Heterogeneous Catalysis

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CO_2 Cycloaddition Reactions Catalyzed by an Ionic Liquid Grafted onto a Highly Cross-Linked Polymer Matrix**

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In recent years, room-temperature ionic liquids (ILs) have attracted much attention owing to their unique properties such as non-volatility, non-flammability, and recyclability.[1] Moreover, ILs can be functionalized by designing different cations and anions. Some functional ILs have been synthesized, and their applications in different fields have been reported.[2] Specifically, ILs have shown great potential as catalysts for various reactions.[3]

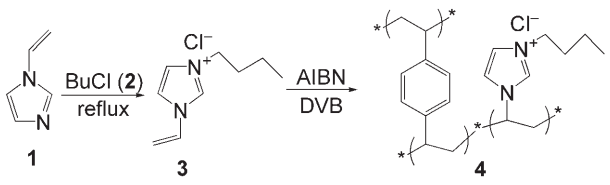
It is known that both homogeneous and heterogeneous catalysts have their advantages and shortcomings. For example, homogeneous catalytic systems usually show higher activity, while heterogeneous catalysts are more easily separated from products. To combine the advantages of heterogeneous and homogenous catalysts has been a topic of interest for years, and immobilization of catalysts on suitable supports is an effective way to do so. Polymeric materials are very attractive supports of catalysts as a result of some unusual advantages.[4] In recent years, immobilization of ILs onto polymers has been studied. For example, Carlin and Fuller prepared a catalytic membrane for heterogeneous hydrogenation which was composed of ILs and poly(vinylidene fluoride)-hexafluoropropylene copolymers with the incorporation of Pd on activated carbon.[5] Vankelecom and co-workers[6] fabricated hydrogenation catalysts that showed excellent activity by impregnation of transition metals and ILs into poly(diallyldimethylammonium chloride). Chi and Kim supported imidazolium salts on polystyrene (PS) resin through covalent bonding. The polymer-supported ILs were highly efficient catalysts for some substitution reactions. In particular, PS[hmim][BF_4] (hmim = 1-*n*-hexyl-3-methylimidazolium cation) showed much higher catalytic activity than the free IL.[7] Kou and co-workers reported that rhodium nanoparticles in ILs stabilized by ionic copolymers displayed excellent lifetimes and activity for arene hydrogenation in ILs.[8]

Conversion of CO_2 into valuable chemicals is of great importance. One of the most successful examples is the synthesis of cyclic carbonates from CO_2 and epoxides (see Scheme S1 in the Supporting Information), and various catalysts have been developed for the reactions, including alkali-metal halides,[9] organic bases,[10] metal oxides,[11] zeolite,[12] titanosilicates,[13] smectites,[14] and metal complexes.[15] However, disadvantages still exist such as low activities, air sensitivity, and requirement of high temperatures and co-catalysts. Recently, it was demonstrated that some ILs are very active catalysts for the cycloaddition of CO_2 to epoxides,[16] and ILs supported on silica have been used as catalyst.[17]

Although the cycloaddition of CO_2 to epoxides to produce cyclic carbonates has been studied extensively, the design of highly effective heterogeneous catalysts is still desirable. In this work, we copolymerized 3-butyl-1-vinylimidazolium chloride ([VBIM]Cl) with the cross-linker divinylbenzene (DVB) to prepare a highly cross-linked polymer-supported IL (PSIL), in which [VBIM]Cl was covalently anchored on DVB-cross-linked polymer matrix. The catalytic performance of the PSIL for the cycloaddition of CO_2 to epoxides was investigated, and it was demonstrated that the catalyst was very active, selective, and stable, and could be easily separated from the products and reused. Synthesis of effective and completely insoluble polymer-supported IL catalysts is an interesting topic. The unique advantage of the highly cross-linked polymeric catalyst is that it is not soluble in any commonly used organic solvents. To the best of our knowledge, this is the first demonstration of supporting an IL on a highly cross-linked polymer matrix to prepare an active and insoluble catalyst.

The route to synthesize the PSIL is shown in Scheme 1. [VBIM]Cl (**3**) was first prepared from 1-vinylimidazole (**1**) and 1-chlorobutane (**2**). The cross-linked polymer with supported IL **4** was synthesized by radical polymerization of [VBIM]Cl (**3**) and DVB using AIBN as the initiator. The composition of the product was determined by elemental analysis (N 2.18, C 82.73, H 7.81, Cl 3.55 %) and indicated that the supporting amount of IL was about 1 mmol per 1 g polymer.

The morphology of the PSIL was observed using scanning electron microscopy (SEM; see Figure S1 in the Supporting



Scheme 1. Synthesis of the cross-linked-polymer-supported ionic liquid **4**. AIBN: azobis(isobutyronitrile).

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Information). The size of the PSIL particles was on the micrometer scale (Figure S1 a in the Supporting Information), and they had a rough surface (Figure S1 b in the Supporting Information).

The catalytic activity of the PSIL for the reaction of CO_2 and propylene oxide (PO) was first studied. The influence of temperature on the yield of propylene carbonate (PC) was investigated at CO_2 pressures of 6 and 10 MPa using the PSIL as catalyst (Figure 1). The yield of PC strongly depended on

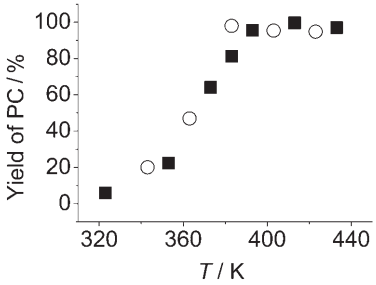


Figure 1. Yields of propylene carbonate versus temperature. Reaction conditions: PO (14.8 mmol), PSIL (0.100 g); ■ 10 MPa CO_2, 10 h; ○ 6 MPa CO_2, 7 h.

the reaction temperature at both pressures. In the lower temperature range, the yield increased with increasing temperature. However, the yield decreased slightly in the high-temperature region. The main reason was that the higher temperature also accelerated the side reactions. On the basis of the preliminary results, other experiments were conducted at 383 K. The dependence of the PC yield on reaction time at 383 K and 6 MPa CO_2 is shown in Figure 2. It illustrates that

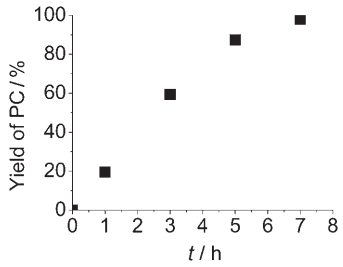


Figure 2. Dependence of the propylene carbonate yields on reaction time. Reaction conditions: PO (14.8 mmol), PSIL (0.100 g), 6 MPa CO_2, 383 K.

the yield of PC increased smoothly with the reaction time and that nearly all the PO could be converted within 7 h. In all the experiments depicted in Figure 2, the by-products were not detectable.

Figure 3 shows the dependence of PC yield on pressure at 383 K with a reaction time of 6 h. An increase in pressure resulted in an increase in the PC yield in the low-pressure region and a decrease of the yield in the high-pressure region. To obtain some evidence to explain this phenomenon, we observed the phase behavior of the CO_2-PO system by using the view cell reported previously.[18] The volume ratio of PO

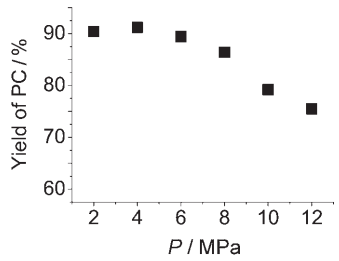


Figure 3. Propylene carbonate yields versus CO_2 pressure. Reaction conditions: PO (14.8 mmol), PSIL (0.100 g), 383 K, 6 h.

to that of the view cell was the same as that in the reaction system. It was demonstrated that there were two phases in the system under all the experimental conditions studied. The top phase was a CO_2-rich phase and the bottom phase was a PO-rich phase. The concentration of CO_2 in the bottom phase increased with increasing pressure. This favored the reaction, considering that CO_2 was a reactant. On the other hand, the concentration of PO in the bottom phase decreased as the pressure was increased, a condition which was not favorable to the reaction because PO was also a reactant. In addition, more PO was extracted into the CO_2-rich phase at higher pressures which reduced the reaction rate.[2f] The competition of these opposite factors resulted in a maximum in the pressure versus yield curve.

To evaluate the PSIL catalyst described here, the activities of various catalysts for the cycloaddition of CO_2 to PO were examined under the same reaction conditions (Table 1). 1-

Table 1: Activities of various catalysts for the cycloadditon reaction of CO_2 and propylene oxide.[a]

Entry	Catalyst	Active sites [mmol]	Yield [%]
1	1-vinylimidazole	0.200	0.75
2	1-butyl chloride	0.200	0.12
3	[BMIM]Cl	0.200	92.8
4	[VBIM]Cl	0.200	75.3
5	PVBIMCl[b]	0.200[c]	45.6
6	PSIL **4**	0.200[d]	97.4

[a] Reaction conditions: PO (29.6 mmol), 6 MPa CO_2, 383 K, 7 h; [b] Synthesized by direct polymerization of [VBIM]Cl; [c] Calculated using the amount of [VBIM]Cl; [d] Calculated using the amount of [VBIM]Cl.

Vinylimidazole and 1-chlorobutane showed negligible catalytic activities(Table 1, entries 1 and 2, respectively). The catalytic activity of the PSIL (Table 1, entry 6) was comparable to or even better than those of the liquid catalysts 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and [VBIM]Cl, a monomer of the PSIL (Table 1, entries 3 and 4, respectively). The main reason for this was that miscibility of the two liquid catalysts and the substrate was very poor, and there was an IL phase in the reaction system at the beginning which was observed in our experiments using the view cell.[18] The inter-phase mass transfer reduced the reaction rate, while the PSIL microparticles synthesized in this work could be well dispersed in the reaction mixture

under stirring. Moreover, another advantage of the solid PSIL was that it was insoluble in the product, whereas the liquid catalysts were soluble in the product. Table 1 also shows that the PSIL was much more active than poly[VBIM]Cl (PVBIMCl; Table 1, entry 5), which was synthesized by direct polymerization of [VBIM]Cl without the cross-linker DVB. This is easy to understand if it considered that the density of the active sites in PVBIMCl was much larger than that in the PSIL, which resulted in insufficient use of the active sites. Note also that PVBIMCl was soluble in the product which was unfavorable with respect to the easy separation of the catalyst from the products. Therefore, the cross-linker in the PSIL not only prevented the dissolution of the catalyst but also enhanced the activity.

Experiments were also carried out to examine the recyclability of the catalyst using PO as the substrate. In each cycle, PSIL as a solid catalyst was recovered by filtration and then rinsed with tetrahydrofuran, acetone, and methanol, respectively. After drying, the catalyst was reused for the next run. The yields of PC for the five repeated runs are shown in Figure 4. There was no considerable decrease in the yield of PC, indicating that the catalyst was not only insoluble in the reaction mixture but was also very stable.

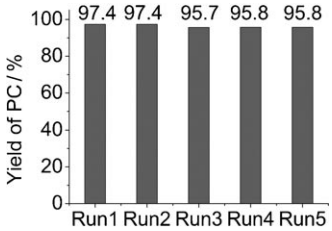
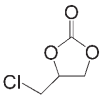
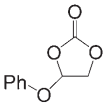
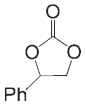
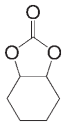


Figure 4. Reuse of the catalyst. Reaction conditions: PO (29.6 mmol), PSIL (0.200 g), 6 MPa CO_2, 383 K, 7 h.

The SEM images of the catalyst after reuse five times are also shown in Figure S1 c,d in the Supporting Information. The morphology of the PSIL was not changed considerably after being reused five times. The thermogram of the PSIL is shown in Figure S2 in the Supporting Information. It can be observed that the PSIL was thermally stable up to 243 °C, which was much higher than the temperature used for the cycloaddition of CO_2 to epoxides. Both the SEM image and the thermogram provide further evidence for the high stability of the catalyst.

Using PSIL as the catalyst, cycloadditions of CO_2 with other epoxides were also examined at 383 K and 6 MPa (Table 2). The results showed that the PSIL was active for all the substrates used. Epichlorohydrin and glycidyl phenyl ether were the most active substrates, and excellent yields of carbonates were achieved in 3 h (Table 2, entries 1 and 2, respectively). Styrene oxide (Table 2, entry 3) showed less activity with only 79.1 % yield obtained after 7 h, which may have resulted from the low reactivity of its β-carbon center. A much longer reaction time was needed to complete the conversion of cyclohexene oxide (Table 2, entry 4), the reason for which may be that its special cyclic molecular structure

Table 2: Catalytic activity of the reaction of various epoxides with CO_2.[a]

Entry	Epoxide	Carbonate	Reaction time [h]	Yield [%]
1			3	95.8
2			3	96.4
3			7	79.1
4			72	93.1

[a] Reaction conditions: epoxide (14.8 mmol), catalyst PSIL (0.100 g), 6 MPa CO_2, 383 K.

hampered the nucleophilic attack from the chloride and therefore decreased the rate of ring opening.

In conclusion, [VBIM]Cl can be supported on a DVB cross-linked polymer by covalent bonds simply by copolymerization of [VBIM]Cl and DVB. The polymer-supported ionic liquid is very active, selective, and stable for the cycloaddition of CO_2 to epoxides. Also, it can be easily separated from the products and reused. We believe that this route can be used to support some other ILs on highly cross-linked polymer matrixes to prepare polymer/functional IL composites, which are stable, insoluble in organic solvents, and have desired functions.

Experimental Section

CO_2 was supplied by Beijing Analytical Instrument Factory with a purity of 99.995 %. 1-Chlorobutane, azobis(isobutyronitrile) (AIBN), propylene oxide (PO), and epichlorohydrin were A.R. grade (Beijing Chemical Plant). Divinylbenzene (DVB) was purchased from FLUKA, and 1-vinylimidazole was provided by Aldrich. Other epoxides were supplied by ACROS ORGANICS. Styrene epoxide was purified by distillation and AIBN was recrystallized three times before use. Other chemicals were used as received.

The procedures to prepare 3-butyl-1-vinylimidazolium chloride ([VBIM]Cl) were similar to that reported.[8] Thus, 1-chlorobutane (18.50 g, 200 mmol) and 1-vinylimidazole (5.50 g, 58.3 mmol) were added to a 25 mL two-necked flask equipped with a magnetic stirrer. The mixture was heated at reflux for 24 h in an oil bath at 70 °C under the protection of nitrogen with stirring. Then, the reaction mixture was cooled down to room temperature. The top phase was poured out, and the solid residue was washed three times with ethyl acetate and then dried at 50 °C for 12 h under vacuum.

DVB-cross-linked polymers with the supported [VBIM]Cl were prepared by radical copolymerization. In a typical experiment, DVB (3.2 g, 24.6 mmol), [VBIM]Cl (0.5 g, 2.68 mmol), and AIBN (0.05 g) were dissolved in chloroform (150 mL) in a three-necked flask under nitrogen protection. The mixture was maintained at 70 °C at reflux for 48 h with stirring. The cross-linked-polymer-supported IL (PSIL) formed was collected by filtration and washed separately with tetrahydrofuran, acetone, and methanol. Then, the solid was dried

under vacuum at 50 °C followed by grinding before use. The product was characterized by thermogravimetric analysis (TGA, PERKIN-ELMER7 Series Thermal Analysis System) at a heating rate of 20 °C min^{-1}. The morphology of the PSIL was observed by scanning electron microscope (JEOL JSM 6700F). The compositions of the polymer were determined using a Flash EA1112 analyzer.

The cycloaddition reactions were carried out in a 10 mL stainless steel reactor with magnetic stirrer with known amounts of PO and PSIL charged into the reactor. The reactor was heated to desired temperature, and CO_2 was added to a suitable pressure under stirring. The mixture was kept at this pressure during the reaction. After the reaction, the reactor was cooled to 0 °C by using iced water and CO_2 was released and passed through a cold trap with *N*,*N*-dimethylformamide as absorbant. After the catalyst was precipitated, the product was analyzed by GC (Agilent 4890 D) with acetophenone as the internal standard. The retention time of the products were compared with available authentic standards. The purity and structure of the product obtained at some typical experimental conditions were also checked by NMR spectroscopy and GC-MS methods. The procedures for other epoxides were similar, and the products were analyzed at room temperature on a Bruker 400 MHz NMR spectrometer using $CDCl_3$ as solvent.

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