

Synthesis of diphenylmethane derivatives in Lewis acidic ionic liquids

Donghong Yin^{a,*}, Changzhi Li^{a,b}, Liang Tao^a, Ningya Yu^{a,*},
Shan Hu^a, Dulin Yin^a

^a *Institute of Fine Catalysis and Synthesis, and Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education), Hunan Normal University, Changsha 410081, Hunan, PR China*

^b *Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian 116023, Liaoning, PR China*

Received 24 August 2005; received in revised form 9 October 2005; accepted 10 October 2005

Available online 10 November 2005

Abstract

Diphenylmethane and its derivatives were prepared via Friedel–Crafts benzylation reaction using ionic liquids of 1-butyl-3-methylimidazolium chloride–ZnCl₂ (BmimCl–ZnCl₂), 1-butyl-3-methylimidazolium chloride–FeCl₃ (BmimCl–FeCl₃) and 1-butyl-3-methylimidazolium chloride–FeCl₂ (BmimCl–FeCl₂) as both reaction media and Lewis acid catalysts. In comparison with the reaction performed in conventional organic solvent, faster reaction rate and higher selectivity to target products were achieved in such ionic liquids media. The effects of reaction temperature, reaction time, and the ratio of metal chloride to BmimCl, as well as the amount of ionic liquids on the Friedel–Crafts benzylation were also investigated. It was found that increasing reaction temperature led to high catalytic activity and selectivity, and that the excess amount of Lewis acidity of ionic liquid was detrimental to the reaction. Moreover, these ionic liquids could be conveniently recovered for recycled use; in particular, BmimCl–ZnCl₂ with moisture-stability could be reused at least eight times without loss of catalytic activity.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Friedel–Crafts reaction; Benzylation; Diphenylmethane; Ionic liquids; Catalysts

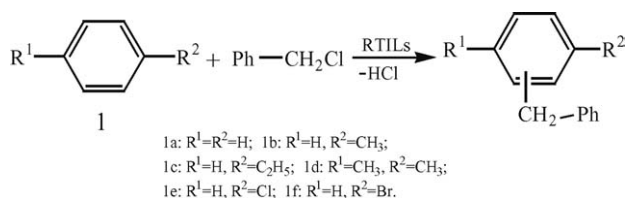
1. Introduction

Diphenylmethane and its derivatives generally prepared via Friedel–Crafts benzylation reaction (Scheme 1) are industrially important compounds used as pharmaceutical intermediates [1] and fine chemicals [2,3]. In the fragrance industry diphenylmethane has been used as both a fixative and a scented soap, as a synergist in some insecticides [4,5] and as a plasticizer [6] for dyes [7]. Also, diphenylmethane has been employed to improve the thermal stability of polyester [8], and the stability and lubricating properties of jet fuels [9]. Furthermore, the substituted diphenylmethanes have been utilized as solvents for pressure-sensitive reaction materials [10] and as insulating staffs, adhesives, and epoxy resin curing agents in chemical industry.

Traditionally, diphenylmethane and its derivatives are prepared via Friedel–Crafts reactions by using H₂SO₄, HF, AlCl₃, FeCl₃, or ZnCl₂ [11] as acid catalysts. However, all these acid catalysts are toxic and corrosive and product isolation is full of difficulties, resulting in severe pollution. To overcome these problems, Lewis acids have been supported in different solids, such as MCM-41 [12], hydroxyapatite (HAP) [13], and fluorapatite (FAP) and have been used as heterogeneous catalysts for the Friedel–Crafts reaction of benzyl chloride with benzene and its derivatives. Such heterogeneous catalysts gave rise to good yields of monoalkyl products with reducing the isolation problems. In spite of the above-mentioned advantages for the use of supported acids, preparations of catalysts are generally tedious, furthermore, these catalysts deactivate rapidly due to the build-up of coke. Hence, there is still a need to develop an easy-clean technology more suitable for the synthesis of diphenylmethane and its derivatives.

The desirable properties of room temperature ionic liquids, such as lack of vapor pressure, wide liquid range, and nonvolatility, have made them excellent reaction media and environmental

* Corresponding authors. Tel.: +86 731 8872576; fax: +86 731 8872531.
E-mail addresses: yindh@hunnu.edu.cn (D. Yin), yuningya@yahoo.com.cn (N. Yu).



Scheme 1. Friedel–Crafts reactions of benzene and its derivatives with benzyl chloride.

benign solvents. Ionic liquids have been regarded as an alternative to conventional organic solvents and applied in electrochemistry [14], extraction [15,16], biocatalysis [17] and catalysis [18]. Chloroaluminate ionic liquids have been reported as both solvent and Lewis acid catalyst for Friedel–Crafts reactions [19–24], but they have a deadly deflection of moisture-sensitivity and, hence, are difficult to reuse. Recently, Xiao and Malhotra [25] have reported on the Friedel–Crafts alkylations of benzene in $FeCl_3$ –pyridinium-based ionic liquids under mild conditions with good conversion, and the catalyst could also be recycled and reused. It is well known that the zinc or iron-containing ionic liquids are more moisture-stable than chloroaluminate ionic liquid [26–28], moreover, their acidic property can be easily modified by adjusting the composition of cations and metal halide, hence, they maybe suitable candidates for Friedel–Crafts reactions.

In this paper, diphenylmethane and its derivatives were synthesized via Friedel–Crafts benzylation reaction of benzyl chloride with benzene and the corresponding derivatives, respectively, for the first time in ionic liquids of 1-butyl-3-methylimidazolium chloride– $ZnCl_2$ (BmimCl– $ZnCl_2$), 1-butyl-3-methylimidazolium chloride– $FeCl_3$ (BmimCl– $FeCl_3$) and 1-butyl-3-methylimidazolium chloride– $FeCl_2$ (BmimCl– $FeCl_2$). Easy separation of the products, accelerating reaction rate, and high selectivity of monoalkylated products were obtained. All these ionic liquids could be reused, especially; BmimCl– $ZnCl_2$ could be recycled for eight times without noticeable drop in activity.

2. Experimental

2.1. General procedures for the synthesis of ionic liquids

1-Butyl-3-methylimidazolium chloride (BmimCl) was synthesized according to the method outlined in the previous reports [29]. BmimCl– $ZnCl_2$, BmimCl– $AlCl_3$, BmimCl– $FeCl_3$ and BmimCl– $FeCl_2$ ionic liquids were synthesized according to the procedures described in the recent literature [26].

2.2. Determination of the acidity of ionic liquids

Acetonitrile was used as a base probe molecule to determine the acidity of ionic liquids; the detail process was similar to that outlined in the previous literature [20].

2.3. Reaction procedure and analysis

In a typical reaction procedure, an appropriate amount of ionic liquid was placed in a 10 ml round-bottom flask equipped

with a stirrer, a reflux condenser and a thermometer, followed by adding 3.9 g (50 mmol) of sodium-dried benzene and 0.64 g (5 mmol) benzyl chloride subsequently. After refluxing for appropriate time, the reaction mixture was placed for a while for the formation of two phases. The upper clear liquid was pipetted off for gas chromatography analysis, and the ionic liquid phase was washed with hexane (3×3 ml), purified in vacuo and directly reused in subsequent runs. All analyses were carried out with a HP 5973 GC–MS equipped with a HP-5 column ($30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$). The concentration of reactants and products was directly given by the system of GC–MS chemstation according to the area of each chromatograph peak.

3. Result and discussion

3.1. Result of acidity determination

Previous literature reported that the Lewis acidic strength of BmimCl– $AlCl_3$ ionic liquids could be adjusted by varying the molar fraction of $AlCl_3$ [20]. Here, we used acetonitrile as a basic probe molecule to determine the acidity of the ionic liquids which contain metal halide $ZnCl_2$, $FeCl_3$ or $FeCl_2$. The principle of this experiment is as follow: if acetonitrile, a weak Lewis base, is mixed with Lewis acid, the interaction between these two compounds will exhibit a correlated band in IR spectra. As can be seen from Fig. 1, there were only two characteristic ν_{CN} stretching vibration bands of acetonitrile at 2250 and 2287 cm^{-1} , when acetonitrile was mixed with the ionic liquid with a $ZnCl_2$ /BmimCl molar ratio of 0.9 (n), indicating that there is no interaction between the ionic liquid and acetonitrile. However, when n was higher than 1.0, an additional band appeared at around 2312 cm^{-1} and a monotonic blue shift of all these bands were observed with an increase of the molar ratio of $ZnCl_2$ to BmimCl (n). The band around 2312 cm^{-1} is an indicative of Lewis acid–base

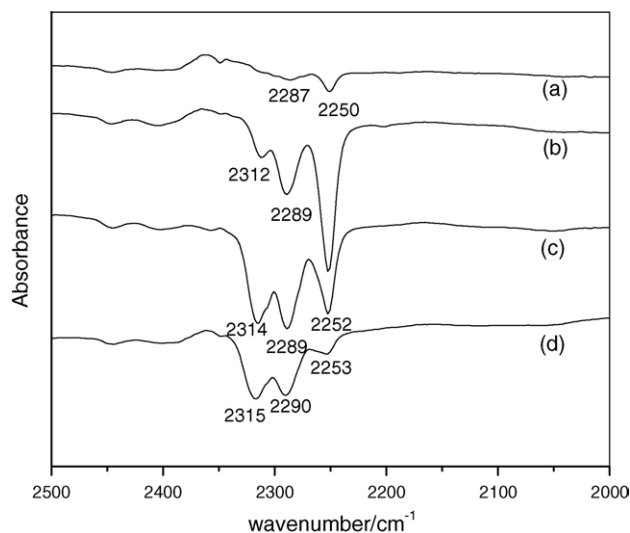


Fig. 1. IR spectra of mixtures of acetonitrile and BmimCl– $ZnCl_2$ ionic liquid: (a) molar ratio of $ZnCl_2$ to BmimCl=0.9; (b) molar ratio of $ZnCl_2$ to BmimCl=1.0; (c) molar ratio of $ZnCl_2$ to BmimCl=1.5; (d) molar ratio of $ZnCl_2$ to BmimCl=2.0.

interaction between the ionic liquid and acetonitrile. Moreover, the intensity of IR band around 2312 cm^{-1} become stronger with the increase of the fraction of ZnCl_2 , implying that the increased amount of ZnCl_2 leads to a stronger Lewis acid–base interaction between the ionic liquid and acetonitrile. The results indicate that the Lewis acidic strength of ionic liquids can be modified by varying the fraction of ZnCl_2 in ionic liquid. Using acetonitrile as a probe molecule, Lewis acidity of the ionic liquids containing FeCl_3 or FeCl_2 showed the similar results.

3.2. Comparison of the Friedel–Crafts benzylation between in organic solvents and in ionic liquids

Table 1 summarizes the results of a comparative study of the Friedel–Crafts reactions between benzene and benzyl chloride in several Lewis acid ionic liquids of BmimCl–ZnCl_2 , BmimCl–AlCl_3 , BmimCl–FeCl_3 , and BmimCl–FeCl_2 and in organic solvent. When the Friedel–Crafts reaction was carried out without ionic liquid, benzene acted as both substrate and solvent and the Lewis acid ZnCl_2 supported on hydroxyapatite or fluorapatite as heterogeneous solid catalysts. As can be readily seen from Table 1 that in the organic solvents, both ZnCl_2/HAP and ZnCl_2/FAP showed rather poor activity and selectivity for the diphenylmethane (entries 1 and 2), whereas the enhanced reaction rate was observed when the Friedel–Crafts reaction was performed in ionic liquids (entries 3–10). Typically, high yield of monoalkyl product was achieved within 2 h in ionic liquids. However, the heterogeneous catalysts needed longer reaction time to get the comparable yield. Also, one can easily find the second advantage of ionic liquids from Table 1, that is, the significantly improved selectivity of monoalkyl products. It is well known that alkylation reaction is governed with the mechanism of carbenium ion, strong polarity and electrostatic field of the ionic liquids used as both catalyst and reaction medium may stabilize the intermediate of carbenium ion charged positively

Table 1
The comparative results of the Friedel–Crafts reactions between benzene and benzyl chloride in different solvent^a

Entry	Solvent	Reaction time (h)	Yield (%)	Selectivity (%)
1	Benzene ^b	2	87 (85)	78
2	Benzene ^c	17	98 (95)	77
3	BmimCl–AlCl_3	1	99.1	99.1
4	BmimCl–AlCl_3	2	100	100
5	BmimCl–FeCl_3	1	98.5	100
6	BmimCl–FeCl_3	2	100	100
7	BmimCl–FeCl_2	1	93.2	100
8	BmimCl–FeCl_2	2	96.2	99.7
9	BmimCl–ZnCl_2	1	79.3	98.7
10	BmimCl–ZnCl_2	2	97.7	99.8

^a In ionic liquids at $80\text{ }^\circ\text{C}$, the reaction condition is as follows: 3.9 g (50 mmol) of benzene and 0.64 g (5 mmol) benzyl chloride in 1 ml ionic liquid (molar ratio of $\text{MX}/\text{BmimCl} = 2.0$).

^b Ref. [19], the mixture of benzyl chloride (9 mmol) and benzene (10 ml) was refluxed in the presence of 0.1 g of ZnCl_2/HAP . The datum in brackets is the yield of products after distillation.

^c Ref. [20], the mixture of benzyl chloride (9 mmol) and benzene (10 ml) was refluxed in the presence of 0.1 g of ZnCl_2/FAP . The datum in brackets is the yield of products after distillation.

in the second carbon, thus, resulting in higher conversion and selectivity.

Clearly, there were slight differences in the yield of monoalkyl products when the reaction was performed in different ionic liquids under the same conditions. BmimCl–AlCl_3 and BmimCl–FeCl_3 showed the best catalytic activity in the benzylation of benzene. The activity sequence for the four ILs was as follows: $\text{BmimCl–AlCl}_3 > \text{BmimCl–FeCl}_3 > \text{BmimCl–FeCl}_2 > \text{BmimCl–ZnCl}_2$. The Friedel–Crafts reaction is normally promoted by Lewis acid catalyst whereas basic catalysts exhibit no catalytic activity. Among AlCl_3 , FeCl_3 , FeCl_2 and ZnCl_2 , AlCl_3 and FeCl_3 possess the highest Lewis acidic strength, imparting the highest Lewis acidity to BmimCl–AlCl_3 and BmimCl–FeCl_3 . Thus, BmimCl–AlCl_3 and BmimCl–FeCl_3 showed the greatest catalytic activity. A series of results in Table 1 demonstrated the expected dependency.

3.3. Influence of reaction temperature and reaction time on the Friedel–Crafts reaction

Reaction temperature and reaction time have important effects on the reaction dynamics and thermodynamics, therefore, the influence of varying the reaction time and temperature on the alkylation were studied, and the results are shown in Table 2. As expected, the elevated reaction temperature, which would accelerate the reaction remarkably, led to the increased conversion. Only 57.3% of benzyl chloride conversion was obtained when the reaction was performed at $25\text{ }^\circ\text{C}$ for 47 h, whereas the reaction can be accomplished within 2 h if the reaction temperature was raised to $80\text{ }^\circ\text{C}$. Also, the increase of reaction temperature gave a higher selectivity for diphenylmethane. At $25\text{ }^\circ\text{C}$, the selectivity towards monoalkylation was only 68.7%, and the other 31.3% of products was dialkylation product; however, the selectivity towards monoalkylation always retained a high level between 98.4% and 100%, if the temperature increased from $25\text{ }^\circ\text{C}$ to $80\text{ }^\circ\text{C}$. On the other hand, the prolonged reaction time usually gave rise to an increased conversion, moreover, this tendency became more apparent under elevated reaction temperature. The reaction could be completed within only 2 h at the temperature of $80\text{ }^\circ\text{C}$, whereas only the conversion of 57.3% was obtained if the reaction was performed at $25\text{ }^\circ\text{C}$ even the reaction time was prolonged to 47 h. It should be noted that a longer reaction time is not the precondition to get a higher selectivity for monoalkylated product.

Table 2
The results of Friedel–Crafts reaction of benzene with benzyl chloride in the ionic liquid BmimCl–ZnCl_2 at different temperature and reaction time^a

Temperature ($^\circ\text{C}$)	Time (h)	Yield (%)	Selectivity (%)
25	30	36.9	69.7
25	47	57.3	68.7
80	0.5	58.1	93.8
80	1	78.2	98.7
80	1.5	93.2	99.9
80	2	97.7	99.8
80	3	98.8	98.7

^a Same as in Table 1.

Table 3

The results of Friedel–Crafts reaction of benzene with benzyl chloride in different amounts of BmimCl–ZnCl₂ ionic liquid with various molar ratios of ZnCl₂ to BmimCl

Entry	Amount of IL (ml)	<i>n</i> ^a	Yield (%)	Selectivity (%)
1	1	1.1	5.2	100
2	1	1.5	29.0	100
3	1	2.0	97.7	99.8
4	1	3.0	97.8	98.9
5	0.1	2.0	15.9	98.3
6	0.2	2.0	32.1	99.8
7	0.5	2.0	63.6	99.2
8	2	2.0	95.6	99.6

^a *n* is the molar ratio of ZnCl₂ to BmimCl; reaction time and temperature are 2 h and 80 °C, respectively.

3.4. Influence of ZnCl₂ composition in ionic liquids and the amount of ionic liquids on the Friedel–Crafts reaction

The effects of varying ZnCl₂ composition in ionic liquids and the amount of the ionic liquids on the alkylation reaction of benzyl chloride with benzene were studied and the results are shown in Table 3. ZnCl₂ molar fraction in ionic liquids had a crucial influence on the catalytic activity (entries 1–3): The ionic liquid with *n* = 1.1 exhibited little catalytic activity (entry 1, *n* is the molar ratio of ZnCl₂ to BmimCl); the reaction rate increased remarkably with an increase of *n* from 1.1 to 2.0, indeed, the conversion of benzyl chloride reached 97.7% with selectivity to monoalkylated product close to 100% in 2 h when *n* was equal to 2.0; whereafter, the increase of *n* from 2.0 to 3.0 gave an almost unchanged conversion and a slightly decreased selectivity of monoalkylated product (entry 4). As has been discussed in Fig. 1, with the increase of the amount of ZnCl₂ in ionic liquids, Lewis acidity of ionic liquids became stronger. Since Friedel–Crafts reactions are promoted by Lewis acid catalysts, the elevated acidic strength will improve both the conversion and the selectivity of monoalkylated product. It should be noted that excess Lewis acidity of ionic liquid appears to be detrimental to the reaction presented here.

On the other hand, the amount of ionic liquid in reaction system also had much influence on the reaction of alkylation. When the alkylation reaction of benzyl chloride with benzene were carried out with the varied amount of ionic liquid (0.1, 0.2, 0.5, 1.0 or 2.0 ml ionic liquid/0.32 g benzyl chloride) under the same reaction conditions, it was observed that, with the increase of the amount of the ionic liquid, the yield of benzyl chloride passed through a maximum and then decreased (Table 3, entries 5–7, 3 and 8). The maximum yield of target product was obtained when the amount of ionic liquid was 1 ml, however, an excess of ionic liquid, which resulted in an undesirable increase of acidity in the system, promoted undesirable side-reactions, and thus, reduced the yield of target product, as observed previously.

3.5. Recycling of the ionic liquid in the Friedel–Crafts reaction

One of the advantages of ionic liquids is that products with high purity can be easily separated. Since the sub-

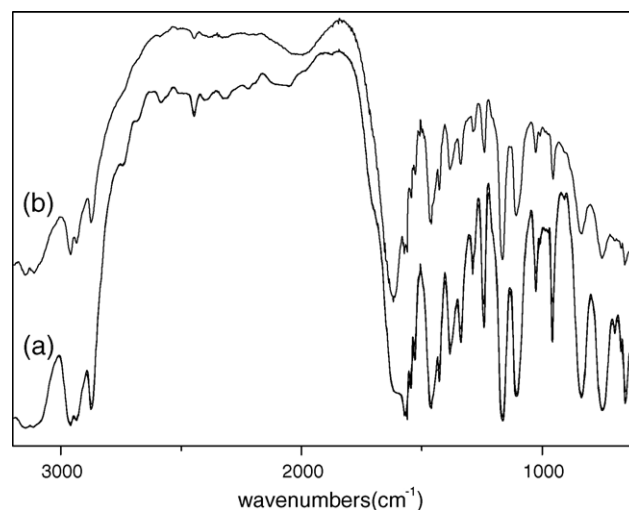


Fig. 2. IR spectra of the fresh ionic liquid of BmimCl–ZnCl₂ (a) and the used one (b).

strates used here are almost insoluble in the ionic liquids and the products are well soluble in benzene and its derivatives, the products with reaction substrates formed a separate phase on the top of the ionic liquids after the completion of the Friedel–Crafts reaction and therefore were easily separated by decantation. Fig. 2 shows the FT-IR spectra of fresh BmimCl–ZnCl₂ and used BmimCl–ZnCl₂. After washed with hexane, the used BmimCl–ZnCl₂ displayed an almost identical spectrum with fresh BmimCl–ZnCl₂, implying that the structure of BmimCl–ZnCl₂ keeps unchanged during the reaction. Based the above results it is logical to conclude that the ionic liquid catalysts with moisture-stability were reusable and the recycle results are shown in Table 4. For moisture-stable

Table 4
Reuse of ionic liquids in the Friedel–Crafts reaction

Entry	BmimCl–MX ^a	Run time	Yield (%)	Selectivity (%)
1 ^b	BmimCl–ZnCl ₂	1	95.7	4.4/36.0/59.6 ^c
2	BmimCl–ZnCl ₂	2	99.4	4.0/35.4/60.5
3	BmimCl–ZnCl ₂	3	98.0	4.6/36.4/59.0
4	BmimCl–ZnCl ₂	4	100	5.9/37.8/56.3
5	BmimCl–ZnCl ₂	5	98.6	4.4/36.6/59.0
6	BmimCl–ZnCl ₂	6	100	5.9/38.7/55.5
7	BmimCl–ZnCl ₂	7	98.6	4.7/36.1/59.2
8	BmimCl–ZnCl ₂	8	100	6.8/37.9/55.3
9 ^d	BmimCl–FeCl ₃	1	100	100
10	BmimCl–FeCl ₃	2	99.6	100
11	BmimCl–FeCl ₃	3	97.1	99.8
12	BmimCl–FeCl ₃	4	85.8	100
13	BmimCl–FeCl ₃	5	19.2	100
14	BmimCl–FeCl ₂	1	96.2	99.7
15	BmimCl–FeCl ₂	2	99.4	99.9
16	BmimCl–FeCl ₂	3	42.6	100
17	BmimCl–AlCl ₃	1	100	100
18	BmimCl–AlCl ₃	2	17.2	100

^a The molar ratio of MX to BmimCl is 2:1.

^b Entries 1–8 are the reaction of toluene (4.6 g) with benzyl chloride (0.32 g) at the temperature of 110 °C in 1 ml of BmimCl–ZnCl₂.

^c The products selectivity (entries 1–8) is the molar ratio of *meta/ortho/para*.

^d Entries 9–18 are the reaction of benzene (3.9 g) with benzyl chloride (0.64 g) at the temperature of 80 °C in 1 ml of different ionic liquids.

Table 5
The results of different aromatic substrates with benzyl chloride

Entry	Substrate	Reaction time (h)	Yield (%)	Selectivity (%)
1	Toluene ^a	1.5	88.8	4.5/36.4/59.1
2	Toluene	2	95.7	4.4/36.0/59.6
3	Toluene	3	99.9	4.7/37.2/58.2
4	Ethyl benzene ^b	2	100	42.5/57.5
5	<i>p</i> -Xylene	1	93.0	100
6	<i>p</i> -Xylene	2	93.2	100
7	<i>p</i> -Xylene	3	94.0	100
8	Chlorobenzene ^b	2	82.3	12/88
9	Bromobenzene ^b	2	78.9	48/52

^a The products selectivity is the molar ratio of *meta/ortho/para*.

^b The products selectivity is the molar ratio of *ortho/para*.

BmimCl–ZnCl₂, repeated use of the catalyst for eight times did not show the decrease in both the yield and the selectivity, indicating clearly that this kind of Lewis acid ionic liquids can be recycled conveniently (entries 1–8). In the cases of BmimCl–FeCl₃ and BmimCl–FeCl₂ with less moisture-stability than BmimCl–ZnCl₂, the yield of the monoalkylated product decreased significantly as the corresponding ionic liquids were recycled for five times and three times, respectively (entries 9–13 and 14–16). Furthermore, the ionic liquids of BmimCl–AlCl₃, which is moisture sensitive, deactivated fast in our study operated in air. Compared with the yield (98.2%) and the selectivity (100%) of the first run, the activity of BmimCl–AlCl₃ in the second run could almost be ignored (entries 17 and 18). These results imply that the ionic liquids with intermediated Lewis acidity and moisture-stability are preferred as catalysts for the alkylation reaction.

3.6. Friedel–Crafts benzylation reaction of different substrates in BmimCl–ZnCl₂

The Friedel–Crafts reactions of benzyl chloride with different activated or deactivated aromatics were carried out in BmimCl–ZnCl₂ to examine the possibility of the wide use of this kind of ionic liquid. The results of the different Friedel–Crafts reactions in BmimCl–ZnCl₂ (molar ratio of ZnCl₂ to BmimCl is 2:1) are showed in Table 5. Because Friedel–Crafts alkylation reaction is governed by the mechanism of carbenium ion [30], the reactants with electric donor groups will undoubtedly stabilize the intermediate of carbenium ion, and, thus, have higher conversion than the reactant without substituted group or the one with electron withdrawing groups. As shown in Table 5, it was observed that the yields and regioselectivities of the first three substrates were very high, and that they did not show many differences each other under the same conditions (Table 5, entries 1–7), whereas chlorobenzene and bromobenzene with strong electron withdrawing group used as reactants showed poorer reaction activity than the three former (entries 8 and 9).

4. Conclusion

The work herein presented a facile method to the preparation of diphenylmethane and its derivatives. The ionic liquids

of BmimCl–ZnCl₂, BmimCl–FeCl₃ and BmimCl–FeCl₂ were found to be novel reaction media and Lewis acid catalysts for the Friedel–Crafts alkylation reactions. These ionic liquids showed fast reaction rate with high selectivity for monoalkylated products. Moreover, the experimental procedure here was quite simple and convenient, and the non-volatile and moisture-stable ionic liquids could be conveniently recovered for recycled use, especially, BmimCl–ZnCl₂ could repeatedly be used at least eight times without loss of catalytic activity. The novel reaction/catalytic media were expected to be promising replacements of homogenous and/or heterogenous catalysts in toxic organic solvents and to find wider applications in related organic synthesis.

Acknowledgements

The project was sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, Ministry of Education [2001–498]. The authors also thank the Natural Science Foundation of Hunan Province for financial support to this project (01JJY3008).

References

- [1] T.W. Bastock, J.H. Clark, Speciality Chemicals, Elsevier, London, 1991.
- [2] B.M. Khadilkar, S.D. Borkar, Chem. Technol. Biotechnol. 71 (1998) 209.
- [3] R. Commandeur, N. Berger, P. Jay, J. Kervennal, Eur. Pat. Appl. EP 0 442 986 (1991) to Atochem S.A.
- [4] A.D. Harford, H.W. Vernon, US Patent, 2 897 112 (1956).
- [5] A. Douglas, H.W. Vernon, British Petroleum Co. Ltd., DE-AS, 1 094 035 (1957).
- [6] N.K. Moshinskaya, V.S. Oliner, L.I. Zhuoiev, SU, 137993 (1960).
- [7] E. Siggel, US Patent, 2 710 849 (1952).
- [8] M.I. Stewart, O.K. Carlson, FMC Corp., US Patent, 3 593 640 (1967).
- [9] A.M. Leus, Ashland Oil & Refining Co., US Patent, 3 529 944 (1967).
- [10] A. Sato, Y. Yida, I. Shimizu, DE-OS, 2 210 133 (1972).
- [11] G.A. Olah, Friedel–Crafts Chemistry, Wiley, New York, 1973.
- [12] X. Hu, G.K. Chuah, S. Jaenicke, Appl. Catal. A 217 (2001) 1.
- [13] S. Sebt, R. Tahir, R. Nazih, S. Boulaajaj, Appl. Catal. A 218 (2001) 25.
- [14] B. Martiz, R. Keyrouz, S. Gmouh, M. Vaultier, V. Jouikov, Chem. Commun. 6 (2004) 674.
- [15] M. Matsumoto, K. Mochiduki, K. Fukunishi, K. Kondo, Sep. Purif. Technol. 40 (2004) 97.
- [16] A.A. Valente, Z. Petrovski, L.C. Branco, C.A.M. Afonso, M. Pillinger, A.D. Lopes, C.C. Romao, C.D. Nunes, I.S. Goncalves, J. Mol. Catal. A 218 (2004) 5.
- [17] C. Chiappe, E. a Leandri, S. Lucchesi, D. Pieraccini, B.D. Hammock, C. Morisseau, J. Mol. Catal. B 27 (2004) 243.
- [18] B. Wang, Y.R. Kang, L.M. Yang, J.S. Suo, J. Mol. Catal. A 203 (2003) 29.
- [19] K. Qiao, Y.Q. Deng, J. Mol. Catal. A 171 (2001) 81.
- [20] L.Y. Piao, X. Fu, Y.L. Yang, G.H. Tao, Y. Kou, Catal. Today 93–95 (2004) 301.
- [21] L. Xiao, K.E. Johnson, R.G. Treble, J. Mol. Catal. A 214 (2004) 121.
- [22] Z.K. Zhao, Z.S. Li, G. Wang, W.H. Qiao, L.B. Cheng, Appl. Catal. A 262 (2004) 69.
- [23] K. Yoo, V.V. Namboodiri, R.S. Varma, P.G. Smirnotis, J. Catal. 222 (2004) 511.

- [24] C. DeCastro, E. Sauvage, M.H. Valkenberg, W.F. Hölderich, *J. Catal.* 196 (2000) 86.
- [25] Y. Xiao, S.V. Malhotra, *J. Mol. Catal. A* 230 (2005) 129.
- [26] A.P. Abbott, G. Capper, D.L. Davies, H.L. Munro, R.K. Rasheed, V. Tambyrajah, *Chem. Commun.* (2001) 2010.
- [27] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, *Green Chem.* 4 (2002) 24.
- [28] D.H. Yin, C. Li, B. Li, L. Tao, D. Yin, *Adv. Synth. Catal.* 347 (2005) 137.
- [29] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, *Chem. Commun.* (1998) 176.
- [30] S. Sebt, R. Tahir, R. Nazih, S. Boulaajaj, *Appl. Catal. A* 218 (2001) 25.