# Immobilized ionic liquid/zinc chloride: Heterogeneous catalyst for synthesis of cyclic carbonates from carbon dioxide and epoxides

Lin-Fei Xiao, Fu-Wei Li, Jia-Jian Peng, Chun-Gu Xia [*]

*State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences and Graduate School of Chinese Academy of Science, Lanzhou 730000, PR China*

## Abstract

Chemical fixation of carbon dioxide with epoxides to form cyclic carbonates proceeds very effectively under mild conditions by using immobilized ionic liquid catalyst in conjunction with zinc chloride without any organic solvents. The reaction temperature, carbon dioxide pressure, effects of different metallic complexes and the amount of immobilized ionic liquid were investigated. The optimum reaction conditions were $110\,^\circ C$ and 1.5 MPa, and the catalyst system was recycled and reused.
© 2006 Elsevier B.V. All rights reserved.

*Keywords:* Immobilized ionic liquid; Carbon dioxide; Cyclic carbonates; Epoxides; Green chemistry

## 1. Introduction

The conversion of carbon dioxide to industrially useful compounds has been a challenge for synthetic chemists and has recently attracted much interest in view of the so-called "sustainable society" and "green chemistry" concepts. As a potential pathway for the effective utilization of carbon dioxide as a non-toxic and cheap $C_1$ building block in organic synthesis, the synthesis of valuable alkylene carbonates via coupling reactions of carbon dioxide and epoxides has attracted much attention due to the great importance in industry. Significance, cyclic carbonates can be used in many applications areas such as aprotic polar solvents, monomers, valuable raw materials and intermediates in the production of pharmaceutical and fine chemicals [1–8].

Although many phosgene-free processes for the synthesis of corresponding five-membered cyclic carbonates have been reported [9–14], the reaction of epoxides with carbon dioxide has also attracted much attention. In the last decades of the 20th century, numerous catalytic systems [15–20] have been developed for the coupling of carbon dioxide and epoxides, such as alkali metal salts [21], alkali metal salts combined with crown ethers or quaternary ammonium salts [22], organoantiomony halide [23],

MgO [24] or Mg–Al mixed oxides [25], ionic liquid [26–31], pophyrin [32], transition-metal complexes [33–44], phenol- and organic-based or sodium iodide [45,46], phthalocyanine [47], polyoxometalate [48] and supercritical carbon dioxide [49–53]. However, currently all these catalysts suffer from low catalytic activity and/or selectivity, low stability; a co-solvent is needed, and high pressure and/or high temperature are required. Development of a highly efficient and environmentally benign catalyst system for the chemical fixation of carbon dioxide with epoxides under mild conditions still remains a challenge. At the same time, the major problem associated with most homogenous catalyst systems is the separation of catalysts from the reaction mixture and the recycling of the catalyst.

Although the ability of ionic liquid has been demonstrated successfully in the chemical fixation carbon dioxide, 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 fixation of carbon dioxide. On the basis of economic criteria and possible toxicological concerns, a new method is to immobilize ionic liquid onto solid supports. Recently, the immobilization of ionic liquid has been successfully used for the hydroformylation [54], hydrogenation [55] and Friedel-Crafts alkylation reaction [56]. Herein, we, for the first time, use the supported ionic liquid as the catalyst in chemical fixation of carbon dioxide.

[*] Corresponding author. Tel.: +86 931 496 8089; fax: +86 931 827 7147.
*E-mail address:* cgxia@lzb.ac.cn (C.-G. Xia).

In order to make the carbon dioxide fixation "greener", a general strategy consists of the conversion of homogeneous catalyst into a heterogeneous catalyst system. With this aim in mind, we used chitosan supported zinc chloride catalyst system for the coupling carbon dioxide and epoxides to form cyclic carbonates [57]. Although this catalyst can be reused, addition of the co-catalyst was needed in every usage. In the present work, we report the first example of the efficient addition of carbon dioxide to epoxides to form cyclic carbonate using recoverable catalysts of the immobilized ionic liquid–zinc chloride catalyst system. This catalyst is very efficient in chemical fixation of carbon dioxide to form cyclic carbonate under mild conditions in high TOF without any additional co-solvent.

## 2. Experiment

### 2.1. Compounds and materials

Tetraethyl orthosilicate (TEOS), (3-chloropropyl)triethoxysilane and propylene oxide were commercially available. Other epoxides used were purchased from Acros Company. Carbon dioxide with a purity of 99.99% was commercially available. Other reagents were analytical grade. 1-(Triethoxysilylpropyl)-3-n-butylimidazolium bromide was prepared according to the procedure in literature [58].

The amount of attached ionic liquid on the $SiO_2$ surface was determined from elemental analysis of nitrogen. All the cyclic carbonates were identified on a GC–MS (HP6890/5973) and a 400 MHz NMR. FTIR spectra was obtained on a Bruker IFS 120HRFT-IR spectrometer.

### 2.2. Preparation of immobilized ionic liquid [56,59]

Imidazole (3.4 g, 53 mmol) was dissolved in 50 ml of dry toluene, 3-chloropyltriethoxysilane (12 ml, 50 mmol) was added to the solution and the mixture was refluxed for 3 h under an argon atmosphere. The solvent was distilled under vacuum ($10^{-3}$ Torr) and an oil containing 3-(N-imidazolyl) propyltriethoxysilane was obtained [Scheme 1, Eq. (1)].

Firstly, 1-(triethoxysilylpropyl)-3-n-butylimidazolium bromide was synthesized by reacting 3-(N-imidazolyl)propyltriethoxysilane with 1-bromobutane in toluene under refluxing for 24 h and then the solvent was distilled off under vacuum. Secondly, 1-(triethoxysilylpropyl)-3-n-butylimidazolium bromide,

together with 40 ml of TEOS, 10 ml of ethanol and 12 ml of water were added into a round bottom flask equipped with a magnetic stirrer. After the formation of a clean and homogeneous liquid mixture, 5 ml of HCl (35 wt.%) was added and the resultant mixture coagulated gradually. After ageing at 60 °C for 12 h, the mixture was then dried in vacuum at 80 °C for 5 h, the resulting solid contained 1-propyl-3-n-butylimidazolium bromide groups bonded to surface silicon atoms. The nitrogen content of the catalyst was found to be 2.3% by elemental analysis of nitrogen (see Scheme 1).
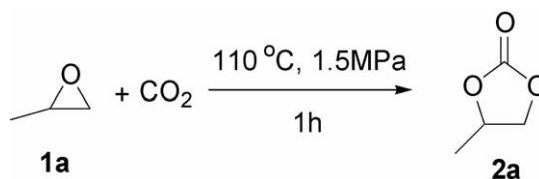
### 2.3. Coupling reaction

The coupling reaction of carbon dioxide and epoxides was carried out in a 50 ml stainless steel autoclave equipped with a magnetic stirrer. For a typical reaction process, the supported ionic liquid (1 g, ionic liquid: 0.82 mmol), $ZnCl_2$ (6.5 mg, 0.05 mmol) and propylene oxide (1a) (10 ml, 0.143 mol) were charged into the reactor without using any co-solvent. The reactor vessel was placed under a constant pressure of carbon dioxide and heated to 110 °C for 1 h. Then the reactor was cooled to ambient temperature, and the resulting mixture was transferred to a 50 ml round bottom flask by filtration. By distillation under vacuum, the product propylene carbonate (2a) was obtained as a colorless liquid. The catalyst separated from the resulting mixture by filtration could be reused directly.
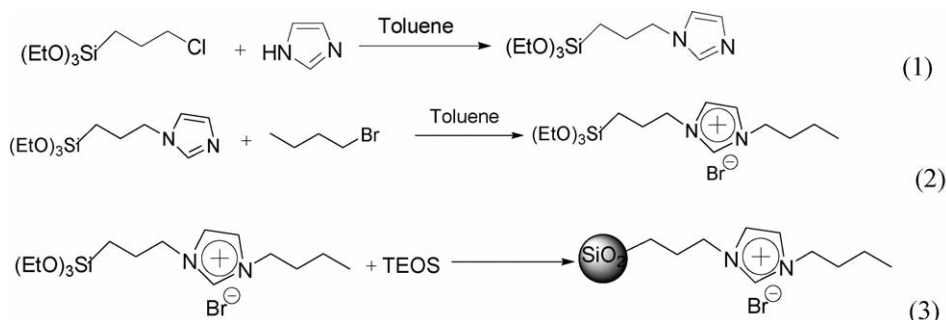
## 3. Results and discussion

### 3.1. Coupling carbon dioxide and propylene oxide (1a) to form propylene carbonate (2a)

Propylene carbonate formed by the cycloaddition of carbon dioxide and propylene oxide is shown in Scheme 2.

The effect of the amount of supported ionic liquid on coupling of carbon dioxide and propylene oxide to form propylene car-

Scheme 2.

Scheme 1. Preparation of the immobilized ionic liquid via the cation (sol–gel method).

Table 1
The effect of the amount of immobilized ionic liquid on coupling carbon dioxide and propylene oxide[a]

| Entry | Immobilized ionic liquid [g] | Yield[b] | TOF[c] |
|---|---|---|---|
| 1[d] | – | – | – |
| 2 | 0.6 | 59 | 1684 |
| 3 | 0.8 | 76 | 2170 |
| 4 | 1.0 | 95 | 2712 |
| 5 | 1.2 | 96 | 2741 |

[a] Reaction conditions: propylene oxide (PO) (10 ml, 0.143 mol), $ZnCl_2$ (6.8 mg, 0.05 mmol); temperature: 110 °C; time: 1 h; $CO_2$ pressure: 1.5 MPa. The selectivity to carbonate are >98%.
[b] Isolated yield.
[c] Moles of propylene carbonate produced per mole of Zn(II) catalyst per hour.
[d] $ZnCl_2$ (6.8 mg, 0.05 mmol) as sole catalyst.

Table 3
The effect of reaction temperature and pressure on coupling of carbon dioxide and propylene oxide[a]

| Entry | Temperature [°C] | Pressure [MPa] | Yield [%][b] | TOF[c] |
|---|---|---|---|---|
| 1 | 90 | 1.5 | 61 | 1742 |
| 2 | 100 | 1.5 | 70 | 1999 |
| 3 | 110 | 1.5 | 95 | 2712 |
| 4 | 120 | 1.5 | 96 | 2741 |
| 5 | 110 | 0.5 | 19 | 543 |
| 6 | 110 | 1.0 | 60 | 1713 |
| 7 | 110 | 2.0 | 95 | 2712 |
| 8 | 110 | 2.5 | 90 | 2570 |
| 9 | 110 | 3.0 | 88 | 2512 |

[a] Reaction conditions: propylene oxide (PO) (10 ml, 0.143 mol), immobilized ionic liquid (1 g), $ZnCl_2$ (6.8 mg, 0.05 mmol); temperature: 110 °C; time: 1 h; $CO_2$ pressure: 1.5 MPa. The selectivity to carbonate are >98%.
[b] Isolated yield.
[c] Moles of propylene carbonate produced per mole of Zn(II) catalyst per hour.

bonate was investigated. The results are summarized in Table 1. Scarcely any reaction occurs when $ZnCl_2$ is used as the sole catalyst (Table 1, Entry 1). While the reaction is conducted with various amounts of supported ionic liquid at 110 °C, the conversion of propylene oxide increases with increasing amount of immobilized ionic liquid. Increasing the amount of $SiO_2$ whose surface is bonded to 1-propyl-3-n-butylimidazolium bromide to more than 1.0 g, only results in a small increases in reactivity. The increase in yield is due to the superfluous immobilized ionic liquid (Table 1, Entries 2–5). Therefore, the adaptable amount of the $SiO_2$, whose surface was bonded to 1-propyl-3-n-butylimidazolium bromide ionic liquid, is 1.0 g.

The effects of different metallic salts on the chemical fixation of carbon dioxide to propylene carbonate were also investigated, and the results are summarized in Table 2.

When these metallic salts are used, the selectivity of propylene carbonate does not change, but the yield of cyclic carbonate is greatly affected by the different metallic positive ions (Table 2, Entries 1–10). Both the selectivity and yield of this reaction are hardly affected by the valence electron of the same metallic element (Table 2, Entries 8 and 9). Among various metallic cations, the reactivity of Zn(II) is the highest. This is probably due to zinc salts, which caused the ring-opening of propylene oxide

Table 2
The effects of different metallic salts on chemical fixation of carbon dioxide[a]

| Entry | Metallic salts | Yield [%][b] | TOF[c] |
|---|---|---|---|
| 1 | $ZnCl_2$ | 95 | 2712 |
| 2 | $ZnBr_2$ | 96 | 2741 |
| 3 | $Zn(OAc)_2$ | 84 | 2398 |
| 4 | $ZnSO_4$ | 85 | 2427 |
| 5 | $CoCl_2$ | 67 | 1913 |
| 6 | $FeCl_3$ | 55 | 1570 |
| 7 | $NiCl_2$ | 71 | 2027 |
| 8 | $CuCl_2$ | 55 | 1570 |
| 9 | CuCl | 50 | 1428 |
| 10 | $AlCl_3$ | 54 | 1542 |

[a] Reaction conditions: propylene oxide (PO) (10 ml, 0.143 mol), immobilized ionic liquid (1 g), metallic salts (0.05 mmol); temperature: 110 °C; time: 1 h; $CO_2$ pressure: 1.5 MPa. The selectivity to carbonate are >98%.
[b] Isolated yield.
[c] Moles of propylene carbonate produced per mole of metallic cation catalyst per hour.

[60]. At the same time, we find that the metallic cation of the main groups can also catalyze the reaction of chemical fixation of carbon dioxide (Table 2, Entry 10).

The activities of various of zinc salts were tested for the synthesis of cyclic carbonates. From Table 2, it can be seen that the activities of anions decrease in the following order: $Br^- > Cl^- > OAc^- > SO_4^{2-}$. Although the activity of $ZnBr_2$ is slightly higher than that of $ZnCl_2$, $ZnCl_2$ is chosen as the catalyst for the coupling of carbon dioxide with epoxides because it is the cheapest Zn(II) salt and has satisfactory activity.

A significant drawback associated with using carbon dioxide as the reagent in organic synthesis is the potential danger associated with operating under high temperature and pressure. So we investigated the effects of temperature and pressure of carbon dioxide. The results are shown in Table 3. The results suggested that increasing the reaction temperature had a pronounced positive effect on the TOF under 110 °C (Table 3, Entries 1–3). However, the enhancement of the reaction temperature up to 110 °C gave only a slight increase in the activity of the catalyst system (Table 3, Entries 3 and 4). In conclusion, increasing the reaction temperature is propitious for the increase in the rate of chemical fixation of carbon dioxide with propylene oxide to form propylene carbonate.

Surprisingly our catalyst system can operate very efficiently at low $CO_2$ pressures. The highest catalytic activity occurs at 1.5 MPa and almost 25% of this optimum TOF is maintained at only 0.5 MPa (Table 3, Entries 3 and 5). Increasing the pressure beyond the optimal level results in a decrease in activity (Table 3, Entries 8 and 9); indicating that, there exists an optimum $CO_2$ pressure. Such a decrease in the activity with increasing pressure of carbon dioxide was also reported previously [26,33,56]. It can be inferred that the introduced $CO_2$ dissolves in propylene oxide or "liquefies" through the formation of a $CO_2$–propylene oxide complex [61]. Too high $CO_2$ pressure may retard the interaction between propylene oxide and the catalyst, resulting in a low TOF.

When the catalyst of immobilized ionic liquid–$ZnCl_2$ is compared with other heterogeneous catalyst system in the literature for the coupling of carbon dioxide and epoxides [24,25,15,41],

these reported values of turnover frequency (TOF) are lower than that obtained in the present work. The reaction temperature for the poly(4-vinylpyridine)-supported zinc halide catalyst [15], but the reaction pressure is higher by 2.0 MPa than the pressure in the present work. A high yield of cyclic carbonates is obtained with Mg–Al mixed oxide catalyst [25] at 100 °C and at low carbon dioxide pressure; however, this catalyst system needs an organic solvent of *N,N*-dimethylformamide and gives a much lower TOF value compared with the present catalyst system. A silica supported chromium–salen complexes catalyst can catalyze this reaction [41], but, higher reaction temperature and $CO_2$ pressure were required compared with this catalyst system. Thus, the present catalyst system is not only effective but has great potential in industry from the standpoints of cost.
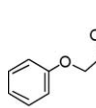
### 3.2. Coupling carbon dioxide and other epoxides to form cyclic carbonates

Under optimized reaction conditions, we examined the reactions of other terminal epoxides (**1b**–**1e**) with $CO_2$. The results are summarized in Table 4. The catalyst system was found to be applicable to a variety of terminal epoxides, forming corresponding cyclic carbonates (**2b**–**2e**) in very high TOF with selectivities higher than 90%.

### 3.3. Possibility of recycling the immobilized ionic liquid–ZnCl$_2$ catalyst system

A series of catalytic cycles were run to investigate the stability of the catalytic activity and recycling. In each cycle, the catalyst was separated by filtration and then used directly for the next run. The results listed in Table 5 show that the catalyst

Table 5
Catalyst recycle studies in coupling carbon dioxide with propylene oxide[a]

| Entry | Recycle no. | Yield [%][b] | TOF[c] |
|---|---|---|---|
| 1 | Fresh | 95 | 2712 |
| 2 | 1 | 93 | 2655 |
| 3 | 2 | 86 | 2455 |

[a] Reaction conditions: propylene oxide (PO) (10 ml, 0.143 mol), immobilization of ionic liquid (1 g), ZnCl$_2$ (6.8 mg, 0.05 mmol); temperature: 110 °C; time: 1 h; $CO_2$ pressure: 1.5 MPa. The selectivity to carbonate are >98%.
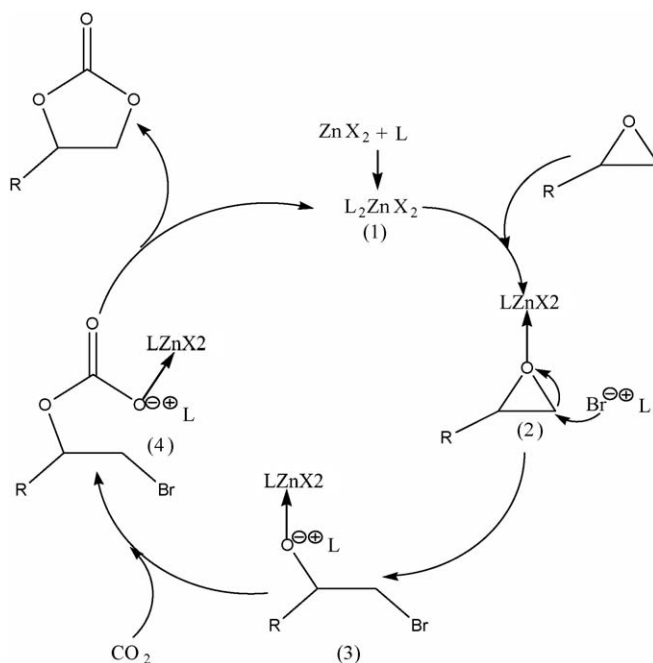[b] Isolated yield.
[c] Moles of propylene carbonate produced per mole of Zn(II)catalyst per hour.

system can be reusable, at least, up to two times with a slight loss of activity, while the selectivity of catalyst system remains. The nitrogen content of the catalyst used in the second time was found to be 2.3% by nitrogen elemental analysis, so a modest decrease in the catalytic activity may be due to the loss of zinc.

### 3.4. Possible mechanism for the present immobilized ionic liquid/ZnCl$_2$-catalyzed coupling of carbon dioxide and epoxides

Based on the above results and previous literature [28,29,31,62], we propose the plausible mechanism for this chemical fixation reaction of $CO_2$ (Scheme 3). The zinc–imidazolium complex (1) was formed by the reciprocity of ZnCl$_2$ and supported ionic liquid, which coordinated the epoxide by replacing one of the immobilized ionic liquid first. At the same time, nucleophilic attack of the dissociated supported ionic liquid on the less sterically hindered carbon atom of the coordinated epoxide occurred (2) to form the active species (3). The insertion of $CO_2$ into the Zn–O bond of (3) would give a

Table 4
Coupling of $CO_2$ and various epoxides[a]

| Substrate | Product | Selectivity [%] | Yield [%][b] | TOF [h$^{-1}$][c] |
|---|---|---|---|---|
| **1b** | **2b** | >98 | 90 | 2069 |
| **1c** | **2c** | 94 | 93 | 2372 |
| **1d** | **2d** | 91 | 83 | 1313 |
| **1e** | **2e** | 98 | 98 | 1445 |

[a] Reaction conditions: epoxides (10 ml), immobilized ionic liquid (1 g), ZnCl$_2$ (6.8 mg, 0.05 mmol); temperature: 110 °C; time: 1 h; $CO_2$ pressure: 1.5 MPa.
[b] Isolated yield.
[c] Moles of propylene carbonate produced per mole of Zn(II)catalyst per hour.



Scheme 3. Proposed mechanism of the coupling of carbon dioxide and epoxides (L, immobilized ionic liquid; L$^{\oplus}$, the cation of immobilized ionic liquid).

zinc carbonate active species (4), which eventually provided the cyclic carbonate.

## 4. Conclusion

The supported ionic liquid/zinc chloride catalyst system exhibits a high activity and selectivity for the synthesis of cyclic carbonates from carbon dioxide and epoxides under mild conditions in a high TOF without any additional co-solvents. The separation of products from the reaction system is very simple. This catalyst system can be reused at least up to two times with slight loss of catalytic activity, while the selectivity of the product cyclic carbonates remains >98%.

## Acknowledgement

## References

[1] D.J. Darensbourg, M.W. Holtcamp, Coordin. Chem. Rev. 153 (1996) 155.
[2] M. Ratzenhofer, H. Kisch, Angew. Chem. Int. Ed. Engl. 19 (1980) 317.
[3] H. Kish, R. Millim, I. Wang, J. Chem. Ber. 119 (1986) 1090.
[4] D.H. Gibson, Chem. Rev. 96 (1996) 2063.
[5] W. Leitner, Coordin. Chem. Rev. 155 (1996) 257.
[6] X. Yin, J.R. Moss, Coordin. Chem. Rev. 181 (1999) 27.
[7] G. Rokicki, Prog. Polym. Sci. 25 (2000) 259.
[8] K. Biggadike, R.M. Angell, C.M. Burgess, R.M. Farrekk, H.E. Weston, J. Med. Chem. 43 (2000) 19.
[9] B.M. Trost, M.T. Chan, J. Org. Chem. 48 (1983) 3346.
[10] V. Bhushan, T.K. Charkraborty, S. Chandrasekaran, J. Org. Chem. 49 (1984) 3974.
[11] J. Sun, S. Fujita, F. Zhao, M. Hasegawa, M. Arai, J. Catal. 230 (2005) 398.
[12] M. Aresta, A. Dibenedetto, J. Mol. Catal. A: Chem. 182 (2002) 399.
[13] J. Sun, S. Fujita, B.M. Bhanage, M. Arai, Catal. Today 93–95 (2004) 383.
[14] J. Sun, S. Fujita, B.M. Bhanage, M. Arai, Catal. Commun. 5 (2004) 83.
[15] H.S. Kim, J.J. Kim, H.N. Known, M.J. Chung, B.G. Lee, H.G. Jang, J. Catal. 205 (2002) 226.
[16] H. Yasuda, L.N. Hen, T. Sakakura, J. Catal. 209 (2002) 547.
[17] W.J. Kruper, D.V. Dellar, J. Org. Chem. 60 (1995) 725.
[18] X. Lu, X. Feng, R. He, Appl. Catal. A: Gen. 234 (2002) 25.
[19] M. Yoshida, M. Ihara, Chem. Eur. J. 10 (2004) 2886.
[20] Y.M. Shen, W.L. Duan, M. Shi, Eur. J. Org. Chem. (2004) 3080.
[21] N. Kihara, N. Hara, T. Endo, J. Org. Chem. 58 (1993) 6198.
[22] G. Rokicki, W. Kuran, Bull. Chem. Soc. Jpn. 57 (1984) 1662.
[23] R. Nomura, A. Ninagawa, H. Matsuda, J. Org. Chem. 45 (1980) 3735.
[24] T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Rujihara, M. Yoshihara, T. Maeshima, Chem. Commun. (1997) 1129.
[25] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, J. Am. Chem. Soc. 121 (1999) 4526.
[26] J.J. Peng, Y. Deng, New J. Chem. 25 (2001) 639.
[27] H.Z. Yang, Y. Deng, F. Shi, Chem. Commun. (2002) 274.
[28] V. Calo, A. Nacci, A. Monopoli, A. Fanizzi, Org. Lett. 4 (2002) 2561.
[29] F.W. Li, L.F. Xiao, C.G. Xia, B. Hu, Tetrahedron Lett. 45 (2004) 8307.
[30] J. Sun, S. Fujita, M. Arai, J. Organometall. Chem. 690 (2005) 3490.
[31] J. Palgunadi, O. Kwon, H. Lee, J.Y. Bae, B.S. Ahna, N.Y. Min, H.S. Kim, Catal. Today 98 (2004) 511.
[32] T. Aida, S. Inoue, J. Am. Chem. Soc. 105 (1983) 1304.
[33] R.L. Addock, S.T. Nguyen, J. Am. Chem. Soc. 123 (2001) 11498.
[34] Y.M. Shen, W.L. Duan, M. Shi, J. Org. Chem. 68 (2003) 1559.
[35] H.S. Kim, J.J. Kim, B.G. Lee, O.S. Jung, H.G. Jang, S.O. Kang, Angew. Chem. Int. Ed. Engl. 39 (2000) 4096.
[36] X. Lü, Y. Zhang, B. Liang, H. Wang, R. He, Chin. J. Catal. 24 (2003) 317.
[37] X. Lü, R. He, Ch.X. Bai, J. Mol. Catal. A: Chem. 186 (2002) 1.
[38] D. Walther, M. Ruben, S. Rau, Coordin. Chem. Rev. 182 (1999) 67.
[39] F.W. Li, C.G. Xia, L.W. Xu, W. Sun, G.X. Chen, Chem. Commun. (2003) 2042.
[40] X. Lu, R. He, C.X. Bai, J. Mol. Catal. A: Chem. 186 (2002) 33.
[41] M. Ramin, F. Jutz, J. Grunwaldt, A. Baiker, J. Mol. Catal. A: Chem. 242 (2005) 32.
[42] H.S. Kim, J.Y. Bae, J.S. Lee, O. Kwon, P. Jelliarko, S.D. Lee, S.H. Lee, J. Catal. 232 (2005) 80.
[43] R. Srivastava, T.H. Bennur, D. Srinivas, J. Mol. Catal. A: Chem. 226 (2005) 199.
[44] X.B. Lu, B. Liang, Y.J. Zhang, Y.Z. Tian, Y.M. Wang, C.X. Bai, H. Wang, R. Zhang, J. Am. Chem. Soc. 126 (2004) 3732.
[45] Y.M. Shen, W.L. Duan, M. Shi, Adv. Synth. Catal. 345 (2003) 337.
[46] Y.M. Shen, W.L. Duan, M. Shi, J. Org. Chem. 68 (2003) 6705.
[47] K. Kasuga, S. Nagao, T. Fukumoto, M. Handa, Polyhedron 15 (1996) 69.
[48] H. Yasuda, L. He, T. Sakakura, C. Hu, J. Catal. 233 (2005) 119.
[49] H. Kawannmi, Y. Ikushima, Chem. Commun. (2003) 896.
[50] J. Sun, S. Fujita, F. Zhao, M. Arai, Appl. Catal. A: Gen. 287 (2005) 221.
[51] X. Lu, J. Xiu, R. He, K. Jin, L. Luo, X. Feng, Appl. Catal. A: Gen. 275 (2004) 73.
[52] Y. Du, F. Cai, D.L. Kong, L.N. He, Green Chem. 7 (2005) 518.
[53] H. Yasuda, L.N. He, T. Takahashi, T. Sakakura, Appl. Catal. A: Gen. 298 (2006) 177.
[54] C.P. Mehnert, R.A. Cook, N.C. Dispenziere, M. Afework, J. Am. Chem. Soc. 124 (2002) 12932.
[55] C.P. Mehnert, E.J. Mozeleski, R.A. Cook, Chem. Commun. (2002) 3010.
[56] M.H. Yalkenberg, C. deCastro, W.F. Hőlderich, Green Chem. 4 (2002) 88.
[57] L.F. Xiao, F.W. Li, C.G. Xia, Appl. Catal. A: Gen. 279 (2005) 125.
[58] P.J. Dyson, M.C. Grossel, N. Srinivasan, T. Vine, T. Welton, D.J. Williams, A.J.P. White, T. Zigras, J. Chem. Soc. Dalton Trans. (1997) 3465.
[59] A.M. Lazarin, Y. Gushikem, S.C. de Castro, J. Mater. Chem. 10 (2000) 2526.
[60] F. Fringuelli, F. Pizzo, S. Tortoioli, L. Vaccaro, J. Org. Chem. 68 (2003) 8248.
[61] R. Nomura, M. Kimura, S. Teshima, A. Ninagawa, H. Matsuda, Bull. Chem. Soc. Jpn. 55 (1982) 3200.
[62] Y.J. Kim, R.S. Varma, J. Org. Chem. 70 (2005) 7882.