

## Lithium Chloride-Imidazolium Chloride Melts for the Coupling Reactions of Propylene Oxide and CO<sub>2</sub>

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A series of lithium chloride-imidazolium chloride (LiCl-[imidazolium]Cl) melts were prepared and their catalytic activities were evaluated for the coupling reactions of propylene oxide and CO<sub>2</sub>. At the constant mole of LiCl, the catalytic activities of LiCl-[imidazolium]Cl melts increased with increasing molar ratio of [imidazolium]Cl/LiCl up to 2, but thereafter decreased rapidly. The variation of alkyl groups on the imidazolium ring showed a negligible effect on the catalytic activity, but the number of alkyl groups present on the imidazolium cation exerts a pronounced effect. Catalysis and electrospray ionization tandem mass spectral analysis results of LiCl-[imidazolium]Cl melts imply that the activity of the melt is strongly related to the amount of LiCl<sub>2</sub><sup>-</sup> generated from the melt.

**Key Words** : Ionic liquids, Lithium chloride, Lithium dichloride, Carbon dioxide, Cyclic carbonates

### Introduction

The synthesis of 5-membered cyclic carbonates by the coupling reactions of epoxides with carbon dioxide has attracted much attention with regard to the reduction and utilization of CO<sub>2</sub>. Cyclic carbonates are being widely used as important components of electrolytes for lithium ion batteries and also as raw materials for the production of various chemicals including ethylene glycol esters, hydroxy-alkyl derivatives, carbamates, alkylene sulfides, polyurethanes, polyesters, and polycarbonates.<sup>1-4</sup>

In this regard, much effort has been devoted to the synthesis of cyclic carbonates utilizing the coupling reactions and, as a result, significant advances have been achieved in terms of catalyst development. The catalytic systems composed of transition metal halides (AlCl<sub>3</sub>, NiCl<sub>2</sub>, MoCl<sub>5</sub>, etc.) and Lewis bases such as amines or phosphines have been successfully employed in the selective formation of cyclic carbonates under a relatively mild condition.<sup>5-10</sup> Zinc(II) complexes have also been used as catalysts, owing to their high activity in the cyclization and copolymerization of CO<sub>2</sub> and epoxides.<sup>11-13</sup>

Recently, there have been a considerable number of articles regarding the use of ionic liquids (ILs) as catalysts and/or solvents in numerous homogeneous and/or heterogeneous reactions,<sup>14,15</sup> such as the coupling reactions of CO<sub>2</sub> with epoxides and Diels-Alder reactions.

Of various types of ILs used for the coupling reactions, imidazolium-based zinc tetrahalide catalysts are most intensively studied due to their outstanding catalytic activities for the coupling reactions.<sup>16,17</sup> In the continuous line of our study to develop high performance catalysts based on ILs, we have found that the activity of a lithium halide can also

be significantly enhanced by the combined use of an imidazolium halide.

Herein, we report the syntheses, reactivities, and spectroscopic characterizations of LiCl-imidazolium chloride (LiCl-[imidazolium]Cl) melts for the coupling reactions of propylene oxide and CO<sub>2</sub> to produce propylene carbonate (PC).

### Experimental Section

Solvents were freshly distilled before use according to the literature procedures.<sup>18</sup> Propylene oxide (PO), imidazole, 1-methylimidazole, 1,2-dimethylimidazole, and LiCl were purchased from Aldrich Chemical Co. and used without further purification. CO<sub>2</sub> was purchased from Sin Yang Gas Co. Imidazole hydrochloride ([HIm]Cl), 1-methylimidazole hydrochloride ([HMIm]Cl), 1-butyl-3-methylimidazolium chloride ([BMIm]Cl), and 1-butyl-2,3-dimethylimidazolium chloride ([BDMIm]Cl) were prepared according to the literature procedures.<sup>19-21</sup> Fourier Transform Infrared (FT-IR) spectra were recorded on a Nicolet 380 spectrophotometer (Thermo Electron Co.). To avoid contact with water and air, FT-IR measurements were performed using a specially designed IR cell equipped with two KRS-5 windows.<sup>22</sup> The thermal properties of LiCl-[imidazolium]Cl melts were determined using a TA Instruments Q10 differential scanning calorimeter (DSC) in the range of -90 to 200 °C at a scan rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. Electrospray ionization tandem mass (ESI-MS) spectra of LiCl-[imidazolium]Cl melts were collected on a Finnigan<sup>TM</sup> TSQ<sup>®</sup> Quantum Ultra<sup>TM</sup> triple quadrupole mass spectrometer. Analytes were detected in the negative mode at 4200 V. Full scan mode was used in the range of 30 to 600 m/z

and data were processed using Xcalibur V. 1.4.

**Synthesis of [BMIm]Cl:LiCl (1:1) melt.** In a 50 mL one-neck flask, [BMIm]Cl (3.49 g, 20 mmol) and LiCl (0.85 g, 20 mmol) were dissolved in methanol (10 mL) and stirred for 1 h at room temperature. After the reaction, the solvent was evaporated to give a pale yellow liquid. The same product was also obtained by heating the mixture of [BMIm]Cl and LiCl at 100 °C for 1 h. Negative-ions ESI-MS spectra:  $m/z$  76.82 [LiCl<sub>2</sub>]<sup>-</sup>, 23%;  $m/z$  160.80 [Li<sub>3</sub>Cl<sub>4</sub>]<sup>-</sup>, 100%;  $m/z$  208.91 [[BMIm]Cl<sub>2</sub>]<sup>-</sup>, 37%.

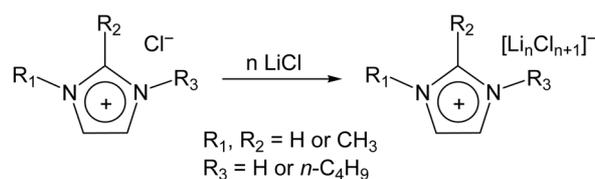
Other LiCl-[imidazolium]Cl melts were prepared in an analogous manner to that employed for the synthesis of [BMIm]Cl:LiCl (1:1) melt. [BMIm]Cl:LiCl (1:2) melt (White solid. Negative-ions ESI-MS spectra:  $m/z$  76.98 [LiCl<sub>2</sub>]<sup>-</sup>, 100%;  $m/z$  118.92 [Li<sub>2</sub>Cl<sub>3</sub>]<sup>-</sup>, 39%;  $m/z$  162.86 [Li<sub>3</sub>Cl<sub>4</sub>]<sup>-</sup>, 42%;  $m/z$  204.92 [Li<sub>4</sub>Cl<sub>5</sub>]<sup>-</sup>, 94%;  $m/z$  246.91 [Li<sub>5</sub>Cl<sub>6</sub>]<sup>-</sup>, 53%;  $m/z$  337.00 [[BMIm]Cl·Li<sub>3</sub>Cl<sub>4</sub>]<sup>-</sup>, 48%); [BMIm]Cl:LiCl (2:1) melt (Pale yellow liquid. Negative-ions ESI-MS spectra:  $m/z$  76.99 [LiCl<sub>2</sub>]<sup>-</sup>, 100%;  $m/z$  209.07 [[BMIm]Cl<sub>2</sub>]<sup>-</sup>, 79%;  $m/z$  383.16 [[BMIm]<sub>2</sub>Cl<sub>3</sub>]<sup>-</sup>, 33%); [BDMIm]Cl:LiCl (1:2) melt (White solid. Negative-ions ESI-MS spectra:  $m/z$  76.96 [LiCl<sub>2</sub>]<sup>-</sup>, 100%;  $m/z$  118.96 [Li<sub>2</sub>Cl<sub>3</sub>]<sup>-</sup>, 37%;  $m/z$  204.90 [Li<sub>4</sub>Cl<sub>5</sub>]<sup>-</sup>, 84%;  $m/z$  246.89 [Li<sub>5</sub>Cl<sub>6</sub>]<sup>-</sup>, 43%;  $m/z$  351.04 [[BDMIm]Cl·Li<sub>3</sub>Cl<sub>4</sub>]<sup>-</sup>, 45%); [BDMIm]Cl:LiCl (1:1) melt (Pale yellow liquid. Negative-ions ESI-MS spectra:  $m/z$  76.97 [LiCl<sub>2</sub>]<sup>-</sup>, 100%;  $m/z$  187.92 [[BDMIm]Cl<sub>2</sub>]<sup>-</sup>, 32%;  $m/z$  223.10 [[BDMIm]<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup>, 31%;  $m/z$  309.05 [[BDMIm]Cl·Li<sub>2</sub>Cl<sub>3</sub>]<sup>-</sup>, 27%;  $m/z$  351.09 [[BDMIm]Cl·Li<sub>3</sub>Cl<sub>4</sub>]<sup>-</sup>, 27%;  $m/z$  411.13 [[BDMIm]<sub>2</sub>Cl<sub>3</sub>]<sup>-</sup>, 31%); [BDMIm]Cl:LiCl (2:1) melt (Pale yellow liquid. Negative-ions ESI-MS spectra:  $m/z$  76.98 [LiCl<sub>2</sub>]<sup>-</sup>, 100%;  $m/z$  223.08 [BDMIm]Cl<sub>2</sub><sup>-</sup>, 76%;  $m/z$  413.19 [[BDMIm]<sub>2</sub>Cl<sub>3</sub>]<sup>-</sup>, 62%).

**Coupling reactions of PO with CO<sub>2</sub>.** All the coupling reactions were conducted in a 200 mL stainless-steel bomb reactor equipped with a magnet bar and an electrical heater. The reactor was charged with an appropriate catalyst and PO and pressurized with CO<sub>2</sub> (4.14 MPa). The bomb reactor was then heated to a specified reaction temperature with the addition of CO<sub>2</sub> from a reservoir tank to maintain a constant pressure. After the completion of the reaction, the product mixture was analyzed using a Hewlett Packard 6890 gas chromatograph equipped with a flame ionized detector and a DB-wax column (30 m × 0.32 mm × 0.25 μm), and a Hewlett Packard 6890-5973 MSD GC-mass spectrometer.

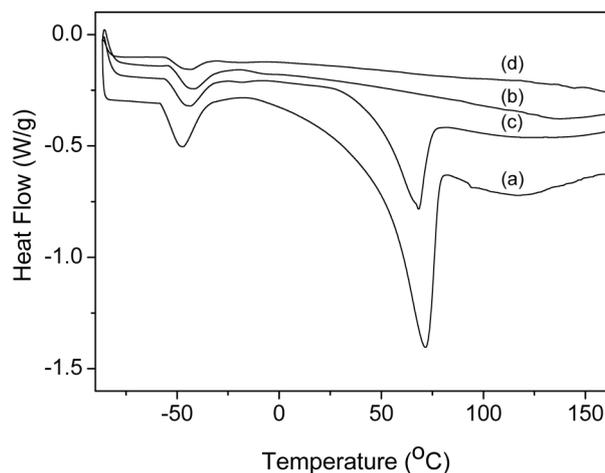
## Results and Discussion

As shown in Scheme 1, a series of LiCl-[imidazolium]Cl melts were prepared by reacting LiCl with [HIm]Cl, [HMIm]Cl, [BMIm]Cl, or [BDMIm]Cl in methanol at room temperature. The same melts were also obtained in the absence of a solvent by heating the mixture of LiCl and [imidazolium]Cl at temperature higher than the melting point of each [imidazolium]Cl.

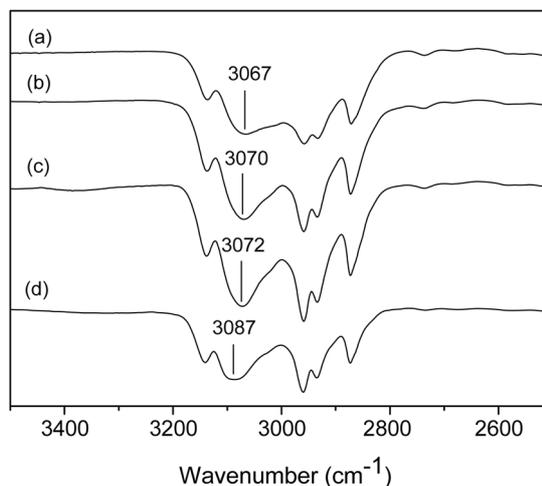
The physical properties of these melts were significantly varied with the molar ratio of [imidazolium]Cl/LiCl. At the molar ratio smaller than 1, the melt exists as a solid. On the



**Scheme 1.** Syntheses of LiCl-[imidazolium]Cl melts.



**Figure 1.** DSC data of (a) [BMIm]Cl and LiCl-[BMIm]Cl melts (b)-(d): the molar ratios of [BMIm]Cl/LiCl are (b) 0.5, (c) 1, and (d) 2.



**Figure 2.** FT-IR spectra of LiCl-[imidazolium]Cl melts. Molar ratio of LiCl to [BMIm]Cl is (a) 0, (b) 0.5, (c) 1, and (d) 2.

contrary, at the molar ratios of 1 or higher, the melts become viscous liquids. The viscosity of the melt decreases with increasing molar ratio of [imidazolium]Cl/LiCl. The thermal behaviors of these melts were studied by DSC in the range of -90 to 200 °C. Figure 1 shows that the LiCl-[BMIm]Cl melts with the molar ratio of 1 exhibits both glass transition and melting temperatures at around -45 and 70 °C, respectively, whereas other melts display only glass transition temperatures at around -45 °C. It is likely that the physical and thermal properties of LiCl-[imidazolium]Cl melts seem to be significantly affected by the variation of the molar ratio

**Table 1.** Coupling reactions of CO<sub>2</sub> and PO in the presence of various catalytic systems<sup>a</sup>

Catalyst	Yield of PC (%)
LiCl	0
[BMIm]Cl	0
LiCl + [BMIm]Cl	3.1 <sup>b,c</sup>
LiCl-[BMIm]Cl melt	58.8 <sup>c</sup>

<sup>a</sup>Molar ratio of PO to catalyst was set at 150. The amount of LiCl was set at 2.36 mmol. Reactions were carried out at 100 °C and 4.14 MPa of CO<sub>2</sub> for 1 h. <sup>b</sup>Admixture. <sup>c</sup>Molar ratio of [BMIm]Cl/LiCl = 1.

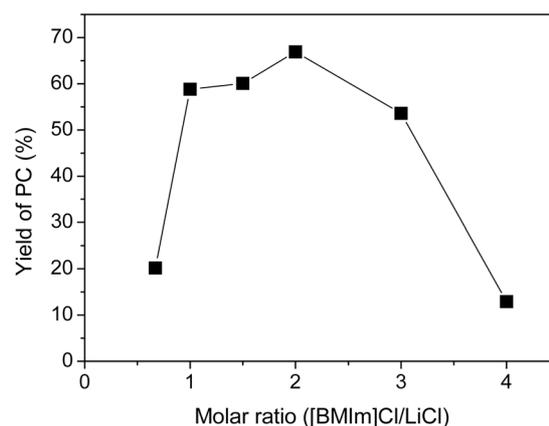
of [imidazolium]Cl/LiCl.

To investigate the formation of LiCl-[imidazolium]Cl melts, FT-IR studies were conducted with LiCl-[BMIm]Cl melts with various molar ratios of [BMIm]Cl/LiCl. As can be seen in Figure 2, all the LiCl-[BMIm]Cl melts display completely different FT-IR spectra from either [BMIm]Cl or LiCl, indicating the strong interaction of LiCl with [BMIm]-Cl and consequently the formation of new species. The broad peaks appeared in the range of 3000-3100 cm<sup>-1</sup> can be assigned as the peak associated with the interaction of aromatic C-H with Cl<sup>-</sup>.<sup>23-25</sup> It is noteworthy that the Cl<sup>-</sup> interaction band at 3067 cm<sup>-1</sup> shifted to a higher frequency upon interaction with LiCl. The degree of the shift increased with increasing content of LiCl in the melt.

The catalytic activities of LiCl-[imidazolium]Cl melts were evaluated for the coupling reactions of CO<sub>2</sub> with PO at 100 °C for 1 h with the molar ratio of PO/catalyst at 150. As shown in Table 1, both [BMIm]Cl and LiCl were completely inactive when they were used alone. The combined use of [BMIm]Cl and LiCl as a simple powdered mixture also showed extremely low activity, but the IL melt obtained from LiCl and [BMIm]Cl in methanol exhibited a dramatic synergy effect for the coupling reaction, implying the important role of an imidazolium cation in the catalysis. Such a synergy effect can be possibly attributed to the enhanced nucleophilicity of Cl<sup>-</sup> resulting from the formation of a new IL species.

The catalytic activity of a LiCl-[BMIm]Cl melt was greatly influenced by the content of [BMIm]Cl in the melt. At the constant mole of LiCl, the activity of the LiCl-[BMIm]Cl melt increased with increasing molar ratio of [BMIm]Cl/LiCl up to 2, but thereafter decreased rapidly, possibly due to the reduced Lewis acidity of the melt with the molar ratios above 2 (Fig. 3).

Previous reports by Kisch on the synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides suggested the parallel requirement of both Lewis acid activation of epoxides and Lewis base activation of CO<sub>2</sub>.<sup>7</sup> It is also reported that the Lewis acidity of a metal chloride such as AlCl<sub>3</sub> can be significantly altered by the interaction with an [imidazolium]Cl.<sup>26</sup> In the case of LiCl-[imidazolium]Cl melt catalyst, lithium center in [Li<sub>n</sub>Cl<sub>n+1</sub>]<sup>-</sup> is expected to act as a Lewis acid to activate an epoxide through an interaction with the oxygen atom of the epoxide, and the chloride ion in [Li<sub>n</sub>Cl<sub>n+1</sub>]<sup>-</sup> is believed to function as a Lewis base to assist ring-opening and CO<sub>2</sub> activation. In consideration of this, it is likely that

**Figure 3.** Dependence of activities of coupling reaction on the molar ratio of LiCl to [BMIm]Cl. The amount of LiCl was set at 2.36 mmol. Reactions were carried out at 100 °C and 4.14 MPa of CO<sub>2</sub> for 1 h.

the most active LiCl-[BMIm]Cl melt ([BMIm]Cl/LiCl = 2) has the most suitable combination of Lewis acidity and Lewis basicity (or nucleophilicity) for the catalysis.

The importance of Lewis acidity in the coupling reaction was further supported from the experiments conducted in the presence of MCl-[BMIm]Cl (M = Li, Na, K, Rb, Cs). As listed in Table 2, the activity of the melt catalyst decreased with the increasing size of the alkali metal ion, *i.e.*, with the decreasing Lewis acidity of the catalyst, again demonstrating the importance of the Lewis acidity.

The effect of alkyl substituent on the imidazolium ring on the coupling reaction of PO with CO<sub>2</sub> was also investigated in the presence of a melt ([imidazolium]Cl/LiCl = 1) at 100 °C. The degree of alkyl substitution on the imidazolium ring exerted a pronounced effect on the catalytic activity. As

**Table 2.** Effect of alkali metal on the coupling reaction<sup>a</sup>

Catalyst	Yield of PC (%)
LiCl-[BMIm]Cl melt	58.8
NaCl-[BMIm]Cl melt	49.5
KCl-[BMIm]Cl melt	39.6
RbCl-[BMIm]Cl melt	17.8
CsCl-[BMIm]Cl melt	5.9

<sup>a</sup>Molar ratio of PO/[BMIm]Cl/MCl was set at 150/1/1 (M = Li, Na, K, Rb, Sc). Reactions were carried out at 100 °C and 4.14 MPa of CO<sub>2</sub> for 1 h.

**Table 3.** Effect of alkyl substituent on the imidazolium cation to the coupling reaction<sup>a</sup>

Melt	Yield of PC (%)
LiCl-[HIm]Cl	3.7
LiCl-[HMIm]Cl	7.2
LiCl-[HDMIm]Cl	57.9
LiCl-[BMIm]Cl	58.8
LiCl-[DMEIm]Cl	60.6
LiCl-[BDMIm]Cl	61.7

<sup>a</sup>Molar ratio of [imidazolium]Cl/LiCl = 1. Molar ratio of PO to catalyst was set at 150. The amount of LiCl was set at 2.36 mmol. Reactions were carried out at 100 °C and 4.14 MPa of CO<sub>2</sub> for 1 h.

listed in Table 3, the melt with two or three alkyl groups on the imidazolium ring showed high activity for the coupling reaction, whereas the melt containing none or one alkyl group on the imidazolium ring exhibited extremely low activity. However, the variation of alkyl group did not give any noticeable change in activity. These results strongly suggest that the electron donation from the alkyl group or groups to the imidazolium ring is of pivotal importance in the catalysis. The order of reactivity was found in the order of increasing electron density on the imidazolium ring: 1-butyl-2,3-dimethylimidazolium chloride ([BDMIIm]Cl)  $\sim$  1,2-dimethyl-3-ethylimidazolium chloride ([DMEIm]Cl)  $>$  1-butyl-3-methylimidazolium chloride ([BMIm]Cl)  $\sim$  1,2-dimethylimidazole hydrochloride ([HDMIIm]Cl)  $>$  1-methylimidazole hydrochloride ([HMIIm]Cl)  $>$  imidazole hydrochloride ([HIm]Cl).

In order to have a better understanding of the nature of LiCl-[imidazolium]Cl melts, ESI-MS spectral analysis was undertaken with the melts of various molar ratios of [BMIm]Cl/LiCl and [BDMIIm]Cl/LiCl. The major lithium species observed in the ESI-MS spectrum of the melt with the molar ratio of [BMIm]Cl/LiCl at 0.5 were  $\text{LiCl}_2^-$  and tetranuclear lithium species,  $\text{Li}_4\text{Cl}_5^-$ . However, at the molar ratios of 1 and 2, the major lithium species were found as  $\text{Li}_3\text{Cl}_4^-$  and  $\text{LiCl}_2^-$  for 1 and  $\text{LiCl}_2^-$  for 2, respectively. The nuclearity of lithium species seems to decrease with increasing molar ratio of [BMIm]Cl/LiCl. These results can be rationalized by assuming that the dissociation of ionic crystal structure of LiCl can be facilitated by the interaction with [BMIm]Cl. Interestingly, the melt prepared from equal moles of [BDMIIm]Cl and LiCl generates  $\text{LiCl}_2^-$  as the major species, suggesting that the additional electron donation from the methyl group at C-2 position is highly effective in dissociating the crystal structure of LiCl, thereby generating mononuclear  $\text{LiCl}_2^-$  species.

From the experimental and ESI-MS spectral results, it is concluded that the catalytic activity of the melt is strongly affected by the nuclearity of lithium species present in the melt and the most active lithium species for the coupling reaction is the mononuclear  $\text{LiCl}_2^-$ . The formation of  $\text{LiCl}_2^-$  can be facilitated by increasing either the molar ratio of [imidazolium]Cl/LiCl or the electron density on the imidazolium ring by introducing alkyl groups. The interaction of LiCl with an [imidazolium]Cl is expected to increase the bond distance of Li-Cl and the nucleophilicity of  $\text{Cl}^-$ . The increased nucleophilicity of  $\text{Cl}^-$  in  $\text{LiCl}_2^-$  is supported by the B3LYP/6-311+G(d) level calculations and natural population analysis. The distance of Li-Cl and the charge on the  $\text{Cl}^-$  of LiCl is increased from 2.025 Å and -0.925 to 2.162 Å and -0.934 in  $\text{LiCl}_2^-$  (Table 4). The electrostatic potentials plotted for LiCl and  $\text{LiCl}_2^-$  also suggests that, as the number of  $\text{Cl}^-$  increases, the negative charge character at chlorine atoms and the bond length of Li-Cl increase at the same time.

The effect of molar ratio of PO/catalyst on the coupling reaction of PO with  $\text{CO}_2$  was studied in the presence of a melt ([BMIm]Cl/LiCl = 2) at 100 °C and 4.14 MPa for 1 h.

**Table 4.** Results of B3LYP/6-311+G(d) level calculations<sup>a</sup>

	LiCl	$\text{LiCl}_2^-$
Bond distance (Å)	2.025	2.162
Charges at Li	0.925	0.868
Charges at Cl	-0.925	-0.934

<sup>a</sup>Charges were obtained by natural population analysis.

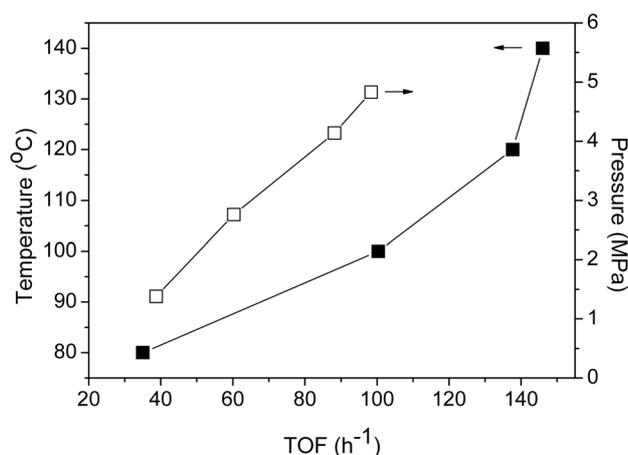
**Table 5.** Dependence of activities of coupling reaction on the molar ratio of PO to catalyst<sup>a</sup>

PO/catalyst	Conversion (%)	TOF ( $\text{h}^{-1}$ ) <sup>b</sup>
300	8.2	24.6
150	66.9	100.4
75	90.4	67.8
50	89.8	44.9

<sup>a</sup>Molar ratio of [BMIm]Cl/LiCl = 2. The amount of PO was set at 20 g (0.345 mol). Reactions were carried out at 100 °C and 4.14 MPa of  $\text{CO}_2$  for 1 h. <sup>b</sup>TOF ( $\text{h}^{-1}$ ): moles of PC/moles of catalyst/h.

The molar ratio of PO to catalyst was varied in the range of 50-300 and the results are listed in Table 5. At the constant mole of PO, the conversions of PO decreased continuously with the increase of the molar ratio of PO/catalyst, indicating that the rate of the coupling reaction is strongly dependent on the catalyst concentration. However, the turnover frequency (TOF) increased with increasing molar ratio up to 150 and then decreased on further increase of the molar ratio. The highest TOF of  $100.4 \text{ h}^{-1}$  was achieved at the molar ratio of 150. The drop in TOF at the molar ratio of 300 seems to be largely attributed to the decreased reaction rate arising from the use of small amount of catalyst (0.46 g, 1.17 mmol). With such a low concentration of catalyst, the chance of PO to interact with the catalyst will be greatly reduced. As the TOF is the multiplication of the molar ratio of PO/catalyst by the conversion, higher TOF does not necessarily mean the higher conversion.

As can be seen in Figure 4, the effects of temperature and pressure were also investigated with the LiCl-[BMIm]Cl



**Figure 4.** Effect of temperature and pressure on the coupling reaction of  $\text{CO}_2$  and PO. Molar ratio of [BMIm]Cl to LiCl was set at 2. The amount of LiCl was set at 2.36 mmol. Reactions were carried out at 100 °C and 4.14 MPa of  $\text{CO}_2$  for 1 h.

melt ([BMIm]Cl/LiCl = 2). The TOF increased steeply with increasing temperature and pressure. The formation of PC was more strongly dependent on the temperature than the pressure of CO<sub>2</sub>. No side product was observed under the experimental conditions.

### Conclusions

Various LiCl-[imidazolium]Cl melts were prepared and the catalytic activities of these melts were evaluated for the coupling reactions of PO and CO<sub>2</sub>. The catalytic activities of LiCl-[imidazolium]Cl melts were found to increase with increasing molar ratio of [imidazolium]Cl/LiCl up to 2 and then decreased on further increase of the molar ratio. Although the variation of alkyl groups showed a negligible effect on the catalytic activity, the degree of alkyl substitution on the imidazolium cation exhibited a pronounced effect, resulting in higher activity with more alkyl-substituted imidazolium. Catalysis and ESI-MS spectral analysis results of LiCl-[BMIm]Cl melts show that the activity of the melt is strongly related to the amount of LiCl<sub>2</sub><sup>-</sup> generated from the melt and the highest activity can be achieved at the molar ratio of [BMIm]Cl/LiCl = 2.

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