



Porous polymer bead-supported ionic liquids for the synthesis of cyclic carbonate from CO₂ and epoxide

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ABSTRACT

Highly cross-linked porous poly(*N*-vinylimidazole-*co*-divinylbenzene) (PVIm) beads of various pore sizes and specific surface areas were synthesized by suspension polymerization. The surfaces of the PVIm beads were then modified with various alkyl halides to obtain various ionic liquid-grafted porous polymer beads (PVIm-RX), which were then used as heterogeneous catalysts in the synthesis of cyclic carbonate from CO₂ and epoxide. All catalytic reactions are carried out under mild conditions (90–130 °C, 0.86–2.17 MPa) in the absence of organic solvents. The effects of texture properties of the PVIm matrix, molecular compositions of the ionic liquid moieties, and catalytic reaction parameters (reaction temperature, pressure, and time) on the catalytic reactivity of cycloaddition reactions were systematically investigated. The results demonstrate that grafted ionic liquids with more nucleophilic anions, bulkier alkyl chains, or hydroxyl groups improve reactivity. Additionally, the incorporation of small amount of ethanol or water into the reaction system could significantly increase reactivity. In addition, textural properties of the polymer matrix (pore size and specific surface area) affected the catalytic reactions. The obtained PVIm-RX heterogeneous catalysts exhibited higher turnover number than those reported for ionic liquids grafted onto porous silica.

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1. Introduction

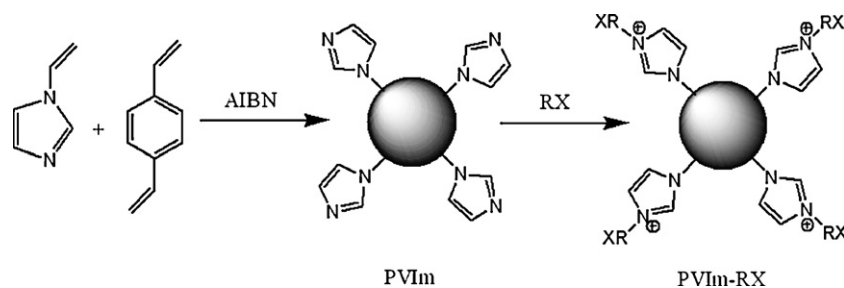
Ionic liquids (ILs) have been known for several decades, but the amount of research on this class of compounds has expanded during the last decade [1–3]. Part of this increase was related to a lack of knowledge of many of the fundamental physical parameters of ILs and to the absence of models to explain their behaviors [4]. However, most importantly, from a practical viewpoint, much of the recent expansion of IL-based chemistry has been related to their utility as environmentally friendly solvents with multiple applications in product synthesis, catalysis, and separation [5–8]. Despite their advantages, some application-related obstacles to the use of ILs have been identified. For example, product purification and IL recycling procedure difficulties, toxicity concerns, and fixed-bed reactor application problems are important issues that need to be addressed prior to industrial scale-up of the use of ILs. The use of a supported IL phase, prepared via immobilization of molecules with IL-like structures onto solid supports, can overcome these difficulties [9–11]. This new class of advanced materials shares the properties of true ILs, but with the benefits associated with a solid support. Moreover, in some

cases, the supported IL can enhance the performance of the solid material.

As an attractive type of support for IL catalysts, polymer materials have garnered attention owing to their low-cost, easy separation, and versatile surface functionalization [12–15]. By grafting ILs onto polymers, a variety of heterogeneous catalysts have been developed in recent years [16]. For example, Carlin and Fuller [17] prepared a catalytic membrane, composed of ILs and poly(vinylidene fluoride)-hexafluoropropylene copolymers with the incorporation of Pd on activated carbon, for heterogeneous hydrogenation. Kim and Chi [18] developed polystyrene resin-supported imidazolium salts through covalent bonding. Their polymer supported (PS) ILs were highly efficient catalysts for some substitution reactions. In particular, PS[hmim][BF₄] (hmim = 1-*n*-hexyl-3-methylimidazolium cation) produced much higher catalytic activity than the free IL.

The conversion of CO₂ into valuable chemicals has commercial benefits, and the synthesis of cyclic carbonate from CO₂ and epoxide has recently received increasing attention [19]. Various catalysts have been developed for such reactions, including alkali-metal halides [20], metal oxides [21], titanosilicates [22], and metal complexes [23,24]. Recently, some homogeneous and heterogeneous ILs were demonstrated to be effective catalysts for the cycloaddition of CO₂ to epoxides [25–27]. With regard to IL-derived

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Scheme 1. Schematic illustration for the synthesis of PVIm-RX.

heterogeneous catalytic systems, most pioneering works have used porous silica as a support [28].

Polymeric materials are promising as substitutes for silica in the synthesis of IL-based heterogeneous catalysts [29,14,30]. Several IL-immobilized polymer catalysts for cycloaddition of CO₂ to epoxide have been developed; however, most of the employed supports generally have low specific surface area and lack pore size consistency [16–18,31]. This lowers the utilization efficiency of the polymer support in both theoretical and practical investigations. In contrast, porous polymer beads synthesized by suspension polymerization possess uniform size, permanent pore structure, and tunable texture properties (pore size and specific surface area), features that are advantageous when grafting ILs onto solid supports.

This study into heterogeneous catalysts used highly cross-linked porous poly(*N*-vinylimidazole-*co*-divinylbenzene) [PVIm] beads of various pore sizes and specific surface areas that were synthesized by suspension polymerization. Various alkyl halides were covalently anchored on the surfaces of as-prepared polymer beads, and a variety of ILs-grafted porous polymer beads (PVIm-RX) were obtained and then used as heterogeneous catalysts for the cycloaddition of CO₂ to epoxide. The catalytic performances of the obtained PVIm-RX, as affected by the molecular composition of the ILs, reaction conditions, and the texture properties of the polymer matrix, were systematically investigated. Compared to previously reported heterogeneous catalysts, those developed in this study have several advantages, including higher surface area, tunable pore size, robust and permanent pore structure, well-defined spherical morphology, and stability in any organic solvent.

2. Experimental

2.1. Materials

1-Bromoethane, 1-bromohexane, 1-bromooctane, 1-bromobutane, 1-chlorobutane, 1-iodobutane, 2-bromoethanol, allyl glycidyl ether (AGE), and toluene commercially obtained from Sigma–Aldrich (St. Louis, MO, USA) were used as received. *N*-Vinylimidazole and divinylbenzene (DVB, 55%), both from Sigma–Aldrich were purified by distillation before use. Azobisisobutyronitrile (AIBN; Sigma–Aldrich) was purified by recrystallization from methanol.

2.2. Synthesis of PVIm beads and PVIm-RX heterogeneous catalysts

Highly cross-linked PVIm beads with varied texture properties were prepared by suspension polymerization in a two-necked, round-bottom flask reactor fitted with a mechanical stirrer and a reflux condenser. At room temperature, the flask was charged with an aqueous phase containing 2 wt% gelatin. The organic phase, a mixture of DVB and *N*-vinylimidazole with specified molar ratios along with a dilute system (toluene and dibutyl phthalate, porogen) and AIBN (0.12 g), was added to the aqueous phase and suspended

by stirring. The temperature was kept constant during the reaction period. Post-reaction, the polymer beads were decanted, washed with water and methanol, and dried in vacuo at 40 °C. Based on the three employed molar ratios of DVB to *N*-vinylimidazole (2:3, 3:3, and 3:2), the obtained polymer beads were described as PVIm1, PVIm2, and PVIm3, respectively. Following the similar procedure to synthesize PVIm2, when the synthesis was performed in the absence of porogen, non-porous polymer beads (PVIm4) were achieved.

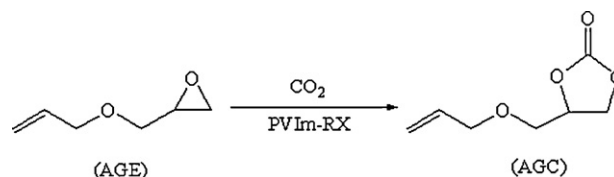
Syntheses of PVIm-RXs were carried out in 100 mL flasks, in which PVIm beads were allowed to react with various alkyl halides (1-bromoethane, 1-bromohexane, 1-bromooctane, 1-bromobutane, 1-chlorobutane, 1-iodobutane, or 2-bromoethanol; molar ratio of *N*-vinylimidazole to alkyl halide = 1:1) in toluene at appropriate reflux temperatures for 24 h. Subsequently, the precipitates were collected, rinsed with dichloromethane, then dried in vacuo to yield PVIm-RX (see Scheme 1).

2.3. Coupling reactions

Allyl glycidyl carbonate (AGC) was synthesized by the coupling reaction between AGE and CO₂ in the presence of a PVIm-RX as illustrated in Scheme 2. All reactions were carried out in a 55 mL stainless-steel reactor with a magnetic stirrer. For a typical reaction, 0.5 g of catalyst was introduced into a reactor containing 40 mmol of AGE. Reactions were carried out under preset carbon dioxide pressures at specified temperatures.

2.4. Characterization

Elemental analysis (EA) was undertaken using Vario EL III (Elementar, Hanau, Germany). During EA, 2 mg of the PVIm-RX samples were subjected to 1100 °C. Sulfanilic acid was used as a standard. Samples for scanning electron microscopy (SEM) were mounted onto silicon plates and dried in air. After osmium coating of the plates, SEM analysis was carried out using a JSM-6700F (Jeol, Tokyo, Japan) microscope at an accelerating voltage of 10 kV. Energy dispersive X-ray spectroscopy (EDS) analysis was performed using an Oxford Link Isis EDS system (Isis Innovation, Oxford, UK) attached to the SEM. Data on thermal transition behavior of the polymer matrix and the polymer supported catalyst were obtained using a thermogravimetric analyzer (TGA; TGA 7, Perkin Elmer, USA) over 30–600 °C range at a scan rate of 10 °C min⁻¹ under a nitrogen



Scheme 2. Coupling reaction between AGE and CO₂ in the presence of PVIm-RX catalysts.

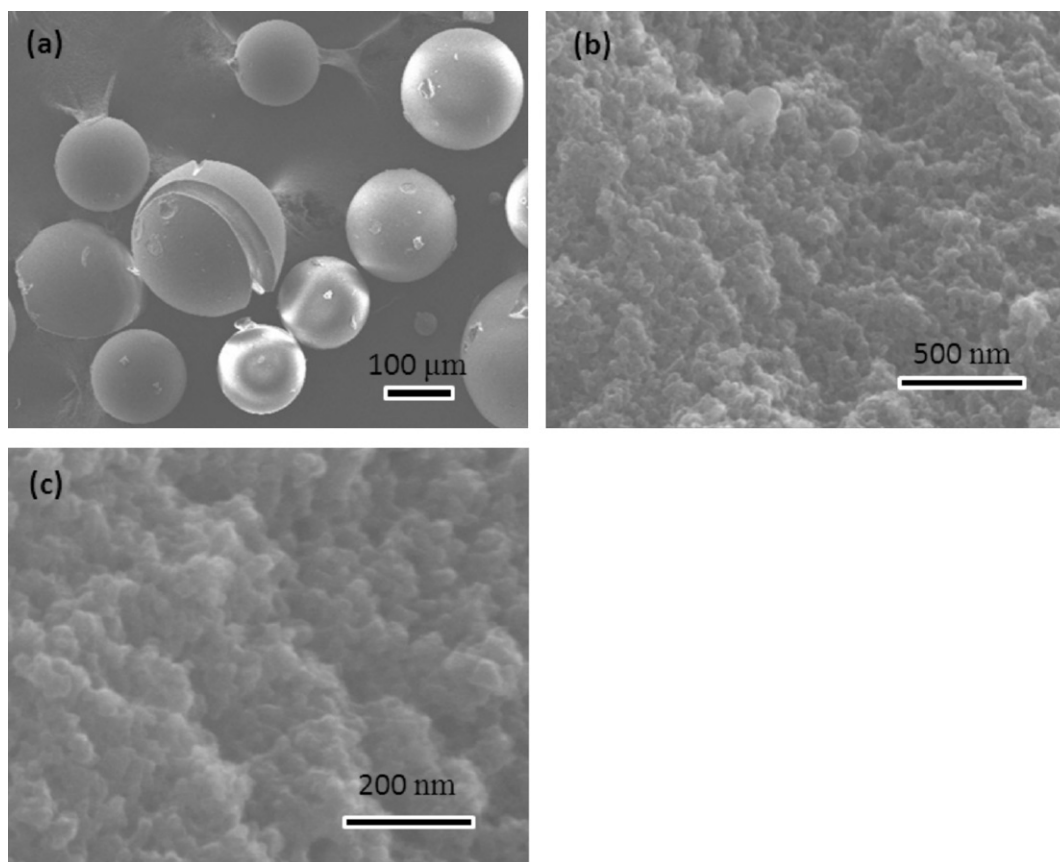


Fig. 1. SEM image of PVIm beads (a), high resolution SEM images of cross-section of PVIm2 (b) and PVIm2-BuBr (c) beads.

atmosphere. Surface area and pore size of the PVIm were measured by nitrogen adsorption at -196°C using a BET (Brunauer, Emmett, and Teller) apparatus (ASAP 2010; Micromeritics, Norcross, GA, USA). Pore size distribution was estimated using the Barrett, Joyner, and Halenda (BJH) algorithm within the Micromeritics supplied software. AGE concentration was determined by gas chromatography (HP 6890; Agilent Technologies, Santa Clara, CA, USA) equipped with a capillary column (HP-5, $30\text{ m} \times 0.25\ \mu\text{m}$) using flame-ionized detector. Dichloromethane was used as an internal standard. The obtained five-member cyclic carbonates were confirmed by comparison with authentic samples obtained from Aldrich.

3. Results and discussion

3.1. Catalyst characterization

As a typical example of the PVIm beads, the morphology of as-prepared PVIm2 beads was examined by SEM observations. Fig. 1a shows that the $150\ \mu\text{m}$ average diameter polymer beads exhibit a spherical morphology. High resolution SEM images (Fig. 1b) revealed that the cross section of the beads is rough with numerous permanent pores in the polymer matrix. Following the grafting of an alkyl halide on the polymer matrix, no marked changes in morphology were observed (Fig. 1c), indicating the presence of permanent pores within IL-grafted polymer bead matrices. EDS spectra of PVIm2-BuCl, PVIm2-BuBr, PVIm2-BuI, and PVIm2-HEtBr showed the presence of chlorine, bromine, iodine, and oxygen, suggesting that the respective alkyl halides had successfully grafted onto the polymer matrix (Fig. 2).

The thermal properties of PVIm2 and PVIm2-BuBr were investigated by TGA. As depicted in Fig. 3a, the TGA trace of PVIm2 was

stable up to 400°C , during heating to 450°C , which corresponds to the pyrolysis temperature of PVIm2. The decomposition of PVIm2-BuBr showed two endothermic steps at 320°C and 450°C (Fig. 3b), which are plausibly attributed to the decomposition of the grafted IL and the polymer matrix, respectively. The results indicate that PVIm2-BuBr is thermally stable up to 290°C .

3.2. Effect of polymer matrix texture on catalytic activity

To investigate the effects of PVIm matrix texture properties on the catalytic reactivity of the cycloaddition reaction, PVIm beads with various specific areas were synthesized. BET analysis results in Table 1 show that the surface area of PVIm beads can be changed by adjusting the mole ratio of DVB and *N*-vinylimidazole. The PVIm1, PVIm2, and PVIm3 surface areas were 905 , 952 , to $1009\ \text{m}^2\ \text{g}^{-1}$, respectively. These results support those in a previous report [32]. Correspondingly, the average BJH pore size of the prepared PVIm beads is tunable within the range of $54.1\ \text{\AA}$ to $75.5\ \text{\AA}$. For further comparative study, non-porous polymer beads with rather low surface area ($<0.1\ \text{m}^2\ \text{g}^{-1}$), PVIm4 were also synthesized.

Table 1
Effect of polymer matrix texture on catalytic activity.

Polymer matrix	PVIm1	PVIm2	PVIm3	PVIm4
Molar ratio (DVB/ <i>N</i> -vinylimidazole)	2:3	3:3	3:2	3:3
Surface area ($\text{m}^2\ \text{g}^{-1}$)	905	952	1009	<0.1
Pore size (\AA)	54.1	75.5	71.0	–
Immobilized amount of IL ($\text{mmol}\ \text{g}^{-1}$)	0.90	0.92	0.78	0.14
AGE conversion (%)	55	65	57	9

Immobilization amount is estimated from EA analysis. Reaction condition: catalyst = $0.5\ \text{g}$; AGE = $40\ \text{mmol}$; temperature = 110°C ; pressure = $0.86\ \text{MPa}$; time = $6\ \text{h}$.

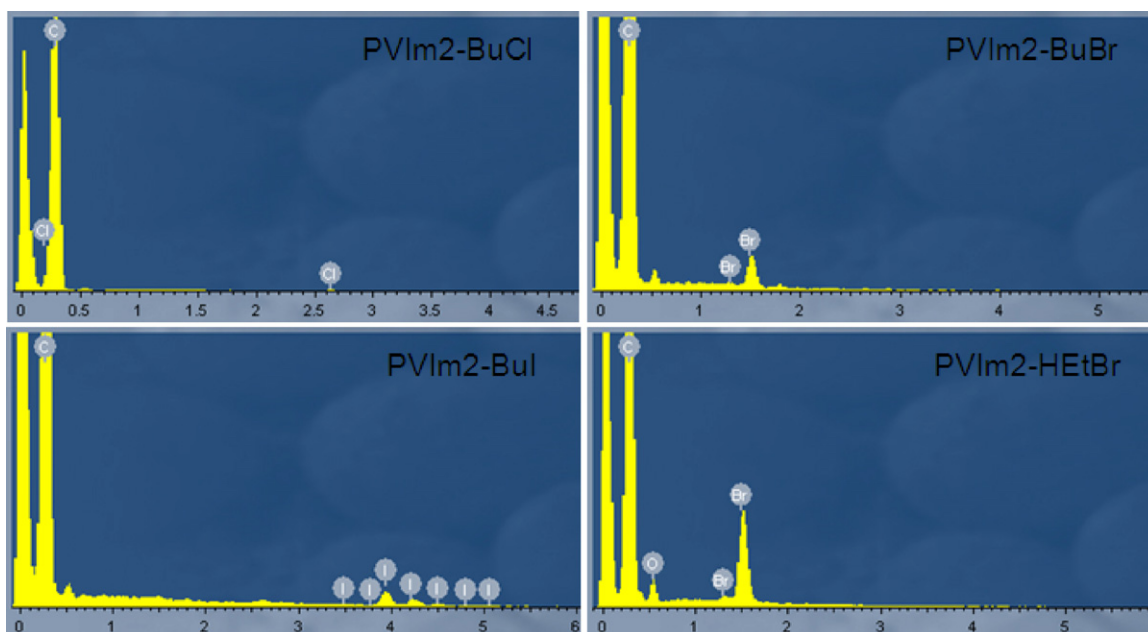


Fig. 2. EDS spectra of PVIm2-BuCl, PVIm2-BuBr, PVIm2-BuI and PVIm2-HEtBr.

After surface modification, using bromobutane, of the as-obtained PVIm beads with various textural properties, the resulting heterogeneous catalysts were used to catalyze the cycloaddition reaction of CO₂ on AGE. As demonstrated in Table 1, the IL-immobilization amount varied in the order of PVIm2 > PVIm1 > PVIm3 > PVIm4, while AGE conversion varied in the order of PVIm2 > PVIm3 > PVIm1 > PVIm4. This difference is related to a combination of molecular composition and polymer matrix texture effects. In general, a low imidazole moiety content and low PVIm surface area resulted in a low IL content, and thus a low AGE conversion. For instance, PVIm4 possessing the lowest surface area owing to its non-porous texture, directly leading to the lowest amount of imidazolium salts, showed the poorest catalytic reactivity (9% AGE conversion). In addition, a small pore size hinders free diffusion of substances, owing to confinement effects, resulting in decreased IL-immobilization and AGE conversion. With regard to PVIm1, although the support matrix possessed the lowest surface area and smallest pore size, the higher imidazole content resulted in PVIm1 exhibiting a relatively high IL-immobilized amount. However, the resulting PVIm1-BuBr catalyst produced the lower AGE

conversion among PVImx-BuBr catalysts, presumably due to confinement effects rendered by the narrow pore sizes within the polymer matrix. In comparison with PVIm1, although PVIm2 used a lower imidazole content, its higher surface area and larger pore size resulted in PVIm2-BuBr producing higher IL-immobilization; thereby leading to higher AGE conversion. Although PVIm3 possessed the highest surface area of the PVIm beads tested and had similar pore size to that of PVIm2, PVIm3 had a low level of IL-immobilization and low AGE conversion. As PVIm3 had the lowest imidazole content, the results suggest that the *N*-vinylimidazole played a major role in the IL-grafting process. Since PVIm2 provided the highest levels of IL-immobilization and catalytic activity, PVIm2 was selected as the polymer support to be used in the following parts of this study (Table 2).

3.3. Effect of alkyl halide on catalytic activity of PVIm2-RX

To investigate the effects of molecular compositions (alkyl chain length and anion type) of grafted ILs on catalytic reactivity, a variety of PVIm2-RXs were employed as heterogeneous catalysts in

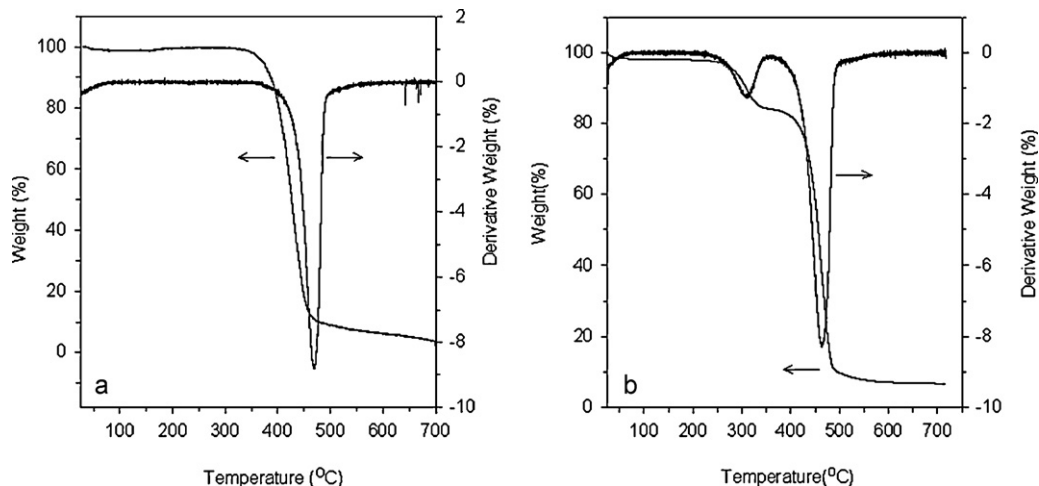


Fig. 3. TGA traces of PVIm2 (a) and PVIm2-BuBr beads (b).

Table 2
Element analysis of PVIm2-RX (X = halogen).

Catalyst	N (%)	C (%)	H (%)	X (%)	Immobilized IL amount (mmol g ⁻¹)
PVIm2-EtBr	2.89	83.90	5.04	8.17	1.02
PVIm2-BuBr	2.83	84.73	5.08	7.36	0.92
PVIm2-HexBr	2.80	85.02	5.28	6.90	0.86
PVIm2-OctBr	2.74	84.98	5.53	6.75	0.84
PVIm2-BuCl	2.95	88.09	5.49	3.46	0.97
PVIm2-Bul	2.67	80.42	4.81	12.1	0.95

cycloaddition reactions. All reactions were performed using the same conditions (110 °C, 1.34 MPa, 6 h) and the same amounts of catalysts and AGE. As shown in Table 3, AGE conversions ranged from 38% to 92% of total available AGE with >99% AGC selectivities. The high selectivities indicate a negligible creation of byproducts in the cycloaddition reactions.

Coupling reactions catalyzed by PVIm2-EtBr, PVIm2-BuBr, PVIm2-HexBr, and PVIm2-OctBr produced AGE conversions of 77%, 85%, 87%, and 82% of the available AGE, respectively (Table 3, runs 1, 2, 3, and 4, respectively). These results suggest that AGE conversion increases with increasing alkyl chain length (from -Et, to -Bu, to -Hex) in the immobilized alkyl halides. However, when the alkyl chain length increased to eight carbons (-Oct), AGE conversion decreased. These results are in agreement with previous reports on the effects of alkyl chain length [27,33]. It is postulated that increasing the bulkiness of the alkyl chain, which more easily forces the halide ions away from the cation, results in a decreasing electrostatic interaction between anion and cation and consequently increasing the availability of the anion. Immobilizing a long alkyl chain (e.g., -Oct) may limit the diffusion of molecules in the polymer matrix pore; thus, slowing the corresponding reaction and leading to lower AGE conversion than that using shorter chain immobilized alkyl halides.

The investigation into the effects of anions, derived from the immobilized alkyl halide, on the catalytic performances of PVIm2-RX used PVIm2-RXs combined with different halide anions [Cl⁻ (PVIm2-BuCl), Br⁻ (PVIm2-BuBr), and I⁻ (PVIm2-Bul)] in cycloaddition reactions between AGE and CO₂. As shown in Table 3, PVIm2-Bul and PVIm2-BuBr exhibited markedly higher catalytic activity than PVIm2-BuCl. The AGE conversions for PVIm2-BuCl, PVIm2-BuBr, and PVIm2-Bul were 38%, 85% and 92%, respectively (Table 3, runs 5, 2, and 6). These marked differences may reflect the nucleophilicity of the anions in the immobilized alkyl halides. The ion radii of Cl⁻, Br⁻, and I⁻ increase and their electronegativity decrease in that order; thus, anion movement away from the imidazole cation in the order of I⁻ > Br⁻ > Cl⁻ reflects their nucleophilicity order. Generally, anions with higher nucleophilicity are favored for AGE conversion [34], a finding that is supported by the increases in AGE conversion (in the order of I⁻ > Br⁻ > Cl⁻) observed in this study.

The PVIm2-Bul catalyst showed the highest AGE conversion (92%) as well as the highest selectivity (99.7%) among the PVIm2-RX catalysts tested. In addition, the turn over number (TON) showed

Table 3
Effect of PVIm2-RX on AGE conversion.

Run	Catalyst	Conversion (%)	Selectivity (%)	TON
1	PVIm2-EtBr	77	>99	60.2
2	PVIm2-BuBr	85	>99	74.0
3	PVIm2-HexBr	87	>99	80.7
4	PVIm2-OctBr	82	>99	77.8
5	PVIm2-BuCl	38	89	28.4
6	PVIm2-Bul	92	>99	77.6

Reaction condition: AGE = 40 mmol; temperature = 110 °C; CO₂ pressure = 1.34 MPa; time = 6 h. TON = (moles of AGC)/(moles of immobilized imidazolium salts).

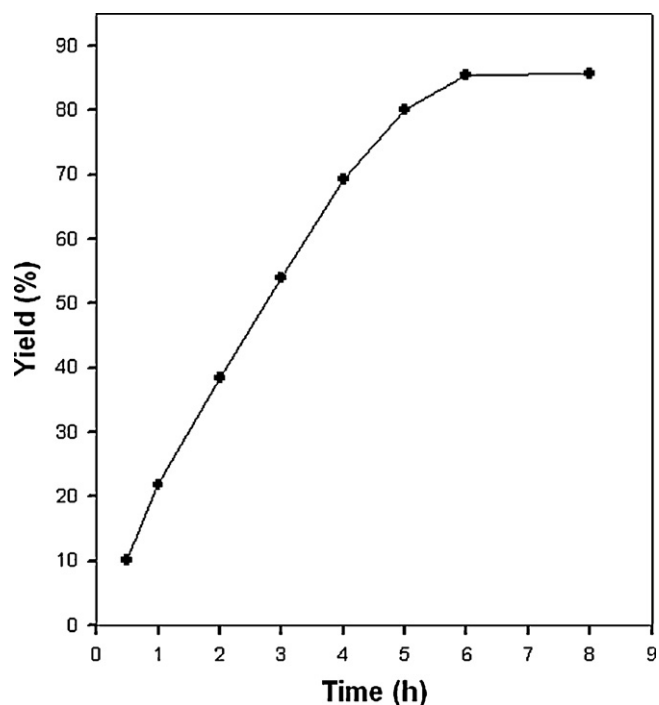


Fig. 4. Time variant yield for PVIm2-BuBr at 110 °C and CO₂ pressure of 1.34 MPa.

the same anion order as the AGE conversion. Of the PVIm2-RX tested, PVIm2-BuBr demonstrated the higher TON (74.0), which was markedly higher than that obtained using the same IL immobilized on commercial silica (TON = 45.5) [35] and on the silicate MCM-41 (TON = 26.6) [36].

3.4. Effect of reaction parameters on the catalytic activity of PVIm2-BuBr

Since the better catalytic activity was obtained with PVIm2-BuBr, the effects of reaction parameters (temperature, time, and CO₂ pressure) were examined using a PVIm2-BuBr-based catalytic system. Initially, the relationship between AGE conversion and reaction time was investigated. Fig. 4 shows that AGE conversion increased with reaction duration up to a reaction time of 6 h, after which AGE conversion did not increase and reaction rate slowed. The results suggest that the CO₂ fixation on AGE was completed within 6 h. Thus, assessments of the other reaction parameters used 6 h reaction times.

The results in Table 4 show that reaction temperature has a strong effect on AGE conversion (runs 2a, 2b, and 2c). In catalytic reactions carried out at 90 °C, 100 °C, and 110 °C, AGE conversions were 49%, 60%, and 65%, respectively. This temperature and conversion rate relationship is attributed to higher reactivity at higher

Table 4
Effect of reaction parameter on catalytic activity.

Run	Temperature (°C)	Pressure (MPa)	Conversion (%)	Selectivity (%)
2a	90	0.86	49	98
2b	100	0.86	60	>99
2c	110	0.86	65	>99
2d	110	1.34	85	>99
2e	110	1.62	94	>99
2f	110	1.82	98	>99
2g	110	2.17	97	99
2h	120	0.86	63	98
2i	130	0.86	59	97

Reaction condition: PVIm2-BuBr = 0.5 g; AGE = 40 mmol; time = 6 h.

Table 5
Effect of catalyst with or without hydroxyl group on AGE conversion.

Catalyst	Conversion (%)	Selectivity (%)
PVIm2-EtBr	77	>99
PVIm2-HEtBr	93	>99
PVIm2-EtBr/EtOH ^a	87	>99
PVIm2-EtBr/H ₂ O ^b	79	>99
PVIm2-EtBr/H ₂ O ^c	89	>99
PVIm2-EtBr/H ₂ O ^d	93	99
PVIm2-EtBr/H ₂ O ^e	95	91

Reaction condition: catalyst = 0.5 g; temperature = 110 °C; pressure = 1.34 MPa; time = 6 h.

^a Ethanol = the same molar amount of immobilized IL.

^b Mole ratio (water:immobilized IL amount) = 0.5.

^c Mole ratio (water:immobilized IL amount) = 1.0.

^d Mole ratio (water:immobilized IL amount) = 5.0.

^e Mole ratio (water:immobilized IL amount) = 10.0.

temperatures. Nevertheless, at reaction temperatures of 120 °C (run 2h) and 130 °C (run 2i), AGE conversion decreased to 63% and 59%, respectively. Although higher reaction system temperatures increase reactivity, the solubility of the CO₂ gas phase in the reaction system decreases with increasing temperatures.

The effects of CO₂ pressure were also investigated. As shown in runs 2c and 2d in Table 4, when the reaction CO₂ pressure increased from 0.86 MPa to 1.34 MPa, AGE conversion increased from 65% to 85%. At higher pressures, 1.62 MPa and 1.82 MPa, AGE conversion increased to 94% and 98%, respectively (Table 4, runs 2e and 2f). Similar effects of CO₂ pressure on catalytic activity have been observed in other catalytic systems [25,37]. During such catalytic reactions, a higher CO₂ pressure can effectively increase the solubility of CO₂ in AGE and thus results in the acceleration of the cyclic carbonate formation. Here, when the catalytic reaction was carried out at a CO₂ pressure of 2.17 MPa, the AGE conversion lowered slightly (97%; Table 4, run 2g) compared with that in the reaction carried out at 1.82 MPa (run 2f). The results indicate that AGE conversion does not keep increasing with pressure, suggesting that a high CO₂ pressure may retard the interaction between AGE and the catalyst. Such retardation may be related to a dilution effect occurring when the reaction pressure reaches equilibrium at a specific temperature, which has been reported to result in lower AGE conversion [37].

3.5. Effect of hydroxyl group on catalytic activity

Sun et al. [38] reported that coordination of an IL hydroxyl group with the halide ion of a hydroxyl-functionalized imidazolium-based IL (HEMIMBr) could initiate reaction activity in the cycloaddition of CO₂ to epoxide. In addition, they reported that incorporation of water or -OH containing compounds into reaction systems can facilitate the cycloaddition reaction in the presence of quaternary ammonium, imidazolium, or phosphonium halide homogeneous catalysts [39]. Furthermore, hydroxyl groups, such as silanols on amine-functionalized SiO₂ catalysts and hydroxyl-functionalized imidazolium-based ILs immobilized on polystyrene, also have been reported to facilitate the chemical fixation of CO₂ [40,41]. Thus, we investigated the role of hydroxyl groups derived from PVIm2-HEtBr, ethanol, and water in the cycloaddition reaction.

The results in Table 5 show that PVIm2-HEtBr exhibits higher conversion (93%) and selectivity (99.8%) in the cycloaddition reaction than the PVIm2-EtBr catalyst (77% conversion and 99.5% selectivity). Surprisingly, by adding a small amount of ethanol or water (i.e., the same amount as the catalyst) into the reaction system, the activity of PVIm2-EtBr was enhanced with AGE conversions of 87% and 89%, respectively; conversions that were higher than that of PVIm2-EtBr alone (77%). Similarly, product selectiv-

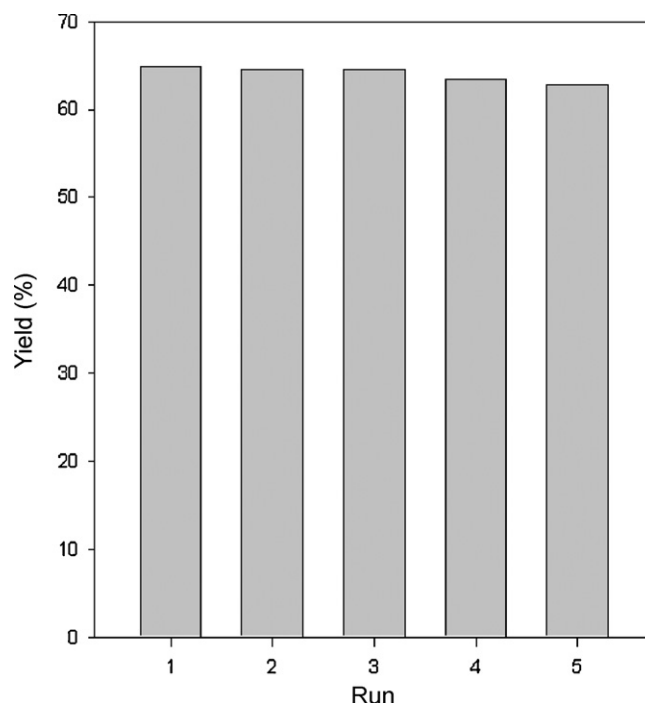


Fig. 5. Effect of recycle catalyst on AGE conversion.

ity was improved in the presence of hydroxyl groups (Table 5). In hydroxyl group-containing catalytic reaction systems, hydroxyl moieties and halide ions function as Lewis acid and Lewis basic sites, respectively, forming acid–base bifunctional catalysts. Their coordination was preferred to the cycloaddition reaction [42]. In the presence of ethanol or water, the H atoms derived from the water or ethanol molecules can coordinate with the O atoms of the epoxide through a hydrogen bond, resulting in the polarization of C–O bonds. At the same time, the halide anion makes a nucleophilic approach to the less sterically hindered C atom of the epoxide. As a result, the epoxide ring opens, leading to a high AGE conversion in the presence of hydroxyl groups [39]. Even though the involvement of water or ethanol into the catalytic reaction system can efficiently promote the catalytic activity, some byproducts might be generated simultaneously under the certain conditions. In our current study, the effect of water amount on the cycloaddition reaction in the presence of PVIm-EtBr was investigated. As is shown in Table 5, when the mole ratio of employed water to immobilized IL ranged from 0.5, 1.0 to 5.0, the AGE conversion increased from 79%, 89% to 93%, respectively. While all the responding selectivity kept above 99%, indicating negligible amount of byproducts. However, further increasing the molar ratio of water to immobilized ionic liquid to 10, the catalytic selectivity decreased to 91%, due to the formation of noticeable amount of glycol determined by GC–MASS analysis.

3.6. Catalyst recycling

To examine the reusability of the prepared catalysts, PVIm2-BuBr was used in reactions carried out for 6 h at 110 °C and under a CO₂ pressure of 0.86 MPa initial CO₂ pressure. After each reaction cycle, the catalyst was recovered by filtration and directly reused for another reaction. The yields of AGC from five consecutive runs are shown in Fig. 5. In each run, the AGC product selectivity remained constant (99%), and AGE conversion changed only slightly after four runs. The results indicate that PVIm2-BuBr exhibits excellent reusability and stability for repetitive use in cycloaddition reactions.

4. Conclusion

A series of highly cross-linked PVIm beads with grafted ILS were synthesized and used as catalysts in cycloaddition reactions of epoxide with CO₂. In an investigation of the effects of molecular composition of grafted ILS on the catalytic activity, it was observed that when the grafted ILS possess a more nucleophilic anion or a bulkier alkyl chain, the corresponding PVIm-RX heterogeneous catalyst exhibited higher activity. Investigation of various reaction parameters indicated that the AGE conversion was highest when the reaction was carried out at 110 °C and at 1.82 MPa of CO₂ pressure. It was also found that the addition of a small amount of ethanol or water into the reaction system could enhance catalytic activity. The incorporation of hydroxyl groups into the grafted ILS can also improve catalytic activity, evidenced by the observation that PVIm2-HEBr produced higher catalytic activity than PVIm2-EtBr. In addition, the textural properties of PVIm (pore size and specific area) affect the catalytic activity of PVIm-RX.

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