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Carboxymethyl cellulose supported ionic liquid as a heterogeneous catalyst for the cycloaddition of CO_2 to cyclic carbonate

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ABSTRACT

The non-toxic biologic material carboxymethyl cellulose (CMC) supported imidazolium-based ionic liquids (ILs), coupling with a series of Lewis acids has been prepared and used as heterogeneous catalysts for the cycloaddition of CO_2 to cyclic carbonate. The as-synthesized catalysts have been characterized by FT-IR, XRD, TGA, SEM etc. Especially, the protonated CMC (HCMC) supporting both the hydroxyl group functionalized IL (1-hydroxypropyl-3-*n*-butylimidazolium chloride, HBimCl) and $NbCl_5$ (HBimCl-$NbCl_5$/HCMC) exhibited the best catalytic performance. It was indicated that HBimCl on HBimCl-$NbCl_5$/HCMC catalyst was highly leaching-resistant even if it was immobilized through non-covalent interaction. The IL and Lewis acid exhibited strong synergistic effects for the cycloaddition reaction. Additionally, the HBimCl-$NbCl_5$/HCMC catalyst exhibited a high activity and excellent selectivity for a wide scope of substrates under optimum conditions and also it was further extended to application in the continuous fixed-bed flow reactor and showed an excellent catalytic stability. No loss of catalytic activity was observed even after 120 h on stream.

1. Introduction

Carbon dioxide (CO_2) is an easily available renewable carbon resource, which has the advantages of being abundant, cheap, non-toxic, and nonflammable in organic synthesis [1–3]. Incorporation of CO_2 into carbonates is a significant transformation because of its potential implications for climate change reduction and the associated economic benefits [4]. Particularly, the five-membered cyclic carbonates are one of the most attractive synthetic protocols utilizing CO_2 as shown in Scheme 1 [5,6]. These products are widely used as monomers, aprotic polar solvents, and as intermediates in the manufacture of fine chemicals [7,8].

Catalysts have been developed to activate CO_2 for cycloaddition in the past decades owing to its inertness [9,10]. A number of homogeneous catalysts have been reported for the synthesis of cyclic carbonates recently, such as alkali metal or transition metal-based binary systems [11–13], salen complex [14,15] and ILs [16–19] etc. Among these homogeneous catalysts, ILs have attracted great attention especially because it owns outstanding properties, like negligible vapor pressure, good chemical and thermal stability and tunable structure [20]. However, homogeneous catalysts have the defects that can not be ignored. For example, it is very hard to separate homogeneous catalyst from products, resulting in the difficulty for further product purification.

Heterogeneous catalysts can avoid these problems to some extent. Naturally, a series of inorganic or organic support immobilizing IL catalysts have been developed. These supports include mesoporous silica [21–23], polymers [24,25], graphene oxide [26], carbon nanotubes [27], etc. It is worth noting that the presence of hydroxyl groups on solid materials could effectively promote the cycloaddition reaction of epoxides with CO_2. Although the great advances of these heterogeneous catalysts have been made, it is definitely essential to develop more effectively heterogeneous catalysts with excellent activity and catalytic stability for the fixation CO_2 under mild conditions. Cellulose and related biopolymers are becoming more and more attractive recently for their excellent properties such as non-toxicity, biocompatibility, biodegradability, non-toxicity, natural abundance and have been employed as supporting materials for CO_2 cycloaddition [28–30]. For examples,

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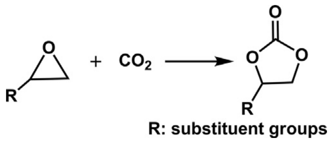

Scheme 1. The synthesis of cyclic carbonate from CO_2 and epoxides.

Roshan et al. [28] immobilized imidazolium-based ionic liquids on carboxymethyl cellulose via a co-dispersing method and examined the catalytic activity in the cycloaddition of carbon dioxide with oxides, demonstrating the synergistic role among the carboxyl moieties, the hydroxyl groups and the anions of the ionic liquid counterparts. However, the deactivation of catalyst has been observed after recycled 4 times. Sun et al. [29] have prepared chitosan (CS) covalently-grafted 1-ethyl-3-methyl imidazolium halide catalysts, which exhibited good activity and selectivity for the reaction with relatively high IL loading. In addition, Tharun et al. [30] have employed quaternized chitosan (QCHT) as a heterogeneous catalyst for the CO_2 cycloaddition. The catalyst displayed only moderate activity and gradual deactivation in catalytic recycles. All these catalysts above have been operated under the batch-wise condition.

On the other hand, although the promising results have been achieved in the batch-wise process, the continuous fixed-bed mode is more preferable from the point of view of the industrial application. In this aspect, Sakakura's group demonstrated that phosphonium halides covalently bound to SiO_2 exhibited excellent catalytic activities for CO_2 cyclicaddition and was proved to be reacted for 1000 h under fixed bed operation condition [31]. However, the synthetic procedures of the catalysts were complicated and the reaction condition was harsh. Hence, it is highly promising to exploit a highly efficient and easily available catalyst which is applicable for a fixed-bed flow reactor under mild conditions.

As we have discussion above, the sodium salt of carboxymethyl cellulose (CMC) is a widely applied material in industry because of its excellent green properties [32]. The protonated CMC (HCMC) is a derivative of the cellulose family with the carboxymethyl group ($-CH_2COOH$) bound, which equipped with abundance hydroxyl groups. In this work, we attempted to immobilize imidazolium-based ILs and Lewis acids on HCMC via a noncovalent linkage to prepare various heterogeneous catalysts. It was found that the combination of the hydroxyl group functionalized imidazolium IL and $NbCl_5$ showed excellent activity and reusability in the cycloaddition of CO_2 with propylene oxide under mild and solvent free conditions. In addition, the present catalyst can be employed in a continuous fixed-bed flow reactor, where the catalyst showed promising catalytic performance for 120 h on stream.

2. Experimental

2.1. Chemical reagents

Sodium salt of carboxymethyl cellulose (NaCMC, 800–1200 mPa s) was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai. Metal chlorides such as $NbCl_5$, $ZnCl_2$, $InCl_3$, $FeCl_3$ and $CaCl_2$ were all purchased from Sinopharm Chemical Reagent Co., Ltd., and used without further purification. CO_2 was supplied by Shanghai Shangnong Gas Factory with a purity of >99.95%. Epoxides were analytical grade and were used directly without further purification. All solvents (analytical grade) were dried by using the standard methods.

2.2. Preparation of catalyst

2.2.1. Preparation of 1- hydroxypropyl-3-n-butylimidazolium chloride (HBimCl)

1-Buthylimidazole (1.69 g, 13.6 mmol) and 3-chloro-1-propanol (1.29 g, 13.6 mmol) were mixed and stirred at 100 °C for 20 h in 50 ml stainless autoclave equipped with a magnetic stirrer under N_2 atmosphere. The resulting mixture was washed 3–4 times with ethyl acetate to remove unreacted impurities. Then product was transferred to 50 ml glass bottle and dried at 70 °C under vacuum for 2 h to obtain slightly yellow and viscous liquid as HBimCl. The ^1H NMR spectra was shown in Fig. 1S. ^1H NMR (400 MHZ, $CDCl_3$):δ0.84 (t, 3H), 1.26 (m, 2H), 1.79 (M, 2H), 2.00 (m, 2H), 3.48 (m, 2H), 4.21 (t, 2H), 4.43 (t, 2H), 4.76 (s, 1H), 7.44 (t, 1H), 7.76 (t, 1H), 10.11 (s, 1H).

2.2.2. Preparation of 1, 3-dibutyl imidazolium chloride (DBimCl)

1-Buthylimidazole (1.69 g, 13.6 mmol) and 1-chlorobutane (1.30 g, 13.6 mmol) were mixed and stirred at 100 °C for 20 h in 50 ml stainless autoclave equipped with a magnetic stirrer under N_2 atmosphere. The resulting mixture was washed 3–4 times with ethyl acetate to remove unreacted impurities. The product was transferred to 50 ml glass bottle, following by drying at 70 °C under the vacuum for 2 h to obtain yellow and viscous liquid product. The ^1H NMR spectra was shown in Fig. 2S. ^1H NMR (400 MHZ), $CDCl_3$:δ0.94 (t, 6H), 1.39 (m, 4H), 1.89 (m, 4H), 4.35 (t, 4H), 7.46 (d, 2H), 10.82 (s, 1H).

2.2.3. Preparation of HCMC

The HCMC was prepared according to previously reported procedures [29]. NaCMC (2 g) was added to 80% ethanol aqueous solution (200 ml), and then HCl (20 ml, 37%) was added and stirred for 45 min. The solid was filtered and then washed with 70% ethanol aqueous solution till the washing solution was neutral and no Cl^- was detected with silver nitrate test. The solid was then dried 2 h under the vacuum to obtain the white powder of HCMC.

2.2.4. Synthesis of HBimCl-M/HCMC catalysts

The IL HBimCl and metal chlorides (Lewis acid) were immobilized on HCMC by co-dispersing the IL (0.068 g, 0.31 mmol) and metal halides (0.155 mmol) in DMF (5 ml) at 100 °C for 5 h under nitrogen atmosphere, and then added the HCMC (0.50 g) and stirred overnight. After the mixture was cooled to room temperature under nitrogen atmosphere, the solvent in the resulting mixture was evaporated under vacuum and washed with anhydrous ethyl ether, followed by drying under vacuum at 40 °C for 2 h to obtain the catalyst HBimCl-M/HCMC, where M represented the different metal halides. For the sake of comparison, $NbCl_5$/HCMC, HBimCl/HCMC, DBimCl/HCMC and DBimCl-$NbCl_5$/HCMC catalysts have also been prepared in a similar method, where the loading amounts of ILs and metal chlorides on CMC were 0.50 mmol g^{-1} and 0.25 mmol g^{-1} respectively, unless otherwise described.

2.3. Characterization

All NMR spectra were recorded on a Bruker AVANCE 400 MHz instrument (400 MHz ^1H NMR) using $CDCl_3$ as solvents. FT-IR spectrum was performed from pressed KBr tablets at room temperature on a Nicolet Fourier transform infrared spectrometer (Magna 550) by pressed KBr tablets at room temperature. The XRD patterns were recorded from D/MAX 2550 VB/PC using CuKα radiation (λ = 1.5406 Å) operated at 40 kV and 200 mA. Surface areas (BET) of the catalysts were measured by N_2 adsorption at 77 K using NOVA 4200 e Analyser after the evacuation of the sample at 100 °C for 12 h. The thermal stability of catalysts was