

Article

# Novel Aryl-Imidazolium Ionic Liquids with Dual Brønsted/Lewis Acidity as Both Solvents and Catalysts for Friedel–Crafts Alkylation

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# Featured Application: In this study, we demonstrate the utility of the tunable aryl-imidazolium magnetic ionic liquids with dual functions as a solvent–catalyst and dual Brønsted–Lewis acidity for the Friedel–Crafts alkylation reaction of p-xylene with benzyl chloride.

**Abstract:** Unique tunable aryl-imidazolium magnetic ionic liquids with dual functions as a solvent–catalyst and dual Brønsted–Lewis acidity (B-L MILs) are applied for Friedel–Crafts alkylation without additional solvents. The catalytic properties of these B-L MILs in the Friedel–Crafts alkylation of p-xylene with benzyl chloride are investigated. The various reaction parameters, including the catalyst dosage, reaction time, reaction temperature, molar ratio of reactants, and reusability, are discussed. The results show that the B-L MIL 5c has more excellent product selectivity (>99%) and reactant conversion (>99%) under the following optimum conditions (reaction temperature = 80 °C, reaction time = 0.5 h, molar ratio of p-xylene to benzyl chloride = 6:1, and catalyst 5c dosage = 1.0 mole %) than traditional catalysts reported in the previous literature. Specifically, due to the mesomeric effect between the FeCl<sub>4</sub> anion and hydrogen atom at cationic moiety, the catalyst B-L MILs with the molar fraction of FeCl<sub>3</sub> equal to 0.5 can be easily recovered and provide satisfactory catalytic activity after being re-used six times.

**Keywords:** tunable aryl-imidazolium Brønsted–Lewis magnetic ionic liquids; dual Brønsted–Lewis acidity; Friedel–Crafts alkylation; homogeneous catalysis; para-substitution; mesomeric effect

# 1. Introduction

Triarylmethanes (TRAMs), diarylalkanes (DIAAs), diphenylmethane (DPM), and their derivatives have been widely used as key intermediates in synthesis, medicine, pharmaceutical, fine chemicals, and industrial chemistry. TRAMs and DIAAs are also used as photochromic agents, dyes, and building blocks for dendrimers. More interestingly, ring-hydroxylated TRAMs have been also reported to exhibit significant antioxidant, antitumor, antitubercular, and anti-inflammatory activities [1–3].



Due to their interesting chemical properties, both TRAM and DIAAs synthesis processes have been receiving increasing attention. Traditionally, they are industrially prepared via a Friedel–Crafts alkylation reaction of electron-rich arenes with benzyl halide using conventional homogeneous Lewis acids such as AlCl<sub>3</sub> [4], FeCl<sub>3</sub> [5], ZnCl<sub>2</sub> [6], BF<sub>3</sub> [7], H<sub>2</sub>SO<sub>4</sub> [8], or their derivatives [9,10] as catalysts in the liquid phase. However, these homogeneous acidic catalysts have a number of inherent shortcomings, including causing equipment corrosion and separation difficulties, being non-reusable and having low regioselectivity, as well as being environmentally hazardous and producing a large amount of acidic liquid waste after the reaction [11,12]. Most acidic catalysts are also expensive and must be used with volatile organic solvents. Therefore, it is very important to develop efficient, green, cost-effective, non-volatile catalysts with high application feasibility.

Ionic liquids (ILs) have been shown to be very promising green solvents with a melting point below 100 °C and excellent properties including extremely low volatility, a wide liquid temperature range, high thermal stability, and extraordinary solubility with many organic compounds [13,14]. Due to these excellent properties, ILs have been applied as solvents and catalysts for organic reactions such as Friedel–Crafts reactions. In 1998, the chloroaluminate IL, [EMIM]Cl-AlCl<sub>3</sub>, was firstly employed to catalyze the Friedel–Crafts reactions, and showed good yields close to 90% at a reaction temperature of 20 °C [15]. Although chloroaluminate IL with high acidic catalytic activity successfully played a good solvent-catalyst role, it has some serious limitations such as its oxophilic property, which easily results in the formation of adducts with C–O functionalities and forming HCl and Al oxides irreversibly with traces of water [16]. To avoid this disadvantage, ILs were used as solvent only for immobilizing the metal triflate as Lewis acidic catalysts to catalyze Friedel-Crafts reactions, and these studies showed good product yields close to 90% under reaction temperatures higher than 80 °C [17–19]. Although metal triflate/ILs catalysts exhibited good catalytic activity, they gave low product yields in a recyclable test due to the non-uniform dispersion of metal triflate immobilized to ILs. Therefore, designing ILs without chloroaluminate systems and with solvent-catalyst properties to improve the above disadvantages is important. Brønsted acidic ionic liquids (BAILs) previously reported in the literature also exhibit the above-mentioned advantages of ILs when compared with traditional Brønsted acidic catalysts [20,21]. Recently, many organic synthesis studies have been focused on applying strong BAILs as a dual solvent-catalyst for reactions such as esterification [22,23], Fisher indole synthesis [24,25], Mannich-type reactions [26], dehydration [27], and Beckmann rearrangement [28]. Moreover, the Friedel–Crafts alkylation that typically requires Lewis acidic catalysts has been also catalyzed by BAILs in recent years [29–34]. For example, both the [HSO<sub>3</sub>-pmim][OTf] and pyrrolidinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)ethanesulfonate ([Pyrro][H(CF<sub>2</sub>)<sub>4</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>3</sub>]) have been used as BAILs catalysts for the Friedel-Crafts alkylation reaction, and they allow this reaction under solvent-free conditions [29,30]. [HSO<sub>3</sub>-pmim][OTf] applied for reactions of electron-rich arene with aldehyde can achieve a 93%–97% product yield with five cycles [29]. [Pyrro][H(CF<sub>2</sub>)<sub>4</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>3</sub>] with a large ionic volume and charge delocalization properties in anion moiety has a low melting point to allow Friedel–Crafts alkylation under low temperature (50 °C) conditions with as high as a 90% yield after reacting for 12–24 h [30].

Iron-containing magnetic ILs have been firstly published in 2004 [35,36], and recent studies on iron-catalyzed organic transformations are of great importance because iron is one of the most inexpensive and non-pollutant metals [37,38]. Unlike AlCl<sub>3</sub>-based catalysts with air- and water-sensitive properties, iron-based catalysts can make reactions both air- and water-stable under mild conditions [39]. Some examples of organic transformations with iron-based ILs as Lewis acidic catalysts or reaction media have been reported [39,40]. 1-Butyl-3-methylimidazolium tetrachloroferrate ([Bmim][FeCl<sub>4</sub>]) has been specifically employed as a catalyst in Friedel–Crafts acylation [41], aryl–Grignard cross-coupling [39], quinazolines synthesis [42], and dimerization reactions [43]. The Lewis acidic ILs are usually used for Friedel–Crafts and coupling reactions because their electron-accepting ability for metals (such as Fe<sup>3+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>) in anion groups can activate the halide from alkyl halide (or acyl halide) [44].

Previous studies have also indicated that the added molar fraction from a metal salt source is an essential factor for Lewis acidic IL activities [18,45–47]. For example, when the molar fraction of AlCl<sub>3</sub> in IL BmimCl–AlCl<sub>3</sub> is below 0.5, this IL exhibits its Lewis basicity because the anion of this IL is Cl and AlCl<sub>4</sub>. When the molar fraction of AlCl<sub>3</sub> is equal to 0.5, BmimCl–AlCl<sub>3</sub> becomes neutral because only the AlCl<sub>4</sub> anion is in IL. Finally, when the molar fraction is more than 0.5, the BmimCl–AlCl<sub>3</sub> IL shows strong Lewis acidity because in this IL, the major anions are the strong Lewis acidic Al<sub>2</sub>Cl<sub>7</sub> [45,46]. Similarly, when BmimCl–ZnCl<sub>2</sub> was used as solvent and catalysts for the synthesis of DPM at 80  $^{\circ}$ C with a reaction time of 2 h, it was found that when the molar fraction of ZnCl<sub>2</sub> to [Bmim][Cl] is lower than 0.67, this IL without Lewis acidic properties had low catalytic activity, and the obtained DPM yield was only 29.0% and even reached as low as 5.2% (0.6 for 29.0% DPM yield and 0.52 for 5.2%, respectively). However, when the molar fraction of  $ZnCl_2$  to [Bmim][Cl] is more than 0.67, the BmimCl-ZnCl<sub>2</sub> IL with increased Lewis acidic properties can give a 97.8% DPM yield with good catalytic activity even after recycling eight times [47]. Another literature reported that BmimCl-FeCl<sub>3</sub> IL has been used as a catalyst for Friedel–Crafts reactions to obtain benzophenone yields of about 20% and 65% with an FeCl<sub>3</sub> molar fraction of 0.52 and 0.6, respectively. However, a sudden drop in benzophenone yield in the fourth run of the recycling experiment occurred in this IL [48]. This was ascribed to the cumulative FeCl<sub>3</sub> loss during each run, which led to an IL sample with an inferior FeCl<sub>3</sub> molar fraction [48]. Therefore, in order to solve the low benzophenone yield in recycling experiment, the two equivalents of anhydrous  $FeCl_3$  must be repeatedly added in this IL [48].

Although studies using ILs as catalysts have been rapidly increasing in number, the cationic structures described in these studies mainly focus on carrying sp3-hybridized carbon atoms as substituents at both nitrogen heterocyclic atoms [13,49,50]. Very recently, a unique series of tunable aryl-imidazolium iron-containing ILs with dual Brønsted-Lewis acidity (abbreviated as B-L MILs) were reported by our group [51]. These B-L MILs have a combination of one proton and sp2 aryl substituents at the nitrogen atoms of the imidazolium core. The physical-chemical properties of B-L MILs are tuned by specific electronic effects (the  $\sigma$ - and  $\pi$ -system) and even by the substituent effect in the aryl moiety [51]. Even though the molar ratio of FeCl<sub>3</sub> to [HPhImX][Cl] ( $X = H, CH_3, OCH_3, and NO_2$ ) is only 0.5 in these B-L MILs systems, they have been shown to have good Lewis acidity [51]. In this study, we demonstrate the utility of the B-L MILs as both solvents and catalysts for the Friedel–Crafts alkylation reaction of p-xylene with benzyl chloride. The influence of various reaction parameters, such as the molar ratio of the reactants, catalyst dosage, reaction time, temperature, and the catalyst recycle are investigated. When compared to the conventional catalysts reported for the Friedel–Crafts alkylation reaction [11,15–19,29,30,47,48,52–54], the dual solvent–catalyst B-L MIL function was found to exhibit high catalytic activity and could be reused after several recycles, thus making the synthesis process greener.

#### 2. Experimental Section

#### 2.1. Chemicals

The B-L MILs were synthesized following the procedure (shown in Scheme 1) discussed in our previous work [51]. p-Xylene was purchased from Sigma-Aldrich (St. Louis, MO, USA), and benzyl chloride (BnCl) was purchased from Acros (Morris Plains, NJ, USA). These two chemicals were used without further purification.



**Scheme 1.** The structures of magnetic ionic liquids with dual functions as a solvent–catalyst and dual Brønsted–Lewis acidity (B-L MILs).

#### 2.2. Catalytic Activity Characterization in the Friedel-Crafts Alkylation Reaction

The catalytic activities of the B-L MILs catalysts (their structures are shown in Scheme 1) were evaluated through the Friedel–Crafts alkylation of p-xylene with BnCl (shown in Scheme 2). The reactions were conducted in a three-necked flask equipped with magnetic stirring and a reflux condensing tube in an oil bath. In each experiment, the B-L MIL was successively quantitatively mixed with p-xylene and BnCl in a reactor, and then the mixture was heated at a desired temperature and stirred for a period of time. The products and B-L MIL catalysts were separated using centrifugation after cooling to room temperature. Then, the reusability of the B-L MIL was characterized. In addition, the effects of key reaction factors including the reaction time, amount of B-L MILs, reaction temperature, and the molar ratio of p-xylene to BnCl were investigated. To be specific, the temperature was studied at a range from 25 °C to 100 °C; the amount of B-L MILs was varied from 0.1 mole % to 1.0 mole %; the reaction time was varied from 10 min to 120 min, and the molar ratio of p-xylene to BnCl was studied in a range from 1 to 10. Finally, the products were analyzed using a gas chromatograph (GC, model: Agilent GC-6890, Santa Clara, California, America) fitted with a capillary column (Supelcowax 10, L × 1.D. = 30 m × 0.32 mm) with an FID (flame ionization detector).



Scheme 2. The Friedel–Crafts alkylation reaction of p-xylene with benzyl chloride (BnCl).

# 3. Results and Discussion

#### 3.1. Structure and Properties Description of B-L MILs

Since the details of the structure (shown in [51]) and property characterization of the B-L MILs 5a–d with dual Brønsted–Lewis properties were published in our previous paper [51], only a brief description is provided here. The B-L MILs 5a–d with close to a 100% atom economy were synthesized using three steps: Ullmann-type coupling, treatment with HCl, and coordination with FeCl<sub>3</sub> (seen in [51]). The

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target samples, 5a–5d, with a 0.5 molar fraction of FeCl<sub>3</sub> in the B-L MILs, were characterized using an elemental analysis (the purity differences of 5a–d between the theoretical and experimental values were both within the expected ratios (within 0.3)), electrospray ionization mass spectrometry (ESI-MS, a fragment peak at m/z = 198.01 corresponding to [FeCl<sub>4</sub>]–, as shown in [51]), UV-vis spectroscopy (three characteristic bands at 534 nm, 619 nm, and 688 nm in [51]), and Raman absorption spectroscopy (a strong band at approximately 330 cm<sup>-1</sup> in [51]). The B-L MILs exhibited good solubility in various organic solvents with the exception of hexane, but they were less soluble in dichloromethane and ethyl ether (seen in [51]). B-L MILs with a sp2-substituted phenyl ring at the nitrogen atom and good charge distribution resulted in good thermal stability [51] and a low melting point (ranging from 65 to 85 °C, as shown in [51]). In terms of the most important tunable acidity, the electron-donating group (EDG) in the para-substitution of the aryl-imidazolium moiety had lower Brønsted acidity and higher Lewis acidity than the electron-withdrawing group (EWG) (as shown in [51]). These properties are related to their sp2-para-substitution effect because the electron-withdrawing and electron-donating groups can influence the charge distribution (calculated using the electrostatic surface potential model) of B-L MILs.

#### 3.2. Catalytic Application in the Solvent-Free Friedel–Crafts Alkylation Reaction

## 3.2.1. Effects of Different B-L MILs on the Friedel-Crafts Alkylation Reaction

The catalytic activity of B-L MILs was examined by using them in a Friedel–Crafts alkylation reaction of p-xylene with BnCl (seen in Scheme 2). The reactions were carried out at 80 °C for 30 min, where the mole ratio of p-xylene to BnCl was 2, and the amount of catalysts remained at 20 mole %. As can be seen from the data in Table 1 (entries 1 to 4), the BnCl conversion was at 51.4%, 20.0%, 98.6%, and 5.0% when 5a-d were used as catalysts, respectively. As also indicated in Table 1 (entries 1 to 4), the DPM selectivity was 95.6%, 41.1%, 91.7%, and 99.5%, corresponding to 5a-d as catalysts, respectively. According to the literature on Lewis acidity determination, CH<sub>3</sub>CN was used as the Lewis base to coordinate the  $FeCl_4$ - anion and obtain a signal of 2310 cm<sup>-1</sup> in Fourier-transform infrared spectroscopy (FT-IR) proven to have Lewis acidity [55]. Similarly, according to our previous research findings, 5c with an electron-donating group ( $-OCH_3$ ) had the obvious 2310 cm<sup>-1</sup> signal [51]. In this Friedel–Crafts alkylation of p-xylene with BnCl, 5c was also confirmed to have better catalytic activity than other B-L MILs. This may be attributed to the fact that the –OCH<sub>3</sub> group has a mesomeric effect that enhances the hydrogen bonding strength between the FeCl<sub>4</sub>- anion and the proton in the imidazolium ring [51]. This effect causes the empty orbital of Fe<sup>3+</sup> in the anion to coordinate with BnCl easily (as seen in Scheme 2). Although all the B-L MILs have the  $FeCl_4$ - anion as the Lewis acidity source, the cationic moiety can influence the Lewis acidity of B-L MILs because of their different EDG and EWG para-substitution effects. Thus, in this work, the B-L MIL 5c was chosen for further study in the Friedel–Crafts alkylation of p-xylene with BnCl.

Entry <sup>a</sup>	B-L MIL	Molar Ratio of IL/BnCl (mole %)	Molar Ratio of p-xylene: BnCl	BnCl Conversion (%) <sup>b</sup>	DPM Selectivity (%) <sup>b</sup>	
1	5a	20.0	2:1	51.4	95.6	
2	5b	20.0	2:1	20.0	41.1	
3	5c	20.0	2:1	98.6	91.7	
4	5d	20.0	2:1	5.0	99.5	
5	5c	0.1	2:1	14.6	99.8	
6	5c	0.3	2:1	96.0	93.0	
7	5c	0.5	2:1	98.9	88.4	
8	5c	0.7	2:1	99.6	81.1	
9	5c	1.0	2:1	99.2	91.0	
10	5c	1.0	4:1	95.0	93.0	
11	5c	1.0	6:1	99.1	96.0	
12	5c	1.0	8:1	98.6	98.3	
13	5c	1.0	10:1	99.3	99.3	
14	5c	1.0	1:1	99.9	75.0	

**Table 1.** The results of the B-L MILs 5a–d application for catalysis in the Friedel–Crafts alkylation of p-xylene with BnCl. DPM: diphenylmethane.

<sup>a</sup> All entry conditions are at a reaction temperature = 80  $^{\circ}$ C and a reaction time = 0.5 h. <sup>b</sup> BnCl conversion and DPM selectivity values are based on GC.

#### 3.2.2. Effects of Reaction Time on the Friedel–Crafts Alkylation Reaction of p-Xylene with BnCl

The reaction time is one key factor that can be used to determine the BnCl conversion and DPM selectivity of this reaction. Therefore, the influence of reaction time is investigated under 20 mole % 5c at a reaction temperature of 80 °C. The reaction times are 10, 20, 30, 60, and 120 min, and the results are presented in Figure 1. It can be clearly observed that the Friedel–Crafts alkylation of p-xylene with BnCl begins to react at 10 min, and that the BnCl conversion increases rapidly with increases in the reaction time, where for 10 to 30 min, the BnCl conversion in 10 min is 22.1%, and at 20 min, it is 41.6% until the equilibrium point (BnCl conversion: 98.6%) is reached at 30 min. The BnCl conversion raises slightly to 98.9% at 60 to 120 min. The DPM selectivity reaches 91.7% at 30 min, and then slightly decreases to 82.9% at 60 min and to 83.6% at 120 min. These results may be due to a uniform molecular collision with the increase in the reaction time [56]. Hence, the optimal reaction time in this reaction is 30 min.



**Figure 1.** The effects of reaction time on the Friedel–Crafts alkylation reaction of p-xylene with BnCl (under 20 mole % 5c, a reaction temperature of 80 °C, and a molar ratio of p-xylene:BnCl = 2:1).

3.2.3. Effects of Catalyst Amounts on the Friedel–Crafts Alkylation Reaction of p-Xylene with BnCl

In this section, the results for a study of the influence of catalyst amounts are shown in Figure 2 and Table 1 (in entries 5 to 9, the reaction temperature condition is 80 °C for 30 min). It can be seen that when the 5c dosage is above 0.3 mole %, the BnCl conversion reaches approximately 95%. However, the BnCl conversion does not increase significantly when the 5c amount is higher than 0.3 mole %, indicating that the BnCl conversion has reached a limiting value when 5c is higher than 0.3 mol %. The DPM selectivity decreases from 93.0% at about 0.3 mole % of 5c to 91.0% at 1.0 mole 0% of 5c. From the point of view of high reaction efficiency and economic green chemistry, the optimal catalyst amount of 1.0 mole % was chosen. It appears that 5c is the predominate catalyst for the Friedel–Crafts alkylation of p-xylene with BnCl under appropriate conditions.



**Figure 2.** The effects of the amount of catalyst on the Friedel–Crafts alkylation reaction of p-xylene with BnCl (at a reaction temperature of 80 °C, a reaction time = 0.5 h, and a molar ratio of p-xylene: BnCl = 2:1).

3.2.4. Effects of Reaction Temperature on the Friedel–Crafts Alkylation Reaction of p-Xylene with BnCl

The reaction temperature is an important key factor affecting the BnCl conversion and DPM selectivity in this Friedel–Crafts alkylation. Therefore, the influence of the reaction temperature was studied at various temperatures ranging from room temperature to 100 °C while keeping the amount of 5c at 1.0 mole % and the reaction time at 30 min. The results are presented in Figure 3. This figure clearly shows that the BnCl conversion increases rapidly to approximately 99.9% when the temperature is increased from 50 to 80 °C and remains above 90% at 100 °C Similarly, DPM selectivity increases rapidly from 0 to 99.9% as the temperature is increased from 25 to 50 °C. Increasing the reaction temperature has the most significant influence on the BnCl conversion and DPM selectivity due to the more vigorous molecular collisions at higher reaction temperatures [56]. Another possible reason for the dramatic changes in BnCl conversion and DPM selectivity may be due to the melting point of B-L MIL 5c (the melting point is about 83 °C). When the reaction temperature is gradually elevated to 80 °C, 5c has been melted to contribute to the homogeneous state with p-xylene and BnCl. However, as temperature is raised to 100 °C, the BnCl conversion and the DPM selectivity do not increase further. This may have been due to the limitations of the chemical reaction equilibrium, given the energy consumption of the reaction. Therefore, 80 °C was selected as the proper reaction temperature.



**Figure 3.** The effects of reaction temperature on the Friedel–Crafts alkylation reaction of p-xylene with BnCl (under a 5c catalyst dosage of 1.0 mole %, a reaction time = 0.5 h, and a molar ratio of p-xylene: BnCl = 2:1).

#### 3.2.5. Effects of the Molar Ratio of p-xylene to BnCl on the Friedel-Crafts Alkylation Reaction

The effects of the molar ratio of p-xylene to BnCl on the Friedel–Crafts alkylation was investigated at 80, 5c 1.0 mole %, with refluxing for 30 min. The molar ratio of p-xylene to BnCl increased from 1 to 10. The results are shown in Figure 4 and Table 1 (entries 9 to 14). It is worth noting that when the molar ratio was 6, the BnCl conversion reached 99.0%, and the DPM selectivity reached 96.0%. When the molar ratio exceeded 6, both the BnCl conversion and DPM selectivity did not increase significantly. This result indicates that the BnCl may have fully reacted, and that the by-products may also have been significantly suppressed when the amount of p-xylene was excessive. Therefore, 6 was selected as the appropriate molar ratio of p-xylene to BnCl.



**Figure 4.** The effects of the molar ratio of p-xylene to BnCl on the Friedel–Crafts alkylation reaction (under a 5c catalyst dosage of 1.0 mole %, a reaction time of 0.5 h, and a reaction temperature of 80.

#### 3.2.6. Catalyst Recycling and Stability

Further investigation, including evaluating the reusability and stability of catalyst 5c for the Friedel–Crafts alkylation reaction of p-xylene with BnCl, was conducted under the optimum conditions obtained by the above-mentioned test (a temperature of 80 °C, a reaction time of 30 min, catalyst 5c amount 1.0 mole %, and a molar ratio of p-xylene to BnCl of 6:1). The 5c could be easily separated from the reaction mixture by centrifugation with drying under a vacuum after washing with hexane 2–3 times. Using this process, six consecutive Friedel–Crafts alkylation procedures were conducted, for which the

results are summarized in Figure 5. The catalytic activity of ILs typically decreases gradually with increases in the catalyst recycle times because the ILs gradually dissolve with the solvent with increases in the number of consecutive reaction times. The striking recycling results shown in Figure 5 show that the product yield was an average of 95.0% with almost no evidence of a decrease in efficiency. Every product yield of the consecutive catalytic run was maintained at a minimum of 90.0% (the first and second run were both 97.0%; the third run was 90.0%, and the fourth run was 92.0%). A 98.0% product yield was even obtained after the sixth reaction run. When compared with some catalysts reported in the literature (shown in Table 2), the 5c had many advantages. Firstly, using 5c can make the reaction solvent-free. Secondly, 5c with air and water stability overcomes the air-sensitive and water-sensitive disadvantages of the AlCl<sub>3</sub>-based systems (AlCl<sub>3</sub>, [EMIM]Cl-AlCl<sub>3</sub>, and [BMIM]Cl-AlCl<sub>3</sub>). Thirdly, the molar fraction of the FeCl<sub>3</sub> in B-L MILs 5c is only 0.5 (compared with [EMIM]Cl-AlCl<sub>3</sub> (molar fraction >0.67), [BMIM]Cl-AlCl<sub>3</sub>, [BMIM]Cl-FeCl<sub>3</sub>, [BMIM]Cl-FeCl<sub>2</sub>, and [BMIM]Cl-ZnCl<sub>2</sub> (both the molar fraction of these four IL >0.67) [15,47,48]). Fourthly, 5c is less expensive than the InCl<sub>3</sub> catalyst. Fifthly, 5c lowers the molar ratio of p-xylene to BnCl, shortens the reaction time, and saves the catalyst. Most importantly, 5c with a specific mesomeric effect can overcome the loss of metal chloride salt in each recycling run and keep the molar fraction equal to 0.5 (when compared with [BMIM]Cl-AlCl<sub>3</sub>, [BMIM]Cl-FeCl<sub>3</sub>, and [BMIM]Cl-FeCl<sub>3</sub> [47,48]). Therefore, 5c can also improve the non-uniform dispersion, and give excellent reusability more than other reported catalysts (when compared with Bi(OTf)<sub>3</sub>/[EMIM][NTf<sub>2</sub>], Cu(OTf)<sub>3</sub>/[BMIM][BF<sub>4</sub>], Sc(OTf)<sub>3</sub>/[BMIM][SbF<sub>6</sub>], [BMIM][B(HSO<sub>4</sub>)<sub>4</sub>], and [Pyrro][H(CF2)<sub>4</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>3</sub>] [16–19,30]) through six consecutive catalytic Friedel–Crafts alkylation runs without a significant loss in product yield (an average of 95.0%). In general, the 5c catalyst with a dual solvent-catalyst function, dual Brønsted-Lewis acidity, and excellent catalytic activity is stable enough. Thus, 5c is a promising material for green chemical processes. The reaction scope (including different reaction substrates and other organic reactions with needing acidic catalysts) and limitation will be expanded to investigate in further follow-up and thorough studies.



**Figure 5.** Examination of reusability of B-L MIL 5c (under reaction temperature =  $80 \degree C$ , a reaction time = 0.5 h, 5c amount =  $1.0 \mod \%$ , and a molar ratio (p-xylene:BnCl) = 6:1).

Catalyst	Reaction Temperature (°C)	Reaction Time (h)	Catalyst Amount	Molar Ratio of Reactants	Re-Used Cycle Number	Product Yield (%)	Reference
5c <sup>a</sup>	80	0.5	1 mole %	6:1	6	95.0	This work
AlCl <sub>3</sub>	130	1	2 wt %	6:1	n.r. <sup>d</sup>	96.5	52
InCl <sub>3</sub>	50	16	10 mole %	10:1	n.r.	75.0	53
PmimCl-FeCl <sub>3</sub> -MCM-41	80	0.75	15 wt %	10:1	n.r.	100.0	11
MZT-11	75	24	1 wt %	10:1	n.r.	92.3	54
[HSO3-pmim][OTf]	40	0.5	20 mole %	2:1	5	93–97	29
[Pyrro][H(CF <sub>2</sub> ) <sub>4</sub> O(CF <sub>2</sub> ) <sub>2</sub> SO	3] 50	24	2 mL	2:1	n.r.	90.0	30
[EMIM]Cl-AlCl <sub>3</sub> <sup>b</sup>	20	1	n.r.	n.r.	n.r.	89.0	15
$[BMIM][B(HSO_4)_4]$	50	1	5 mole %	5:1	n.r.	51.0	16
Bi(OTf) <sub>3</sub> /[EMIM][NTf <sub>2</sub> ]	150	3	5 mole %	2:1	4	91.0	17
$Cu(OTf)_3/[BMIM][BF_4]$	80	24	5 mole %	5:1	n.r.	81.0	18
Sc(OTf) <sub>3</sub> /[BMIM][SbF <sub>6</sub> ]	20	12	20 mole %	2:1	n.r.	92.0	19
[BMIM]Cl-AlCl <sub>3</sub> <sup>b, c</sup>	80	2	1 mL	10:1	1	100.0	47
[BMIM]Cl-FeCl <sub>3</sub> <sup>b, c</sup>	80	2	1 mL	10:1	3	97.1	47, 48
[BMIM]Cl-FeCl <sub>2</sub> <sup>b, c</sup>	80	2	1 mL	10:1	2	99.4	47
[BMIM]Cl-ZnCl2 <sup>b</sup>	80	2	1 mL	10:1	8	98.6	47

Table 2. Comparison of reaction conditions between B-L MIL 5c and previously reported catalysts.

<sup>a</sup> Solvent-free condition in this study. <sup>b</sup> Molar fraction of metal chloride salt must be more than 0.67. <sup>c</sup> The product yield has been drastically reduced in the next recyclable test because of the loss of metal chloride salt in each run. <sup>d</sup> n.r.: not reporte.

## 4. Conclusions

This study was aimed toward applying a series of B-L MILs with different para-substitutions in cationic moiety for the Friedel-Crafts alkylation in an aromatic system. The catalytic activity of the B-L MIL 5c that was examined for the Friedel-Crafts alkylation of p-xylene with BnCl exhibited excellent catalytic activity, in which the BnCl conversion was above 99.0% (DPM selectivity with product yields of 96.0% and an average of 95.0%, respectively) along with the following optimal reaction conditions: molar ratio n(p-xylene): n(BnCl) = 6:1, catalyst 5c amounts: 1.0 mole %, reaction temperature =  $80 \,^{\circ}$ C, and reaction time =  $0.5 \,\text{h}$ . Furthermore, the homogeneous catalyst 5c can be separated easily by centrifugation from the reaction system, and outstanding catalytic activity without significant loss in product yield after six consecutive recycles dual to its specific mesomeric effect was found. The dual solvent-catalyst function and dual Brønsted-Lewis acidity of B-L MIL 5c provided many advantages over the traditional catalysts under consideration. Therefore, this study provides a more extensive platform for organic reactions and meets the green chemistry standards, including operational simplicity, high product yield, no significant loss, and reusability. It is worth mentioning that the molar fraction of the FeCl<sub>3</sub> in the B-L MILs system is only 0.5, which is lower than that of other metal salt sources such as AlCl<sub>3</sub> and ZnCl<sub>2</sub> previously reported (molar ratio >0.67) [18,45–47,57]. Hence, B-L MILs are potentially suitable for the industrial production of DPM derivatives.

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