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Solventless synthesis of cyclic carbonates from carbon dioxide and epoxides catalyzed by silica-supported ionic liquids under supercritical conditions

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Abstract

A silica-supported ionic liquid proved to be an efficient heterogeneous catalyst for solventless synthesis of cyclic carbonates from epoxides and carbon dioxide under supercritical conditions, which requires no additional organic solvents either for the reaction or for the separation of product. The effects of reaction time, temperature and other reaction parameters on the reaction are investigated. High yields with excellent selectivity were obtained. The purity of product separated directly by filtration from the reaction mixture, reached 99% without further purification process. Moreover, the catalyst can be easily recovered by filtration and reused over four times with slight loss of its catalytic activity. The process represents a simple, ecologically safer, cost-effective route to cyclic carbonates with high product quality, as well as easy product recovery and catalyst recycling.

Keywords: Cycloaddition reaction; Solventless synthesis; Cyclic carbonate; Supercritical CO_2; Supported ionic liquid catalyst; Epoxide

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1. Introduction

Development of green processes based on chemical fixation of carbon dioxide has attracted much attention in industrial chemistry from the standpoint of the protection of environment and resource utilization because there are many possibilities for CO_2 to be used as a safe and cheap C1 building block in organic synthesis producing useful organic compounds [1–3]. One of the most promising methodologies in this area is the direct synthesis of five-membered cyclic carbonates via the cycloaddition reaction of CO_2 with epoxides [4] (Scheme 1). These carbonates, e.g. ethylene carbonate and propylene carbonate (PC), can be widely used for various purposes, such as electrolytic elements of lithium secondary batteries, polar aprotic solvents, intermediates for organic and polymeric synthesis, and ingredients for pharmaceutical/fine chemicals in biomedical applications [5]. On the other hand, supercritical carbon dioxide ($scCO_2$) is an attractive substitute solvent, because it combines environmentally benign characters with favorable physico-chemical properties for chemical synthesis [6–12]. Accordingly, CO_2 could be a particularly advantageous reaction medium when CO_2 serves as both a reactant and a solvent. In fact, the cycloaddition reaction of CO_2 to epoxides is very suitable for proceeding under supercritical conditions, because $scCO_2$ possesses high solvating power towards various epoxides [13–16].

Ionic liquids have received a lot of interest during the last few years because they possess some of the most important features, such as the negligible vapor pressure, unique solvation properties, good ion conductivity as well as catalytic activity and selectivity. It has been reported that various kinds of catalytic reactions have smoothly performed in ionic liquids and the ionic liquid itself can be the catalytically active species as well [17–21]. It worth mentioning

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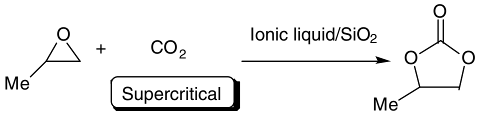

Scheme 1. Synthesis of propylene carbonate from propylene oxide and supercritical CO_2.

that CO_2 can significantly dissolve into the ionic liquid phase, which makes the reactions of CO_2 in it possible and suitable. As a matter of fact, ionic liquids have been reported to be one of most efficient catalysts for CO_2 fixation to produce cyclic carbonate from epoxides [22–27]. Particularly, Kawanami et al. found that 1-alkyl-3-methylimidazolium salts exhibited high rate and effectiveness for the synthesis of cyclic carbonate under supercritical CO_2 and BF_4^- was the most effective among the counter anions $(NO_3^-, CF_3SO_3^-, BF_4^-$ and $PF_6^-)$ of imidazolium salts [23]. In this context, the preparation process using the ionic liquids could become greener and simpler because of easy product separation and catalyst recycling and unnecessary use of volatile and harmful organic solvents. Furthermore, supported ionic liquids with catalytic amounts of ionic liquids attached to easily recyclable solid materials suitable for fixed bed operations, possess promising alternative in heterogenized catalysis [28–35].

Proper use of supercritical carbon dioxide in heterogeneous catalysis may afford enhancement of the reaction rate, control of selectivity, increasing catalyst lifetime, and facilitating separation. Although numerous heterogeneous catalysts have been found to be effective for the chemical fixation of CO_2 [36–44], development of more efficient and environmentally benign catalytic processes for cyclic carbonate synthesis under mild conditions still remains a promising issue.

In the framework of our continuous effort on developing heterogeneous catalysis for the synthesis of cyclic carbonate, we selected one kind of the efficient ionic liquids as shown in Fig. 1, reported by Kawanami et al. [23], and supported it on to amorphous silica for the synthesis of cyclic carbonates from epoxides and carbon dioxide under supercritical conditions. The silica-supported ionic liquid catalysts, denoted by $[C_4\text{-mim}]^+X^-/SiO_2$, were found to exhibit high activity for the solventless synthesis of cyclic carbonates, and high yields with excellent selectivity were obtained at temperature of 160 °C under 8 MPa. In addition, the catalyst can be easily recovered and reused for four times with slight loss of its catalytic activity.

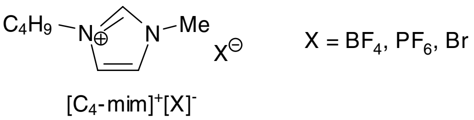

Fig. 1. Formula of 1-butyl-3-methylimidazolium ionic liquids used in this study.

2. Experimental

2.1. Reagents

Silica gel (Surface area: 300–550 m^2/g; Pore volume: 0.70–0.90 ml/g; Granularity: 400 mesh) as a support used in this study was commercially obtained from Qingdao Haiyang Chemical reagents Co., Ltd. The 1-butyl-3-methyl-imidazolium room temperature ionic liquids ($[C_4\text{-mim}]^+X^-$, Fig. 1) were synthesized according to the published methods [45]. Other reagents were of analytic grade and were used without further purification.

2.2. Preparation of the silica-supported ionic liquid catalyst

Silica-supported catalysts were prepared as described previously [32]. A typical example is as follows: to a stirred solution of $[C_4\text{-mim}]^+[BF_4]^-$ (5.0 g, 22 mmol) in acetone, silica powder (20 g, pretreatment at 150 °C in vacuum for 3 h) was added. After being fully stirred, the volatile components of the mixture were removed on a rotary evaporator. Then the resulting material was evacuated in air at 150 °C in vacuo for 3 h, leading to a white powder. Hereafter, the resulting catalyst is denoted by $[C_4\text{-mim}]^+[BF_4]^-/SiO_2$ (The ionic liquid loading: 20 wt%). The specific surface area was determined by means of the BET method using N_2 adsorption at 77 K with a Quantachrome NOVA 2000e instrument. Prior to measurement, the sample was heated in vacuum at 100 °C for 3 h. The BET surface area of the typical supported catalyst (n-Bu_4NBr/SiO_2) was 239 m^2/g. The FT-IR spectra were recorded on a Bruker Eqinox 55 FT-IR spectrophotometer. The FT-IR spectra comparison of the typical supported catalyst $[C_4\text{-mim}]^+[BF_4]^-/SiO_2$ with the support SiO_2 and the active species $[C_4\text{-mim}]^+[BF_4]^-$ undoubtedly indicated the active catalyst was successfully immobilized in the support of silica.

2.3. A representative procedure for the synthesis of cyclic carbonate from CO_2 and epoxide catalyzed by the silica-supported ionic liquid

The cycloaddition reaction of CO_2 to propylene oxide was carried out with a stainless steel autoclave (25 cm^{-3} inner volume).[1] A typical procedure is as follows: prior to the reaction, the catalyst was evacuated at 150 °C for 3 h. In an autoclave, CO_2 (liquid, 4.0 MPa) was added to a mixture of propylene oxide (57.2 mmol), a catalyst ($[C_4\text{-mim}]^+[BF_4]^-/SiO_2$, 1.8 mmol%), and biphenyl (80 mg, an internal standard for GC analysis) at room temperature. The initial pressure was adjusted to 8 MPa at 160 °C and the autoclave was heated at that temperature for 4 h. At the end of the reaction, the autoclave was cooled to ambient temperature and then was further cooled to 0 °C in an

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[1] *Caution.* Experiments using compressed gases such as supercritical fluids are potentially hazardous and must only be carried out using appropriate equipment and safety precautions.