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Ionic liquids grafted on carbon nanotubes as highly efficient heterogeneous catalysts for the synthesis of cyclic carbonates

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ABSTRACT

A variety of multi-walled carbon nanotubes grafted with immidazolium-based ionic liquids (CNT-ILs) were synthesized and utilized as highly efficient heterogeneous catalysts for the production of cyclic carbonates via cylcoaddition reactions of epoxides and CO_2. In comparison with conventional heterogeneous catalysts that employ porous silica and polymer supports, CNT-ILs exhibited significantly enhanced catalytic reactivity towards the cycloaddition reactions. The effects of the IL molecular structure (alkyl chain length and counter anions) and the reaction parameters (temperature, CO_2 pressure, and time) on the catalytic performance of the corresponding heterogeneous catalysts were also systematically investigated.

1. Introduction

Room temperature ionic liquids (ILs) are organic salts with melting points below 100 °C [1–4]. Taking advantage of their unusual properties such as negligible vapour pressure, good thermal stability, wide liquid temperature range, designable properties, and wide electrochemical windows, ILs have been used for a variety of purposes, including catalytic reactions [5,6], CO_2 and SO_2 capture [7], synthesis of metal oxides, and chemical functionalization of various materials [8,9].

CO_2 is an easily available renewable carbon resource with the advantages of being nontoxic, abundant, and economical. One of the most effective applications using CO_2 as a raw material is its coupling with epoxides to afford five-membered cyclic carbonates. These products are important industrial materials as polar aprotic solvents in organic and polymeric syntheses, as ingredients in pharmaceuticals, or as fine chemicals in biomedical synthesis [10–12]. Considering the desire for chemical technology that has minimal environmental impact, a variety of highly efficient green IL catalysts such as imidazolium, pyridinium or ammonium salts have been widely developed to catalyze cycloaddition reactions between CO_2 and epoxides [13–15]. Unfortunately, these homogeneous catalysts tend to cause difficulties in catalyst recovery and product purification. To successfully address these issues, the development of IL-based heterogeneous catalysts is considered as the most effective alternative solution.

IL-based heterogeneous catalysts are generally prepared by grafting ILs onto various solid supports. They not only retain the important physical and chemical features of ILs, such as nonvolatility, nonflammability, and good thermal stability, but also possess a number of advantages in terms of catalyst recovery, regeneration, and reuse. Thus far, a variety of IL-based heterogeneous catalysts, including silica or polymer-immobilized quaternary ammonium salts, alkali halides, imidazolium alkyl halides, and amino acid, have been extensively developed for the synthesis of cyclic carbonates via cycloaddition reactions [16–20]. Although these conventional heterogeneous catalysts demonstrate excellent catalytic performance, the challenge is to develop more efficient catalytic systems that can be practically produced in industries. To this end, two main advanced strategies have primarily been developed. The first is the direct involvement of a certain amount of co-catalysts, including water, alcohol, and metal ions, in the traditional IL-based heterogeneous catalytic systems; these enhanced systems demonstrated significantly improved yields of cyclic carbonates [21–24]. The second involves the chemical modification of grafted IL moieties with functional groups such as —OH and —COOH; these functionalized heterogeneous catalysts also exhibited improved catalytic reactivity toward the cycloaddition reactions [25–27]. On the basis

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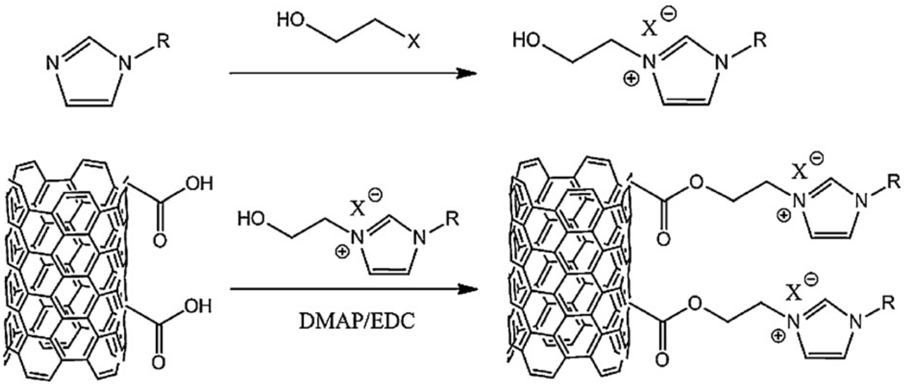

Scheme 1. Schematic illustration for the synthesis of HRImX (top) and CNT-ILs (bottom). R = Me, Et and Bu; X = Cl, Br and I.

of such pioneering research, we have found that most of the related works mainly focused on the development of highly efficient catalytic systems at molecular level. Nevertheless, the range of advanced support materials for the construction of highly efficient heterogeneous catalysts for the CO_2/epoxide cycloaddition reactions remains underexplored. In heterogeneous catalysts, the support materials tend to play an important role in the catalytic performance. Therefore, a careful choice of support materials could provide a third alternative to effectively promote the catalytic reactivity of IL catalysts in the synthesis of cyclic carbonates.

Carbon nanotubes (CNTs) possess many unique properties, such as high specific surface areas, good mechanical properties, and excellent thermal and electrical conductivities [28], making them ideal support candidates for the synthesis of various heterogeneous catalysts. To efficiently immobilize catalysts onto CNT sidewalls, it is critical to activate the graphitic surface of the CNT, which tends to be chemically inert and shows poor solubility [29]. This can be achieved by a conventional oxidation method, which offers a simple yet powerful tool to tailor the CNT surface with carboxylic groups under strongly acidic conditions, and not only endows the CNTs with excellent solubility in polar solvents but also provides flexible handles for the grafts of versatile functionalities onto the CNT sidewalls through diverse chemical protocols [30]. Based on such surface-modified CNTs, although several IL-based heterogeneous catalysts have been developed for the catalysis of diverse reactions such as the hydrogenation of 1-hexene and Diels–Alder reactions [31,32], the use of IL-immobilized CNTs as catalysts for the cycloaddition reactions of CO_2 and epoxides is still relatively unexplored.

Herein, a series of imidazolium-based ionic liquids, bearing hydroxyl groups, different alkyl chain lengths, and various halide counter anions, were synthesized and grafted onto oxidized CNT surfaces to generate various heterogeneous catalysts for the cycloaddition reactions of CO_2 and epoxides. In addition, the effects of catalytic reaction parameters including temperature, CO_2 pressure and time on the cyclic carbonate yield and selectivity were also investigated.

2. Experimental

2.1. Materials

4-Dimethylaminopyridine (DMAP), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC), 2-chloroethanol, 2-bromoethanol, 2-iodoethanol, 1-methylimidazole, 1-ethylimidazole, 1-butylimidazole, toluene, diethyl ether, various epoxides, and multi-walled carbon nanotubes (MWCNTs) were purchased from Aldrich and used as received.

2.2. Synthesis of imidazolium-based Ils

1-Hydroxyethyl-3-methyl imidazolium bromide (HMImBr) was synthesized according to the procedure described in Scheme 1. In a typical reaction, 1-methylimidazole (10 mmol) and 2-bromoethanol (10 mmol) were poured in sequence into a flask containing 50 mL anhydrous toluene while being vigorously stirred under an argon atmosphere. After refluxing for 3 h, toluene was removed. Following a similar procedure, the other HRImX products were also synthesized using 2-chloroethanol and 2-iodoethanol, respectively, instead of 2-bromoethanol.

The NMR data are as follows:

HMImBr. ^{1}H NMR (300 MHz, DMSO-d6): δ 3.74 (q, 2H), 3.90 (s, 3H), 4.27 (t, 2H), 5.18 (s, OH), 7.78 (s, 1H), 7.82 (s, 1H), 9.26 (s, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d6) δ 35.8, 51.6, 59.4, 122.7, 123.4, 136.9 ppm.

HEImBr, ^{1}H NMR (300 MHz, DMSO-d6): δ 1.39 (s, 3H), 3.74 (q, 2H), 4.21(t, 2H), 4.27 (t, 2H), 5.18 (s, OH), 7.80 (s, 1H), 7.88 (s, 1H), 9.56 (s, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d6) δ 15.8, 51.7, 52.6, 59.4, 122.3, 123.1, 137.4 ppm.

HBImBr, ^{1}H NMR (300 MHz, DMSO-d6): δ 0.67(s, 3H), 1.15 (t, 2H), 1.74 (t, 2H), 3.75 (q, 2H), 4.23 (t, 2H), 4.31 (t, 2H), 5.19 (s, OH), 7.90 (s, 1H), 7.92 (s, 1H), 9.38 (s, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d6) δ 13.7, 19.5, 31.8, 51.6, 53.1, 59.2, 122.5, 123.4, 136.5 ppm.

2.3. Synthesis of MWCNTs supported IL

Prior to the grafting of the IL on the MWCNTs, pristine MWCNTs were oxidized to introduce —COOH groups on their surfaces according to the reported procedures [33]. In a typical experiment, MWCNTs (1.2 g) were added to a flask containing a mixture of concentrated sulfuric acid and nitric acid (600 mL; 3:1 by volume). After 10 h at 70 °C, the resulting ink-like solution was diluted with deionized water and then filtered through a 0.22-μm polycarbonate film. The solid product was rinsed with deionized water until the filtrate tested neutral. The resultant oxidized MWCNTs were collected and dried in a vacuum oven at 100 °C for 12 h.

In a typical IL grafting process, the oxidized MWCNTs (0.2 g) were dispersed in anhydrous DMF. Thereafter, DMAP (0.3 g), EDC (0.3 g), and HMImBr (0.9 g) were added to the obtained CNT sol. The esterification reaction was performed at 60 °C for 24 h. Upon completion, the resulting mixture was filtered and washed with deionized water. The resultant HMImBr-grafted MWCNTs (CNT-HMImBr) were collected and dried under vacuum at 60 °C for 12 h. Following the similar procedure, CNT-HMImCl, CNT-HMImI, CNT-HEImBr, and CNT-HBImBr were also synthesized.