case of DMC2, the remaining K⁺ ions were removed by washing the precipitate seven times with a mixture of distilled H₂O and *t*-BuOH whilst decreasing the quantity of H₂O and increasing the amount of *t*-BuOH. Elemental analyses revealed the following results: DMC1 (Zn 25.14%, Co 8.53%, K 1.43%); DMC2 (Zn 30.85%, Co 9.81%, no K⁺ ions were detected). DMC0 consisted of pure Zn₃[Co(CN)₆]₂, which was prepared in the absence of a complexing agent.

2.3. Catalyst characterization

Fourier transform infrared spectra (FTIR) were measured on an Analect RFX-65A FTIR spectrophotometer (Analect, USA). The surface morphologies of the DMC catalysts were

Table 1

Conditions used for the preparation of the different DMC catalysts^a.

Catalyst	Times of washing	Crown ether:K ⁺ molar ratio
CDMC1	1	2
CDMC2	1	1
CDMC3	2	2
DMC0	1	0
DMC1	1	0
DMC2	7	0

^a K₃[Co(CN)₆] (1.66 g) was used at 45 °C. ZnCl₂ (2.5 g) was used in CDMC1, CDMC2, CDMC3, DMC1 and DMC2 catalysts. A smaller amount of ZnCl₂ (1.02 g) was used in DMC0.

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