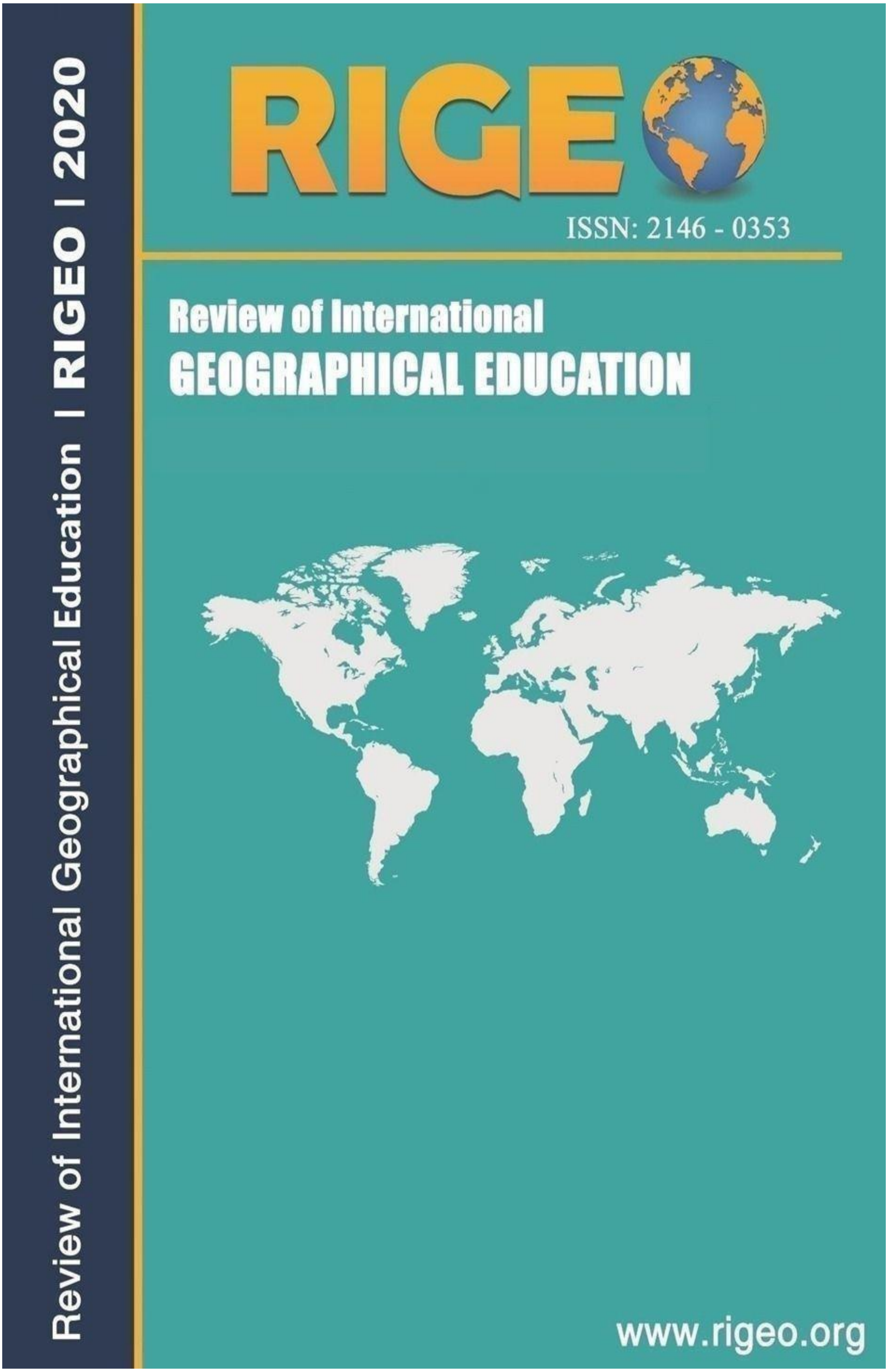

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A process where ionic liquids catalyze the cycloaddition of carbon dioxide to propylene oxide

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Abstract:

Experiments on the cycloaddition of carbon dioxide to propylene oxide at room temperature ionic liquids based on 1-n-butyl-3-methylimidazolium and n-butylpyridinium salts have been conducted, all without the need of additional organic solvents. The most active catalyst, with about 100% selectivity, was determined to be 1-n-butyl-3-methylimidazolium tetrafluoroborate. A high conversion rate required an appropriate molar ratio of CO to propylene oxide. The catalyst for the process, an ionic liquid, may be recycled. Five-membered cyclic carbonates are excellent aprotic polar solvents and are used extensively as intermediates in the production of drugs and pesticides. The formation of cyclic carbonates *via* cycloaddition of epoxides and carbon dioxide, which is one of the routes for carbon dioxide chemical fixation,1 has received much attention as regards the utilization of carbon resources and the reduction of CO pollution.

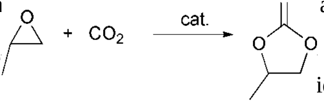
Cycloaddition between epoxides and carbon dioxide using org2anic and inorganic compounds such as metal halides,2,3 onium halides, metal complexes4h6 and MgO,7 Mg*È*Al mixed oxides,8 KI*È*ZnO,9 *etc*. as catalysts generally occur at low rates unless high temperature, high carbon dioxide pressure, long reaction time and/or high catalyst/substrate ratios are used. More recently, propylene carbonate has also been syn- thesized from supercritical carbon dioxide (sc-CO)*È*propylene oxide mixture with phthalocyaninatoaluminium chloride*È* tetrabutylammonium bromide as catalyst, which necessitates a

Results and discussion

E†ect of the ionic liquid and its amount on the cyclo2addition

The results of the cycloaddition of CO to propylene oxide in a series of ionic liquids consisting of BMIm` or BPy` and Cl~, BF ~, PF ~ (Table 1) indicated that both the cations and anions have a strong impact on the catalytic 2activities, entries 1*È*4. BMImPF and BPyBF , used as catalysts, showed the lowest catalytic activities with that of BMImPF being the worst. The conversion of propylene oxide could, however, be greatly increas4ed if 6BMImCl catalyst was employed, and even better catalytic performance was achieved with the ionic liquid consisting of the BMIm` cation and BF ~anion (entry 4).
6 4

The e†ect of the amount of BMImBF catalyst on the cycloaddition was examined. The conversion of propylene oxide increased with increasing amount of BMImBF4 under the same6 reaction conditions, entries 5*È*7, although the TONs
higher reaction pressure and larger 4
molar ratio.10
CO_2/propylene
oxide
4
decreased correspondingly. There was no detectable conver- sion of propylene oxide if no ionic liquid catalyst was used.



The catalytic performances of combined ionic liquids were also tested. Only a moderate improvement in catalytic activity was obtained when a added to
$BMImBF_4$’
entry 8; howe

Recently, the iquids as environmentally benign media for catalytic processes or chemical extractions has become widely recognized and accepted.11,12 Room temperature ionic liquids have negligible vapor pressure, excellent thermal stability and special charac- teristics in comparison with conventional organic and inorga- nic solvents. Many reactions catalyzed with ionic liquids and showing high performance have been reported.13h17 This o†ered some new clues that using ionic liquids as catalysts for those traditionally acid*È*base synthetic reactions may be not only possible but also practical and 6even highly efficient. Our new appro6ach, reported herein, involves the use of room tem- perature ionic liquids based on 1-*n*-butyl-3-methyl- imidazolium (BMIm) and *n*-butylpyridinium (BPy) salts as catalytic media for the cycloaddition of carbon dioxide to pro- pylene oxide, and the possibility of recycling the ionic liquids.
enhanced if a small amount of BMImCl was added to BMImPF , entry 9. This indicates that the PF_4 ~ anion is not a favorable component for the BMIm` cation-containing ionic liquid as the catalyst towards cycloaddition, while some synergism may exist between BF ~ and Cl~, which could enhance the catalytic performance of BMImBF ionic liquid as the catalyst if4 the results of entries 5 or 6 are compared with that of entry 8.

Although varied conversions of propylene oxide were obtained with di†erent ionic liquids, it is worth noting that the selectivity for the desired propylene carbonate product was essentially 100%, since GC-MS analysis showed that there were no other detectable products.

E†ect of the amount of added CO_2 and temperature on the cycloaddition

Since the best catalytic activity was obtained with BMImBF ionic liquid, the e†ect of the amount of carbon dioxide added

Table 1 E†ect of the ionic liquid and its amount on the cycloaddition reactiona

Entry	Ionic liquid	Amount added/mmol	$P(CO_2)$/MPa	Conversion (%)	Selectivity (%)	TONb
1	BMImPF$_6$	(1.5)	2.0	11.3	100	7.8
2	BPyBF$_4$	(1.5)	2.0	25.3	100	16.8
3	BMImCl	(1.0)	2.0	63.8	100	63.8
4	BMImBF$_4$	(0.75)	2.5	67.4	100	89.9
5	BMImBF$_4$	(1.5)	2.5	80.2	100	53.5
6	BMImBF$_4$	(2.0)	2.5	90.3	100	45.2
7	BMImBF$_4$	(2.5)	2.5	100	100	40.0
8	BMImBF$_4$]BMImCl	(1.5]0.2)	2.0	90.5	100	53.2
9	BMImPF$_6$]BMImCl	(1.5]0.2)	2.0	45.3	100	26.6

a Reaction conditions: 110 ¡C, 6 h. b TON: mol propylene carbonate converted per mol of ionic liquid.

Table 2 E†ect of the amount of CO$_2$ added and the temperature on the cycloaddition reactiona

Entry	BMImBF$_4$/mmol	$P(CO_2)$/MPa	CO$_2$ added/g	CO$_2$/propylene oxide molar ratio	T/¡C	Conversion (%)	TON
1	1.5	1.5	4.1	0.93	110	80.7	53.8
2	1.5	2.0	5.8	1.32	110	90.1	60.1
3	1.5	2.5	8.0	1.82	110	80.2	53.5
4	1.5	3.5	11.7	2.66	110	74.3	49.5
5	1.5	4.5	16.5	3.75	110	69.4	46.3
6	2.5	2.5	8.0	1.82	rt	24.1	9.6
7	2.5	2.0	5.8	1.32	rt	35.8	14.3
8	2.5	2.5	8.0	1.82	65	55.2	22.1
9	2.5	2.5	8.0	1.82	90	77.5	31.0
10	2.5	2.5	8.0	1.82	100	96.8	38.7
11	2.5	2.5	8.0	1.82	110	100	40.0
12	2.0	2.5	8.0	1.82	110	90.3	45.2
13	0.75	2.5	8.0	1.82	110	67.4	89.9
14	0.4	2.0	5.8	1.32	130	97.7	244.3
15	0.2	2.5	8.0	1.82	140	82.3	411.5
16	0.2	2.0	5.8	1.32	140	89.9	449.5

a Reaction: 6 h.

and the reaction temperatures was further examined using the BMImBF$_4$ ionic liquid system. From the results in Table 2, entries 1È5, it can be seen that insufficient or excessive amounts of CO$_2$ result in relatively lower conversions, that is there exists an optimum CO$_2$Èpropylene oxide molar ratio for high conversion, *ca.* 1.3, which seems to have little relation to the amount of ionic liquid used. Since the amount of ionic liquid used in this work was 0.02È0.3 ml and since only a very small portion of CO$_2$ may be dissolved in the ionic liquid, it can be conjectured that the CO$_2$ introduced was dissolved in the propylene oxide or “liquifiedÏ through the formation of a CO$_2$Èpropylene oxide complex, which has been postulated on the basis of the appearance of a new absorption band in the UV spectrum of a saturated solution of CO$_2$ in propylene oxide.18 Too much CO$_2$ may retard the interaction between propylene oxide and the ionic liquid catalyst, thus resulting in a lower conversion.

As expected, the reaction temperature has a strong impact on the reaction rate. It is worth noting that the BMImBF$_4$ ionic liquid exhibited some activity even at room temperature, entries 6 and 7. When the amount of ionic liquid was fixed at 2.5 mmol, conversion of propylene oxide increased with increasing temperature, with 110 ¡C being high enough for complete conversion of propylene oxide, entry 11. If the reac-tion temperature was further increased to 130 or 140 ¡C, the amount of the ionic liquid catalyst could be greatly reduced and high TONs could be achieved, entries 14È16.

The possibility of recycling the BMImBF$_4$ ionic liquid catalyst

In order to investigate the possibility of recycling the BMImBF$_4$ ionic liquid catalyst, a recycle experiment was conducted. BMImBF$_4$ (12.5 mmol) was placed in the autoclave, then 0.5 mol propylene oxide and CO$_2$ with an initial pressure

autoclave successively and reacted at 110 ¡C for 6 h. After this time, the resulting mixture was distilled at 83È86 ¡C/2 mmHg to give the desired propylene carbonate product of 100% purity, as analyzed by GC-MS. The reactor containing the used ionic liquid after distillation was charged with propylene oxide and CO$_2$ again. This procedure was repeated for 5 cycles. The conversion and yield results are listed in Table 3. Since the ionic liquid is non-volatile and thermally stable, the desired product could be easily separated from the ionic liquid by simple distillation, and satisfactory yields could be obtained. After the ionic liquid catalyst had been used 5 times, the catalytic activity was only slightly decreased. This indi- cates that the ionic liquid catalyst for the cycloaddition of CO$_2$ to propylene oxide is recyclable.

Although the reaction mechanism for the cycloaddition of CO$_2$ to propylene oxide is not clear at this stage, it can be conjectured, based on the experimental results, that BMIm` may act as the main active site for the activation of the CO$_2$Èpropylene oxide complex mentioned above, since the non-nucleophilic BF$_4$~ and PF$_6$~ ions cannot form covalent bonds with the epoxide.19 The nature of the anion, BF$_4$~, PF$_6$~, Cl~, *etc.*, has a strong impact on the physicochemical

Table 3 Stability of the ionic liquid catalysta

Cycle number	PO conv. (%)b	PC yield (%)b	TON
1	100	90.7	40
2	100	91.8	40
3	98.2	90.5	39.3
4	97.5	89.2	39.0
5	96.1	86.9	38.4

a Reaction conditions: 110 ¡C, 6 h. b PO \ propylene oxide; PC \propylene carbonate.

of 4.0 MPa at room temperature were introduced into the -

properties of BMIm`; for example, BMImBF$_4$ is soluble in water while BMImPF$_6$ is insoluble in water and much less ionic than BMImBF$_4$. Such an impact or modulation caused or controlled by the anions would result in an enhancement or inhibition of the interaction between the BMIm` active sites and CO$_2$ Èpropylene oxide complex. Thus, the following reaction pathway is tentatively proposed:

CO$_2$]PO] CO$_2$ÈPO

CO$_2$ÈPO]Q` H CO$_2$ÈPOÉÉÉQ`] PC]Q`

where PO \propylene oxide; PC \propylene carbonate; CO$_2$ ÈPO \CO$_2$ Èpropylene oxide complex; Q`\BMIm`.

In conclusion, BMImBF$_4$ room temperature ionic liquid is an e†ective catalyst for the cycloaddition of CO$_2$ to propylene oxide with excellent selectivity and relatively short reaction time. The resulting product can be separated from the ionic liquid by simple distillation, while the ionic liquid catalyst is recyclable.

Experimental

1-*n*-Butyl-3-methylimidazolium tetrafluoroborate (BMImBF$_4$) and hexafluorophosphate (BMImPF$_6$) were synthesized according to the procedures reported in the literature.20,21 *n*-Butylpyridinium tetrafluoroborate (BPyBF$_4$) was synthesized using the same procedure. BMImBF$_4$, BMImPF$_6$, BPyBF$_4$ and BMImCl were used as the only catalyst without any other additives.

All cycloaddition reactions were performed in a 90 cm^3 stainless steel autoclave equipped with a magnetic stirrer. For each typical reaction, ionic liquid (0.2È2.5 mmol) and propylene oxide (100 mmol) were successively charged into the reactor without any additional solvent, and then CO$_2$ was introduced at room temperature. Since the autoclave could be conveniently and precisely weighed in a balance, the amount of CO$_2$ added was also measured by weight. The autoclave was heated up to the desired temperature with stir-ring for 6 h. After cooling, the resulting liquid mixture was analyzed with a HewlettÈPackard 6890/5793 GC-MS equipped with a HP 5MS column (30 m long, 0.25 mm i.d., and 0.25 lm film thickness). The concentration of reactant and product was directly given by the GC-MS Chemstation

system according to the area of each chromatograph peak. Isolated yields of propylene carbonate were based on the propylene oxide added.

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