

Supported basic ionic liquid: Highly effective catalyst for the synthesis of 1,2-propylene glycol from hydrolysis of propylene carbonate

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Abstract

Hydrolysis of propylene carbonate to 1,2-propylene glycol was performed by using a SBIL catalyst. The effects of temperature, reaction time, the molar ratio of water to propylene carbonate, choice of catalyst, and the amount of catalyst were investigated. It was found that more than 99% yield and selectivity were obtained in the presence of SBIL under the optimum conditions. Additionally, the catalyst could be reused at least up to five times with slight loss of catalytic activity.

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Keywords: Supported basic ionic liquid; Hydrolysis; Propylene carbonate; Propylene glycol

1. Introduction

1,2-Propylene glycol is chemicals of acknowledge commercial importance. It can be used in many applications areas such as antifreeze agents, brake fluids, intermediates in the production of pharmaceuticals and fine chemicals, the diol component in the manufacture of polyurethanes and the starting point for the manufacture of poly(propylene glycol)s. Therefore, a number of routes leading to the manufacture of 1,2-propylene glycol, such as the addition of water to 1,2-propylene oxide [1], the preparation from propene via 1,2-diacetoxypropane followed by saponification thereof [2], the single-stage hydrogenolysis of dihydroxyacetone [3], the hydrogenolysis of glycerol [4–6] and the hydrolysis of propylene carbonate [7–10]. However, currently all these methods suffered from low selectivity and/or yield of 1,2-propylene glycol, and high pressure and high temperature are required. Development of a method for the manufacture of 1,2-propylene glycol with high selectivity and yield under mild conditions still remains a challenge.

In recent years room temperature ionic liquids have attracted increasing interest in the area of green chemistry [11–17]. Room temperature ionic liquid was initially introduced as an alternative green reaction media, but today it has marched far beyond showing its significant role in controlling the reac-

tion as catalyst [18–22]. Numbers of acidic ionic liquids and neutral ionic liquids have been developed and successfully applied to catalyze esterification reaction [23–26], cleavages of ethers [27,28], alkylation [29–32], aldol condensation [33], epoxidation [34], Michael addition [35–38], protection of carbonyls [39], Koch carbonylation [40] and chemical fixation of carbon dioxide [41–46], since the first successful use of dialkylimidazolium chloroaluminate as a catalyst in Friedel-Crafts acylations [18]. Recent, basic ionic liquids have aroused unprecedented interest because they showed more advantages such as catalytic efficiency and recycling of the ionic liquid than the combination of inorganic base and ionic liquid for some base-catalyzed processes [47–49]. Basic ionic liquids have been successfully utilized to catalyze the Michael addition [50,51], Heck reaction [52] and Markovnikov addition [53].

Although the ability of ionic liquid has been demonstrated successfully in many reactions, the chemical industry still prefers to use heterogeneous catalyst system, because of the ease of separation and the possibility to use a fixed-bed reactor, a solid catalyst is highly advantageous for the chemical reaction. On the basis of economic criteria and possible toxicological concerns, a new method is to immobilize ionic liquid onto solid supports [54–57]. Recently, the supported ionic liquid has been used for the hydroformylation [58,59], hydrogenation [60], Friedel-Crafts alkylation reaction [61], Mizoroki–Heck reaction [62], chemical fixation of carbon dioxide [63–66], hydroamination reaction [67], aldol reaction [68], epoxidation [69]. Herein,

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we, for the first time, use the supported basic ionic as the catalyst in hydrolysis of propylene carbonate.

2. Experiment

2.1. Materials and analysis

Chloromethylated polystyrene (4–5% Cl content and 2% cross-linked with divinylbenzene) and the hydroxide containing ion exchange resin (exchange capacity 5.0 mmol/g) was commercially available. Propylene carbonate was prepared according to the procedure in the literature [41,45]. Other reagents were analytical grade and were used as received.

The amount of attached ionic liquid on the polystyrene was determined from elemental analysis of nitrogen. The reaction mixture was identified on a GC–MS (HP 6890/5973). FT-IR spectra was obtained on a Bruker IFS HRFT-IR Spectrometer.

2.2. Preparation of supported ionic liquid 1 [70]

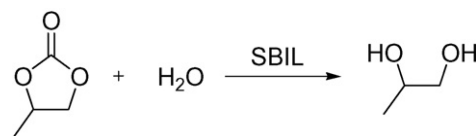
A mixture of polystyrene resin (10.0 g) and 1-methylimidazole (4.0 mL, 51.1 mmol) in toluene (100 mL) was refluxed for 24 h. After cooling to room temperature, the reaction mixture was filtered, and the supported ionic liquid 1 (SIL 1) was washed with toluene, 0.1 mol/L HCl, water and methanol, followed by drying under reduced pressure to give SIL 1 (Scheme 1). The loading of the ionic liquid was obtained to be 3.6 mmol/g by the means of the nitrogen content obtained from elementary analysis.

2.3. Preparation of supported basic ionic liquid 2 and 3 [50,52]

Solid potassium hydroxide or potassium hydrogen carbonate (50.0 mmol) and SIL 1 (10.0 g) were added to water (100 mL), and the mixture was stirred vigorously at room temperature for 24 h. then the mixture was filtrated and washed with water until neutral, followed by drying under reduced pressure to give the supported basic ionic liquid 2 (SBIL 2) and supported basic ionic liquid 3 (SBIL 3) (Scheme 1).

2.4. Characterization of ionic liquid

IR is known to be useful for detecting functional group in the molecular. We found the absorption maximum of imidazole



Scheme 2. The hydrolysis of propylene carbonate.

in SIL 1 at 1570 cm^{-1} , the hydroxyl band of SBIL 2 appears at the 3392 cm^{-1} and the absorption maximum of bicarbonate in SBIL 3 at 1404 cm^{-1} . Therefore, the FT-IR data also provide evidence that we have obtained supported ionic liquid

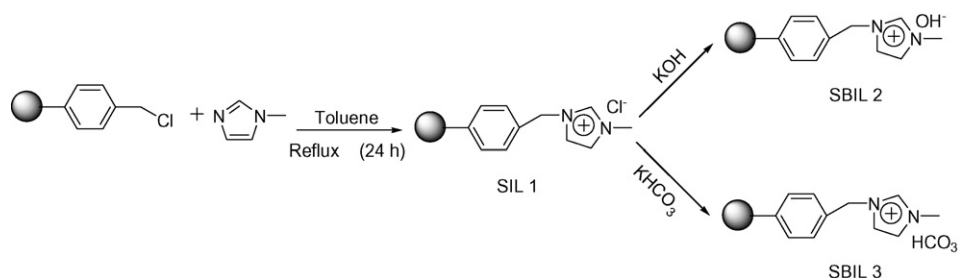
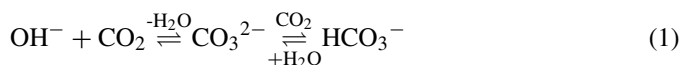
2.5. Hydrolysis of propylene carbonate for the manufacture of 1,2-propylene glycol

The hydrolysis of propylene carbonate for the manufacture of 1,2-propylene glycol was carried out in a 50 mL stainless steel autoclave equipped with a magnetic stirrer (Scheme 2). For a typical reaction process, the supported ionic liquid (175 mg), propylene carbonate (2.55 g) and water (0.81 g) were charged into the reactor. The reactor was heated to $140\text{ }^{\circ}\text{C}$ for 4 h. Then the reactor was cooled to ambient temperature, and the resulting mixture was transferred to a 50 mL round bottom flask by filtration. The catalyst separated from the resulting mixture by filtration could be reused directly. Qualitative analyses were conducted with a HP 6890/5973 GC–MS and quantitative analyses were carried out over a Agilent 6820 GC.

3. Results and discussion

3.1. Catalytic hydrolysis of propylene carbonate in the presence of SBIL

The activities of different supported ionic liquid were tested for the hydrolysis of propylene carbonate to produce 1,2-propylene glycol. Table 1 shows that the SBIL 3 exhibits the highest activity. Excellent selectivity (>99%) and yield (>99%) of 1,2-propylene glycol was obtained in the presence of SBIL 3. The activity of SBIL 3 is higher than that of SBIL 2 and a simple hydroxide containing ion exchange resin was probably due to the reaction of OH^- , CO_2 and H_2O (Eq. (1)).



Scheme 1. Preparation of the supported ionic liquid.

Table 1
The effects of catalyst on the hydrolysis of propylene to form 1,2-propylene glycol^a

Entry	Catalyst	Amount of catalyst (mg)	Selectivity (%)	Yield ^c (%)
1	SIL 1	175	>99	28
2	SBIL 2	175	>99	76
3	IER ^b	126	>99	85
4	SBIL 3	175	>99	>99
5	SBIL 3	50	>99	79
6	SBIL 3	75	>99	87
7	SBIL 3	100	>99	95
8	SBIL 3	125	>99	97
9	SBIL 3	150	>99	98

^a Reaction conditions: propylene carbonate (25 mmol), water (50 mmol), temperature 140 °C, reaction time 4 h.

^b IER was the hydroxide containing ion exchange resin.

^c GC yield.

The amount of catalyst has significant effect on the yield of the 1,2-propylene glycol. As shown in Table 1, the amount of the SBIL 3 had a positive effect on the hydrolysis of propylene carbonate to form 1,2-propylene glycol. While the reaction was conducted with various amounts of SBIL 3, the propylene conversion and 1,2-propylene glycol yield uniformly increased with increasing amount of SBIL 3. When the amount of SBIL 3 was 175 mg, a satisfaction selectivity (>99%) and yield (>99%) of 1,2-propylene glycol were obtained (Table 1, entry 3). Therefore, the optimum amount of SBIL 3 was 175 mg.

Temperature has a significant effect on the yield of 1,2-propylene glycol when the temperature varied from 100 to 150 °C. Table 2 shows that the yield of 1,2-propylene glycol increased with increasing the reaction temperature under 140 °C. However, the continuous enhancement of the temperature beyond 140 °C gave only a very slightly increase in the yield of 1,2-propylene glycol. When the reaction was carried out at 140 °C, a satisfaction of the selectivity (>99%) and yield (>99%) of 1,2-propylene glycol were obtained (Table 2, entry 4). Hence, the optimum temperature was 140 °C for hydrolysis of propylene carbonate to form 1,2-propylene glycol.

A significant drawback associated with the hydrolysis of propylene carbonate is that a large number of water is necessary in this reaction. So we investigated the effects of the molar ratio of water to propylene carbonate. The results are shown in Table 3.

Table 2
The effects of temperature on the hydrolysis of propylene to form 1,2-propylene glycol^a

Entry	Temperature (°C)	Selectivity (%)	Yield ^b (%)
1	100	>99	25
2	120	>99	72
3	130	>99	96
4	140	>99	>99
5	150	>99	>99

^a Reaction conditions: propylene carbonate (25 mmol), water (50 mmol), SBIL 3 (175 mg), reaction time 4 h.

^b GC yield.

Table 3
The effects of the different molar ratio of water to propylene carbonate on the hydrolysis of propylene carbonate^a

Entry	Molar ratio	Selectivity (%)	Yield ^b (%)
1	1:1	>99	92
2	1.2:1	>99	95
3	1.4:1	>99	97
4	1.6:1	>99	98
5	1.8:1	>99	>99
6	2:1	>99	>99

^a Reaction conditions: propylene carbonate (25 mmol), SBIL 3 (175 mg), temperature 140 °C, reaction time 4 h.

^b GC yield.

When the molar ratio of water to propylene carbonate is 1:1, 1,2-propylene glycol was obtained at 92% yield. With increasing the molar ratio of water to propylene carbonate under 1.8:1, the yield of 1,2-propylene glycol was increased. The excellent selectivity (>99%) and yield (>99%) of 1,2-propylene glycol was given when the molar ratio of water to propylene carbonate is 1.8:1. It was obvious that nearly no change of the 1,2-propylene glycol yield had been taken place when the molar ratio of water to propylene carbonate was increased further (Table 3, entries 4,5). So the optimum molar ratio of water to propylene carbonate was kept about 1.8:1, at which the satisfaction selectivity and yield of 1,2-propylene glycol were obtained.

The effects of the reaction time on hydrolysis of propylene carbonate to form 1,2-propylene glycol was investigated. The results are summarized in Table 4. Reaction time has significant effect on the yield of 1,2-propylene glycol when the reaction time varies from 0.5 to 4.0 h in the presence of SBIL 3. When the reaction carried out for 0.5 h, the dissatisfactory yield (41%) was obtained (Table 4, entry 1). The yield of 1,2-propylene glycol could be improved to >99% when the reaction time was increased from 0.5 to 4 h (Table 4, entries 1–5). In order to obtain an excellent yield of the product, 4.0 h was the optimum reaction time.

3.2. Possibility of recycling the supported basic ionic liquid 3 catalyst

A series of catalytic cycles were run to investigate the constancy of the catalyst activity and recycle. In each cycle, the catalyst was separated by filtration and then used for the next

Table 4
The effects of the reaction time on the hydrolysis of propylene carbonate^a

Entry	Reaction time (h)	Selectivity (%)	Yield ^b (%)
1	0.5	>99	41
2	1.0	>99	63
3	2.0	>99	91
4	3.0	>99	96
5	4.0	>99	>99

^a Reaction conditions: propylene carbonate (25 mmol), water (45 mmol), SBIL 3 (175 mg), temperature 140 °C.

^b GC yield.

Table 5
Catalyst recycle studies in hydrolysis of propylene carbonate^a

Entry	Reuse	Selectivity (%)	Yield ^b (%)
1	Fresh	>99	>99
2	1	>99	>99
3	2	>99	>99
4	3	>99	>99
5	4	>99	98
6	5	>99	98

^a Reaction conditions: propylene carbonate (25 mmol), water (45 mmol), SBIL 3 (175 mg), temperature 140 °C, reaction time 4 h.

^b GC yield.

experiment directly. The results listed in Table 5 show that this catalyst can be reusable for at least up to five times with slight loss of activity, while the selectivity of catalyst remain almost the same.

4. Conclusion

The supported basic ionic liquid (SBIL) exhibited a high activity for the hydrolysis propylene carbonate to 1,2-propylene glycol. It was found that excellent yield (>99%) of 1,2-propylene glycol, more than 99% selectivity, could be achieved in the presence of SBIL 3. This catalyst can be reused at least up five times with slight loss of catalytic activity, while the selectivity of the 1,2-propylene glycol remains more than 99%.

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References

- [1] C.K. Weissmehl, H.J. Arpe, *Industrielle Organische Chemie*, second ed., Verlag Chemie, Weinheim, 1978, pp. 259–260.
- [2] J.R. Valbert, U.S. Patent 3,715,388 (1973).
- [3] E. Gehrler, W. Harder, U.S. Patent 5,306,847 (1994).
- [4] A.D. Mohanprasad, K. Pim-Pahn, R.S. Willam, J.S. Galen, *Appl. Catal. A Gen.* 281 (2005) 225–231.
- [5] G.L. Daniel, H.S. Brent, *J. Catal.* 232 (2005) 386–394.
- [6] S. Ludwig, E. Manfred, U.S. Patent 5,616,817 (1997).
- [7] J.S. Buchanan, J.G. Santiesteban, Z. Jiang, U.S. Patent 6,573,396 (2003).
- [8] M. Tojo, K. Oonishi, U.S. Patent 6,479,689 (2002).
- [9] M. Tojo, K. Oonishi, U.S. Patent 6,346,638 (2002).
- [10] M.A. Pacheco, C.L. Marshall, *Energy Fuels* 11 (1997) 2–29.
- [11] P.J. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* 39 (2000) 3772–3789.
- [12] T. Welton, *Chem. Rev.* 99 (1999) 2071–2083.
- [13] L.A. Blanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, *Nature* 399 (1999) 28–29.
- [14] R.A. Brown, P. Pollet, E. Mckoon, C.A. Eckert, C.L. Liotta, P.G. Jessop, *J. Am. Chem. Soc.* 123 (2001) 1254–1255.
- [15] W. Leitner, *Nature* 423 (2003) 930–931.
- [16] X.F. Yang, M.W. Wang, C.J. Li, *Org. Lett.* 5 (2003) 657–660.
- [17] A. Kumar, S.S. Pawar, *J. Org. Chem.* 69 (2004) 1419–1420.
- [18] J.A. Boon, J.A. Levinsky, J.L. Pflug, J.S. Wilkes, *J. Org. Chem.* 51 (1986) 480–483.
- [19] R. Sheldon, *Chem. Commun.* (2001) 2399–2407.
- [20] Y.J. Kim, R.S. Varma, *Tetrahedron Lett.* 46 (2005) 7447–7449.
- [21] B.C. Ranu, R. Jana, *J. Org. Chem.* 70 (2005) 8621–8624.
- [22] A.L. Zhu, T. Jiang, D. Wang, B. Han, L. Liu, J. Huang, J. Zhang, D.H. Sun, *Green Chem.* 7 (2005) 514–517.
- [23] J.Z. Gui, X.H. Cong, D. Liu, X.T. Zhang, Z.D. Hu, Z.L. Sun, *Catal. Commun.* 5 (2004) 473–477.
- [24] T. Joseph, S. Sahoo, S.B. Halligudi, *J. Mol. Catal. A Chem.* 234 (2005) 107–110.
- [25] H.P. Zhu, F. Yang, J. Tang, M.Y. He, *Green Chem.* 5 (2003) 38–39.
- [26] J. Fraga-Dubreuil, K. Bourahla, M. Rahmouni, J.P. Bazureau, J. Hamelin, *Catal. Commun.* 3 (2002) 185–190.
- [27] G. Driver, K.E. Johnson, *Green Chem.* 5 (2003) 163–169.
- [28] G.J. Kemperman, T.A. Roeters, P.W. Hilberink, *Eur. J. Org. Chem.* 9 (2003) 1681–1686.
- [29] J. McNulty, S. Cheekoori, J.J. Nair, V. Larichev, A. Capretta, A.J. Robertson, *Tetrahedron Lett.* 46 (2005) 3641–3644.
- [30] Y.R. Jorapur, C.H. Lee, D.Y. Chi, *Org. Lett.* 7 (2005) 1231–1234.
- [31] H.Y. Shen, Z.M.A. Judeh, C.B. Ching, *Tetrahedron Lett.* 44 (2003) 981–983.
- [32] E.J. Corey, Y. Bo, J. Busch-Petersen, *J. Am. Chem. Soc.* 120 (1998) 13000–13001.
- [33] M. Horikawa, J. Busch-Peterson, E.J. Corey, *Tetrahedron Lett.* 4 (1999) 3843–3846.
- [34] E.J. Corey, F.Y. Zhang, *Org. Lett.* 1 (1999) 1287–1290.
- [35] J.S. Yadav, B.V.S. Reddy, G.J. Baishya, *Org. Chem.* 68 (2003) 7098–7100.
- [36] B.C. Ranu, S.S. Dey, *Tetrahedron* 60 (2004) 4183–4188.
- [37] L.W. Xu, J.W. Li, S.L. Zhou, C.G. Xia, *New J. Chem.* 28 (2004) 183–184.
- [38] F.Y. Zhang, E.J. Corey, *Org. Lett.* 2 (2000) 1097–1100.
- [39] Z. Duan, Y. Gu, Y. Deng, *Catal. Commun.* 7 (2006) 651–656.
- [40] K. Qiao, C. Yokoyama, *Catal. Commun.* 7 (2006) 450–453.
- [41] L.F. Xiao, F.W. Li, C.G. Xia, *Appl. Catal. A Gen.* 279 (2005) 125–129.
- [42] V. Calo, A. Nacci, A. Monopoli, A. Fanizzi, *Org. Lett.* 4 (2002) 2561–2563.
- [43] H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, *Chem. Commun.* (2003) 896–897.
- [44] J.M. Sun, S.-I. Fujita, M. Arai, *J. Organomet. Chem.* 690 (2005) 3490–3497.
- [45] F.W. Li, L.F. Xiao, C.G. Xia, B. Hu, *Tetrahedron Lett.* 4 (5) (2004) 8307–8310.
- [46] J.J. Peng, Y.Q. Deng, *New J. Chem.* 25 (2001) 639–641.
- [47] P. Formentin, H. Garcia, A. Leyva, *J. Mol. Catal. A Chem.* 214 (2004) 137–142.
- [48] H. Chen, D.R. Justes, R.G. Cooks, *Org. Lett.* 7 (2005) 3949–3952.
- [49] C.P. Mehnert, N.C. Dispenziere, R.A. Cook, *Chem. Commun.* (2002) 1610–1611.
- [50] B.C. Ranu, S. Banerjee, *Org. Lett.* 7 (2005) 3049–3052.
- [51] S.Z. Luo, X.L. Mi, L. Zhang, S. Liu, H. Xu, J.P. Cheng, *Angew. Chem. Int. Ed.* 45 (2006) 3093–3097.
- [52] Y. Liu, Y. Lu, G. Gao, Q. Yang, M. He, *Catal. Commun.* 7 (2006) 985–989.
- [53] J.M. Xu, B.K. Liu, W.B. Wu, C. Qian, Q. Wu, X.F. Lin, *J. Org. Chem.* 71 (2006) 3991–3993.
- [54] T. Welton, *Coord. Chem. Rev.* 248 (2004) 2459–2477.
- [55] M.H. Valkenberg, C. Castro, W.F. Hölderich, *Green Chem.* 4 (2002) 88–93.
- [56] S. Lee, *Chem. Commun.* (2006) 1049–1063.
- [57] Z.F. Fei, T.J. Geldbach, D.B. Zhao, P.J. Dyson, *Chem. Eur. J.* 12 (2006) 2122–2130.
- [58] A. Riisager, R. Fehrmann, M. Haumann, B.S.K. Gorle, P. Wasserscheid, *Ind. Eng. Chem. Res.* 44 (2005) 9853–9859.
- [59] C.P. Mehnert, R.A. Cook, N.C. Dispenziere, M. Afework, *J. Am. Chem. Soc.* 124 (2002) 12932–12933.
- [60] C.P. Mehnert, E.J. Mozeleski, R.A. Cook, *Chem. Commun.* (2002) 3010–3011.
- [61] M.H. Valkenberg, C. Castro, W.F. Hölderich, *Appl. Catal. A Gen.* 215 (2001) 185–190.
- [62] H. Hagiwara, Y. Sugawara, K. Isobe, T. Hoshi, T. Suzuki, *Org. Lett.* 6 (2004) 2325–2328.

- [63] L.F. Xiao, F.W. Li, J.J. Peng, C.G. Xia, *J. Mol. Catal. A Chem.* 253 (2006) 265–269.
- [64] G. Lai, J. Peng, J. Li, H. Qiu, J. Jiang, K. Jiang, Y. Shen, *Tetrahedron Lett.* 47 (2006) 6951–6953.
- [65] T. Takahashi, T. Watahiki, S. Kitasumi, H. Yasuda, T. Sakakura, *Chem. Commun.* (2006) 1664–1666.
- [66] J. Wang, X. Yue, F. Cai, L. He, *Catal. Commun.* 8 (2007) 167–172.
- [67] S. Breitenlechner, M. Fleck, T.E. Miller, A. Suppan, *J. Mol. Catal. A Chem.* 214 (2004) 175–179.
- [68] M. Gruttadauria, S. Riela, P.L. Meo, F. D'Anna, R. Noto, *Tetrahedron Lett.* 45 (2004) 6113–6116.
- [69] L.L. Lou, K. Yu, F. Ding, W. Zhou, X. Peng, S. Liu, *Tetrahedron Lett.* 47 (2006) 6513–6516.
- [70] J.W. Byun, Y.S. Lee, *Tetrahedron Lett.* 45 (2004) 1837–1840.