Short communication

Coconut shell activated carbon tethered ionic liquids for continuous cycloaddition of CO_2 to epichlorohydrin in packed bed reactor

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ARTICLE INFO

ABSTRACT

Various ionic liquids (ILs) were in situ prepared on coconut shell activated carbon (CSAC) granules. Cycloaddition of CO_2 to epichlorohydrin (ECH) was continuously carried out in a packed-bed reactor without using solvent or cocatalyst. The conversion rates of ECH over the CSAC tethered Bmim/Br, Bmim/BF$_4$, Bmim-OH/Br and Bmim-COOH/Br were 63.4%, 74.5%, 83.4% and 85.9% at 140 °C and 1.4 MPa, respectively. The selectivities to epichlorohydrin carbonate (ECHC) were over 98% for the four catalysts. The ECH conversion stabilized at 82% for the CSAC tethered Bmim-COOH/Br after 50 h of continuous performance in the packed bed reactor.

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1. Introduction

The addition of CO_2 to epoxides offers an alternative way to produce cyclic carbonates without involving the hazardous phosgenes that are used in industry. The reaction mechanism was widely discussed. Recently, some ionic liquids (ILs) [1–4], ammonium and phosphonium salts [5–8], have been reported as catalysts for the transformation of CO_2 to organic carbonates. Great efforts have been dedicated to immobilize ILs in order to facilitate catalyst recycling. In particular, mesoporous silicas such as MCM-41 and SBA-15 have been the focus of a number of studies because of their large surface area, high pore volume and opened structure. Although these catalysts show excellent conversion rate and selectivity in the cycloaddition reactions, they are only applicable to a batch reactor and must be separated after each batch. In addition, the cycloaddition of CO_2 to epoxides is a triphasic reaction system in batch reactor, in which CO_2 must dissolve in a solvent or epoxides to accomplish its diffusion to the catalyst surface. Therefore, the reaction is restricted by the solubility of CO_2. Supercritical CO_2 (scCO$_2$) may offer a complete miscibility in the ILs, but it must be operated under a high pressure condition [9–11].

At the current stage, high costs, low thermal stability of catalysts, and a lack of effective and feasible catalytic reaction systems that can work under mild and solvent-free conditions are still the challenges for large scale production. Therefore, the crucial factor is to design novel supported catalysts and feasible catalytic reaction system that

can be performed for continuous performance in a packed-bed reactor, because packed bed reactor has many attractive features, especially, continuous flow operation for large scale production under constant operating conditions. The cycloaddition of CO_2 to epichlorohydrin (ECH) is exothermic, which may promote generation of by-products. Hence, continuous flow-through process in packed bed reactor might bring away the heat and keep a constant operation temperature. Moreover, gas–solid biphasic catalysis may be achieved by flowing of CO_2 and gaseous epoxides through the solid catalyst in a column. Thus, the reactants can directly get access to the catalyst surface, promoting the reaction as well as avoiding the use of solvents. Chen et al. [12] reported continuous cycloaddition of CO_2 in a spiral capillary reactor, in which 2-hydroxyl-ethyl-tributylammonium bromide (HETBAB) was dissolved in epoxide, and the gas–liquid reaction occurred at 160 °C and 3.5 MPa. Hatton et al. [13] reported that a continuous flow cycloaddition of CO_2 in N,N-dimethylformamide (DMF) and the catalyst N-bromosuccinimide was dissolved in DMF. To our best knowledge, the only reported solid catalyst for carrying out the reaction in a packed-bed reactor was amorphous silica immobilized phosphonium salts by Sakakura et al. [14]. A mixture of propylene oxide and scCO$_2$ was continuously introduced into the reactor. The experiments were conducted at 160 °C under a high pressure of 10 MPa.

Prospective catalysts applicable to a packed-bed reactor must have a high mechanical strength, good abrasion resistance and big particle size. To process powdery carriers, e.g. mesoporous silica grafted ILs, ammonium or phosphonium salts into macrosized granules for application in a packed-bed reactor, the powdery catalysts are normally mixed with an adhesive binder and subjected to annealing at high

temperature. Unfortunately, the supported organics can not stand annealing at a high temperature. Coconut shell activated carbon (CSAC), a cheap and readily available biomass material, has high mechanical strength, good abrasion resistance and an inherent granular structure as well as high surface area and pore volume [15,16]. Its applicability in a continuous packed-bed process has ever been industrially demonstrated. This paper attempted to *in situ* prepare ILs on the CSAC granules as shown in Scheme 1, and explored the feasibility of continuous cycloaddition of CO_2 to ECH in a packed bed reactor under solvent-free and relatively low-pressure conditions. Continuous performance in a packed bed reactor might be extended to continuously remove CO_2 for upgrading biogas or natural gas.

2. Experimental

2.1. Preparation of CSAC tethered imidazolium ILs

The covalent immobilization amount of imidazolium ILs on the CACS depends on the concentration of surface hydroxyl groups. In order to increase the hydroxyl group amount, CACS granules were subjected to oxidation according to a report [15]. Raw CSAC (15.0 g) granules were washed with boiling water and treated with HNO_3 (300 mL, 20 wt.%) in a backflow device at 85 °C for 4 h, then the granules were separated, thoroughly washed with distilled water and dried at 105 °C for 24 h.

The CSAC tethered imidazolium ILs were synthesized as described in Scheme 1. The oxidized CSAC (10 g) granules and (3-chloropropyl)trimethoxysilane (CPTMS, 0.81 g, 0.41 mmol) were mixed in toluene (300 mL) and refluxed at 105 °C for 24 h under nitrogen atmosphere. The solid was separated by suction filtration and washed with ethanol. The physically adsorbed CPTMS on the solid was extracted with ethanol in a Soxhlet extractor for 24 h, vacuum filtrated and dried at 70 °C for 7 h in vacuum. The silanized CSAC granules (10 g) and imidazole (0.279 g, 0.41 mmol) were placed in toluene (200 mL) and refluxed at 105 °C for 12 h, followed by filtration and vacuum drying at 70 °C for 7 h. A mixture of CSAC tethered imidazole (10 g) and n-butyl bromide (0.56 g, 0.41 mmol) was heated in toluene (200 mL) at 105 °C for 12 h to achieve CSAC tethered Bmim/Br.

To obtain carboxyl functionalized ILs, the CSAC tethered imidazole (10 g) was mixed with 2-bromobutyric acid (0.68 g, 0.41 mmol) in a flask and refluxed at 105 °C for 12 h, then filtrated and washed with anhydrous ethanol, and vacuum dried at 70 °C for 10 h. The as-prepared product is the CSAC tethered Bmim-COOH/Br. Bmim-OH/Br were also synthesized in a similar way as described above. The CSAC tethered imidazole (10 g) was mixed with bromoethanol (0.51 g, 0.41 mmol) for preparation of the CSAC tethered Bmim-OH/Br.

To obtain CSAC tethered Bmim/BF_4, a mixture of NH_4BF_4 (0.43 g, 0.41 mmol) and the CSAC tethered Bmim/Br (10 g) was added in acetone (300 mL) to reflux for 12 h at 57 °C, then separated by suction filtration. The process was repeated until Br^- were totally exchanged, which might be identified by adding a drop of 0.1 wt.% $AgNO_3$ solution to the filtrate. The final product was filtrated and washed three times with anhydrous ethanol and then dried in vacuum at 70 °C for 10 h. The as-prepared product is the CSAC tethered Bmim/BF_4.

The materials used to prepare the CSAC tethered ILs and characterization experiments were described in the supporting information.

2.2. Cycloaddition of CO_2 to ECH in packed bed reactor

The cycloaddition reaction of CO_2 to ECH was carried out in a packed-bed reactor without using solvent (Figure S1). The packed column has an inner diameter of 1 cm and a length of 40 cm. The flow rates of ECH and CO_2 were 1 mL·min^{-1} and 50 mL·min^{-1}, respectively. The catalyst (3–5 g) was placed at the middle of the column with both ends filled with quartz granules. The reaction temperature was investigated in a range of 110–150 °C and the pressure was 1.0–1.5 MPa. ECH and epichlorohydrin carbonate (ECHC) were identified and quantified by gas chromatography equipped with a capillary column and FID detector (GC112A Gas Chromatograph, DB-5 Column, 30 m × 0.53 nm).

3. Results and discussion

The surface oxygen-containing groups on the raw and the oxidized CSAC were identified and quantified by Boehm titration. The phenolic hydroxyl amount on the raw CSAC was enhanced by oxidization with 20% HNO_3. The Boehm's titration results suggested that the concentration of phenolic hydroxyl on the oxidized CSAC was increased to 0.376 from 0.118 mmol/g for the raw CSAC. The FT-IR spectra and XPS analyses of intermediates to prepare the CSAC tethered ILs were discussed in the supporting information (as seen in Figure S2–S6). The FT-IR spectra of four CSAC tethered ILs were shown in Figure S7. Few differences were observed among four spectra. Since the oxidized CSAC carrier contained lots of –OH, C═O and COOH, some characteristic groups like –OH and COOH on Bmim-OH/Br and Bmim-COOH/Br can not be distinguished
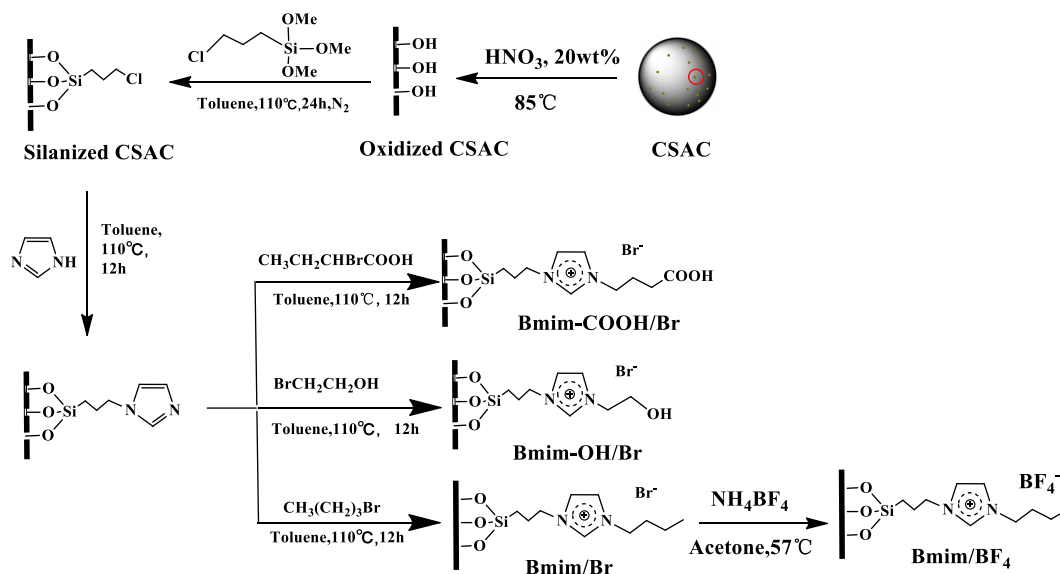
Scheme 1. Preparation of the CSAC tethered imidazolium ILs.

from each other. In spectrum of the immobilized Bmim/BF₄, the stretching vibration of B–F was observed at 1040 cm⁻¹ [17]. For three tethered ILs containing Br⁻, a band attributed to the stretching vibration of C–Br appeared at 623 cm⁻¹ [18].

Thermal stability of the immobilized ILs was significant for continuously catalytic performance in packed bed reactor. It can be observed that the organic moieties on four CSAC supported ILs began to decompose over 300 °C as seen in Figure S8. The unsupported imidazolium ILs would decompose at 260 °C as reported [19]. The amounts of N element in the CSAC supported ILs were determined by Elemental Analyzer. Elemental analysis showed that the amounts of N element were 2.41%, 2.39%, 2.33% and 2.59% for Bmim/Br, Bmim/BF₄, Bmim-OH/Br and Bmim-COOH/Br, respectively. Their respective concentrations of ILs on the CSAC were 0.861, 0.853, 0.832 and 0.925 mmol/g.

The cycloaddition reaction of CO_2 and ECH was carried out in packed bed reactor without using solvent. A temperature range of 110–150 °C was investigated under a pressure of 1.4 MPa. When the reaction temperature was below 120 °C, the conversions of ECH over four catalysts were less than 40% as seen in Fig. 1. The main reason for it was that ECH was in liquid state at a temperature below 120 °C and only a small quantity of CO_2 was dissolved in ECH without a solvent. In these cases, the catalytic reactions occurred in a triphasic system, and gaseous CO_2 was difficult to disperse onto the surface of the catalysts. However, a gas–solid biphasic reaction system was obtained as the temperature was increased to 130 °C due to gasification of ECH. It allowed easy access of the reactants to the surface of the catalysts. Therefore, the ECH conversion increased rapidly to 79.3% from 35.8% over Bmim-COOH/Br in the packed bed reactor as the temperature reached 130 °C. However, the ECH conversion increased slowly with further increase of the temperature, probably because the rapidly increased conversion after gasification of ECH would greatly reduce the concentration of ECH, decreasing the conversion rate of ECH. Meanwhile, the four catalysts displayed a high selectivity to ECHC at 140 °C. However, the selectivity to ECHC obviously declined when the reaction temperature reached 150 °C, probably because high temperature accelerated some side reactions such as polymerization or isomerization [18,20,21].

In terms of a gas–solid reaction system at 140 °C, the pressure of CO_2 would be another significant factor affecting the cycloaddition as seen in Fig. 2. The selectivity to ECHC was over 98% for the four catalysts at 1.4 MPa. The conversions of ECH were slowly increased with the pressure above 1.2 MPa. The pressure was adjusted by increasing the partial pressure of CO_2, whereas ECH was pumped in with a constant flow rate in all experiments. According to the reported mechanism [22–24], the supported imidazolium ionic liquids firstly interact with epoxides, then the intermediate combines CO_2. Therefore, further increase in the
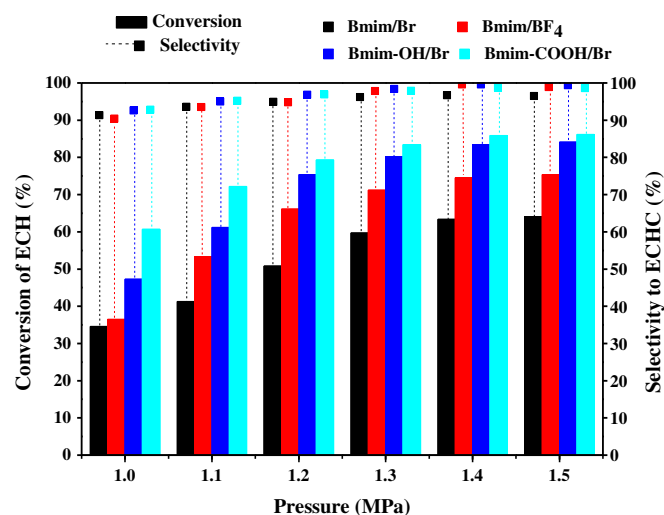

Fig. 2. Effect of the pressure of CO_2 on the conversion of ECH and the selectivity to ECHC in the packed bed reactor without using solvent at 140 °C.

pressure has relatively slight effect on the conversion rate of ECH. The conversion of ECH reached a highest value at 1.4 MPa. Therefore, 140 °C and 1.4 MPa would be the optimal conditions for the cycloaddition reaction over the CSAC tethered ILs in the packed bed reactor. The highest conversions were 63.4%, 74.5%, 83.4% and 85.9% for Bmim/Br, Bmim/BF₄, Bmim-OH/Br, Bmim-COOH/Br, respectively. Correspondingly, their TOF values (the TOF was defined as the number of the converted epoxide molecules per hour on per active catalytic site) were 84.9, 99.8, 112.6 and 115 h⁻¹, respectively. In comparison, blank experiments were conducted over the oxidized CSAC and the CPTMS silanized CSAC under the same condition, and no ECHC was detected in the outflow mixture. The mechanism for cycloaddition of CO_2 had been widely discussed before [22–24]. Hydroxyl or carboxyl groups on the CSAC tethered Bmim-OH/Br and Bmim-COOH/Br could form hydrogen bond with oxygen in ECH resulting in the polarization of C–O bond, which played a synergistic role with Br⁻ to promote the cycloaddition.

The catalytic activity of Bmim-COOH/Br was varied with liquid hourly space velocity (LHSV) as shown in Figure S9. The conversion of ECH and selectivity to ECHC declined with the augment of LHSV. When LHSV increased, ECH might self-aggregate at the high temperature and result in the decline of the selectivity. When the LHSV reached 6 h⁻¹, the conversion stayed steady at ~82% and the impact of external diffusion could be ignored. A short duration test was carried out over the
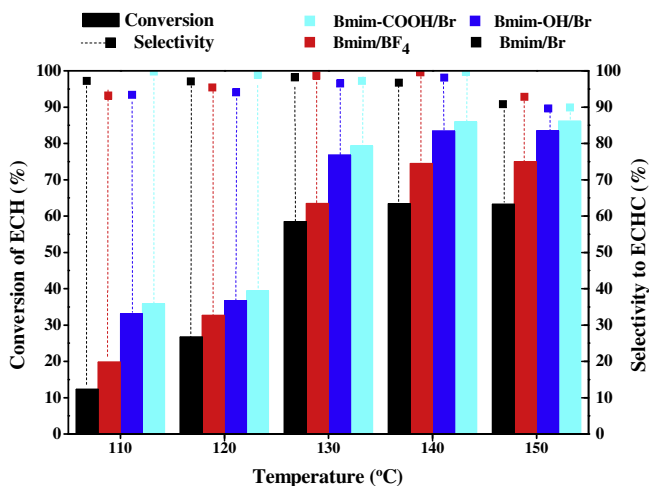

Fig. 1. Effect of temperature on the conversion of ECH and selectivity to ECHC in the packed bed reactor without using solvent under a pressure of 1.4 MPa.
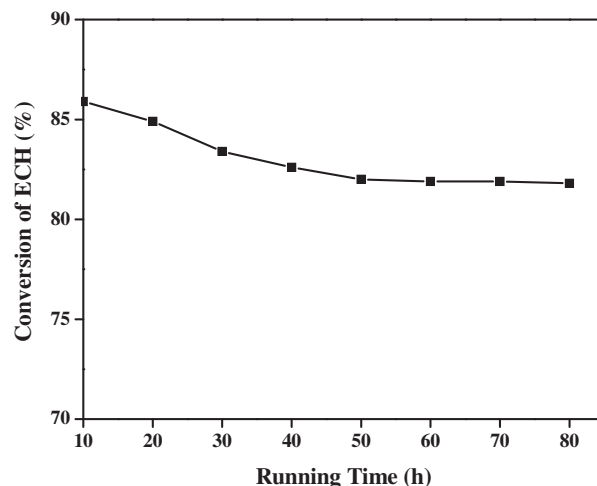

Fig. 3. Plot of the conversion of ECH vs time in the packed bed reactor over the CSAC tethered Bmim-COOH/Br at 140 °C and 1.4 MPa.

CSAC tethered Bmim-COOH/Br at 140 °C and 1.4 MPa as shown in Fig. 3. The catalytic cycloaddition reaction continuously proceeded for 80 h. It can be observed that the conversion of ECH slightly decreased in the beginning 50 h. However, 50 h later, it stabilized at 82%. In fact, the CSAC tethered ILs exhibited relatively stable catalytic activity.

Although many references reported higher conversions, the cycloaddition reactions were conducted in batch reactors [25–27]. The only continuous performance in packed-bed reactor was reported by Takahashi et al. [14]. The cycloaddition of CO_2 to propylene oxide was carried out over SiO_2 immobilized C_3H_6-P(n-Bu)$_3$Br. The conversion of the epoxide was 80%, but with supercritical CO_2 as reactant at a high pressure of 10 MPa.

4. Conclusions

CSAC granule tethered ILs were successfully synthesized and might be used in the packed-bed reactor. A gas–solid biphase reactive system may be formed at a temperature higher than the boiling point of ECH. Thus, there is no need using a solvent to absorb CO_2 and transport it to the catalyst surface. Moreover, the cycloaddition of CO_2 to ECH can proceed in a way of continuous feeding. Among the investigated four catalysts, Bmim-OH/Br and Bmim-COOH/Br exhibited more active catalytic performance. Probably, carboxyl or hydroxyl might form hydrogen bond with the O atom of ECH, which polarized the C–O bond in ECH and promoted the reaction. Although the duration test of 80 h is not enough for evaluating a catalyst, it still indicated that CSAC granules tethered ILs is a prospective catalyst for efficient and environmentally friendly cycloaddition of CO_2.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2015.05.004.

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