

## Diphenylmethane Synthesis Using Ionic Liquids as Lewis Acid Catalyst

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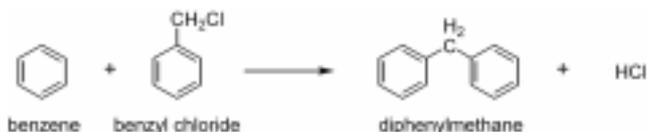
**Abstract**—Friedel-Crafts alkylation of benzene with benzyl chloride was studied by using organochloroaluminate ionic liquids as Lewis acid catalyst. The reaction was performed in the temperature range of 40 to 70 °C at benzene/benzyl chloride=17, where selectivity to diphenylmethane was high. The optimum AlCl<sub>3</sub>/BMIC ratio of the ionic liquid for the benzylation reaction was 2. Superior performance was obtained with butyl group constituting the cationic species of the ionic liquid. Stirring speed had a major impact on catalytic activity of the BMIC-AlCl<sub>3</sub> ionic liquid; benzyl chloride conversion decreased substantially from 98 to 68% as stirring speed was reduced from 900 to 500 rpm, and eventually no reaction took place at 200 rpm. BMIC-AlCl<sub>3</sub> ionic liquid was more active than Fe-MCM-41 at the expense of a small drop in selectivity but still higher than 96% selectivity was obtained. The ionic liquid could be easily recovered after phase separation. The performance of BMIC-AlCl<sub>3</sub> ionic liquid was maintained after the second run with 97.4% conversion and 95.6% selectivity, but a sudden drop in activity was observed after the third run with only 26.8% conversion.

Key words: Friedel-Crafts Alkylation, Diphenylmethane, Ionic-liquid, Fe-MCM-41

### INTRODUCTION

Considerable interest has recently been manifested in the use of room temperature ionic liquids as a solvent/catalyst for industrial reactions including polymerization, alkylation, acylation, and Diels-Alder reactions [Simon et al., 1998; Adams et al., 1998; Lee, 1999; Welton, 1999; Earle et al., 1998; Marsh et al., 2002]. Room temperature ionic liquids typically consist of nitrogen-containing organic cation and inorganic anions, physicochemical properties of which can be finely tuned for a range of applications by varying the ionic species [Gordon et al., 1998]. They are good nonvolatile solvents for a wide range of organic, inorganic, and polymeric materials, which can be easily separated from the reactant/product by gravity settling due to density differences [Freemantle, 1998]. In addition, organochloroaluminate ionic liquids, typically a mixture of a quaternary ammonium salt such as 1,3-dialkylimidazolium chloride with aluminum chloride, can serve as Lewis acid when the molar ratio of aluminum trichloride to dialkylimidazolium chloride is greater than 1 [Chauvin and Oliver-Bourbigou, 1995]. The ionic liquids can be characterized by <sup>1</sup>H-NMR and elemental analysis [Bonhote et al., 1996].

The Friedel-Crafts alkylation of aromatic compounds is an important synthetic tool employed for the preparation of many fine chemical intermediates, and is usually carried out in the presence of homogeneous acids such as AlCl<sub>3</sub>, BF<sub>3</sub>, HF, or H<sub>2</sub>SO<sub>4</sub>. However, these acidic reagents present problems of catalyst separation/recovery, corrosion, toxicity and unwanted waste by-products such that environmentally benign catalysis involving solid acid catalysts has been actively investigated as an alternative [Clark and Rhodes,



Scheme 1. Friedel-Crafts alkylation of benzene to diphenylmethane.

2000]. Diphenylmethane is widely used as fragrance fixative, additive to agrochemicals, dyes, and polyesters and prepared typically by the Friedel-Crafts alkylation of benzene with benzyl chloride (Scheme 1) in the presence of a Lewis acid catalyst, AlCl<sub>3</sub>. Montmorillonite-supported zinc (Clayzinc), iron pillared clays (FePILCs), zeolites, sulfate-promoted Fe<sub>2</sub>O<sub>3</sub>, and recently an Fe-containing mesoporous molecular sieve have been reported as active/selective and environmentally friendly catalysts for the reaction [Clark and Rhodes, 2000; Pai et al., 1997; Singh and Pandey, 1999; Koyande et al., 1998; He et al., 1998].

In this work, diphenylmethane synthesis by benzene alkylation was studied using organochloroaluminate ionic liquids as Lewis acid catalyst. Effects of ionic liquid composition, reaction parameters (temperature, reactant ratios, stirring speed), and catalyst recycling on the catalyst performance were investigated. Comparison of catalytic activity was also made with Fe-MCM 41, which has recently been reported to be an active heterogeneous catalyst for the same reaction [He et al., 1998].

### EXPERIMENTAL

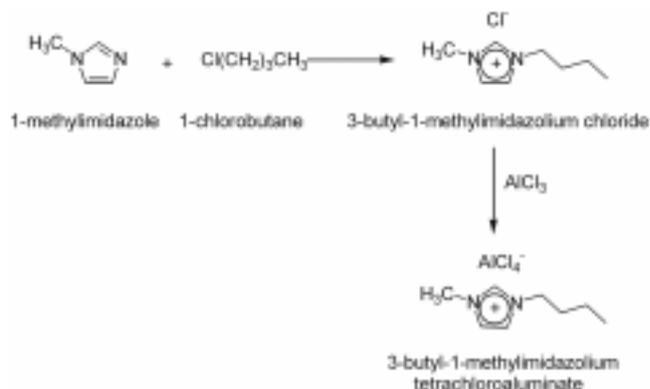
#### 1. Preparation of the Ionic Liquid

Organochloroaluminate ionic liquid was prepared as described in the references [Huddleston et al., 1998; Wilkes et al., 1982; Bonhote et al., 1996]. To prepare the organic cation, 1-methylimidazole (99+%, Aldrich) was reacted with either 1-chlorobutane (99%, Al-

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<sup>‡</sup>This paper is dedicated to Professor Baik-Hyon Ha on the occasion of his retirement from Hanyang University.



**Scheme 2.** Synthesis of organochloroaluminate ionic liquid.

drich) or 1-chloro propane (99.5%, Aldrich). As an inorganic anion, aluminum trichloride (99.5%, Junsei Chemical Co.) was used. The ionic liquid was synthesized in a dry box purged with nitrogen due to sensitivity of the material to moisture in air. First, 1-methylimidazole and 1-chlorobutane of 1 to 1 mole ratio were mixed inside a 250 ml 3 neck flask fitted with a condenser and placed in a constant temperature bath maintained at 70 °C and stirred vigorously for 48-72 h. After brown colored 3-butyl-1-methylimidazolium chloride was obtained, the liquid was cooled to room temperature and excess reactant remained was removed in a rotary evaporator. The mole ratio of 3-butyl-1-methyl-imidazolium chloride to aluminum trichloride was adjusted to 1 : 1, 1.5 : 1, 2 : 1, and 2.5 : 1, respectively, and the mixture was stirred for 12 h at room temperature to produce the final product of 3-butyl-1-methylimidazolium tetrachloroaluminate ionic liquids (BMIC- $\text{AlCl}_3$ ). Overall synthesis stoichiometry is shown in Scheme 2. Following the same procedure described above, 1-chloropropane was also used to prepare the cationic precursor with a different alkyl group. 3-Propyl-1-methyl-imidazolium chloride to aluminum trichloride was then adjusted to 2 : 1 ratio to produce 3-propyl-1-methylimidazolium tetrachloroaluminate (PMIC- $\text{AlCl}_3$ ).

## 2. Catalytic Reaction

Benylation of benzene was carried out for 4 h using a 50 ml 3 neck round flask placed inside a constant temperature bath which was maintained at 40-70 °C and atmospheric pressure. The experimental apparatus is basically identical to the one used by us earlier [Chung et al., 1998]. The standard set of reaction conditions is described in Table 1. Initially, 26 ml benzene (99.5%, Oriental Chemi-

**Table 1.** Reaction conditions of benzylation of benzene

Parameter	Spec.
Benzene	292.5 mmol
Benzyl chloride	17.4 mmol
Temperature	60 °C
Stirring speed	900 rpm
Reaction time	4 h
Pressure	1 atm
Catalyst	BMIC- $\text{AlCl}_3$ , 0.25 g

<sup>a</sup>3-butyl-1-methylimidazolium tetrachloroaluminate ionic liquid. mole ratio of benzene : benzyl chloride = 17 : 1.

cal Industries) and 0.25 g of ionic liquid (1 wt% reaction mixtures) were put into the reactor. After reaction temperature was established, benzyl chloride (99%, Aldrich) was introduced to the mixture and reaction was initiated by vigorous mechanical stirring (900 rpm). At regular intervals, samples were taken and neutralized by using NaOH solution (0.1 N), and product was analyzed with a gas chromatograph (Shimadzu GC-14A) equipped with FID and CBP-20 capillary column.

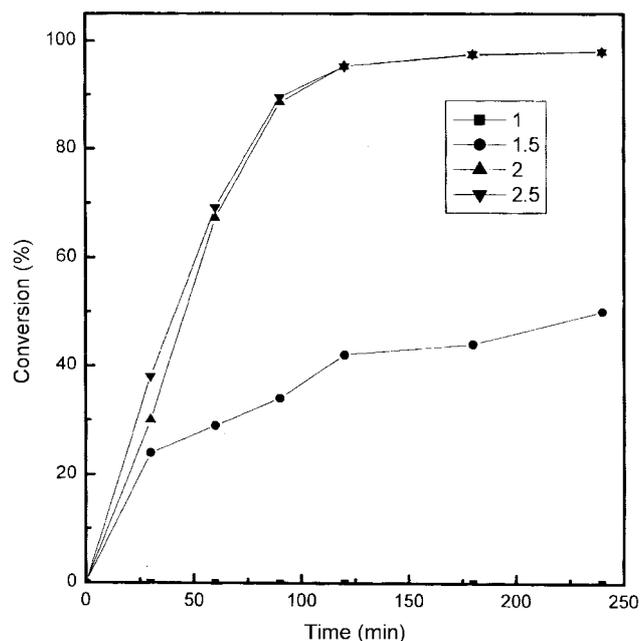
## RESULTS AND DISCUSSION

Catalytic activities of 3-butyl-1-methyl imidazolium tetrachloroaluminate ionic liquids (BMIC- $\text{AlCl}_3$ ) prepared with different molar ratio of aluminum trichloride ( $\text{AlCl}_3$ ) to 3-butyl-1-methylimidazo-

**Table 2.** The conversion of benzyl chloride and selectivity to diphenylmethane in benzylation of benzene using different catalysts

Catalyst	$\text{AlCl}_3/\text{BMIC}$	Si/Fe	Conversion of benzyl chloride (%)		Selectivity to diphenylmethane (%)	
			2 h	4 h	2 h	4 h
BMIC- $\text{AlCl}_3$	1	-	0	0	0	0
BMIC- $\text{AlCl}_3$	1.5	-	42.0	50.3	100	100
BMIC- $\text{AlCl}_3$	2	-	95.3	97.9	96.1	96.1
BMIC- $\text{AlCl}_3$	2.5	-	95.3	98.1	96.3	96.1
PMIC- $\text{AlCl}_3$	2	-	78.6	91.8	97.6	89.4
Fe-MCM-41 <sup>a</sup>	-	15	11.5	20.9	100	100
Fe-MCM-41 <sup>b</sup>	-	50	71.9	99.4	98.7	98.5

<sup>a</sup>Fe(III) $\text{Cl}_3$  grafting. <sup>b</sup>direct synthesis. Reaction conditions are the same as those specified in Table 1.



**Fig. 1.** Benzyl chloride conversion profiles using ionic liquid catalysts prepared at different  $\text{AlCl}_3/\text{BMIC}$  mole ratios.

lium chloride (BMIC) are summarized in Table 2 and their conversion profiles are shown in Fig. 1. No reaction took place when the  $\text{AlCl}_3/\text{BMIC}$  ratio was 1, and with  $\text{AlCl}_3/\text{BMIC}=1.5$ , benzyl chloride conversion was limited to ca. 50% after 4h reaction. When the  $\text{AlCl}_3/\text{BMIC}=2$ , benzyl chloride conversion increased to >95% after 2 h and remained almost constant afterwards. Selectivity to diphenylmethane was ca. 96%. Small amounts of heavier product (not identified) by polyalkylation and rearrangement were observed, and their formation increased with conversion, but not to a significant extent. Virtually identical results were obtained with  $\text{AlCl}_3/\text{BMIC}=2.5$ , indicating that the optimum  $\text{AlCl}_3/\text{BMIC}$  ratio of the ionic liquid for the benzylation reaction is 2. It is known that when  $\text{AlCl}_3/\text{BMIC}<1$ , the ionic liquid formed contains a mixture of  $[\text{AlCl}_4^-]$  and highly complexing  $\text{Cl}^-$  anions and basic in nature, while it becomes neutral at  $\text{AlCl}_3/\text{BMIC}=1$ , and acidic when  $\text{AlCl}_3/\text{BMIC}>1$  by the formation of excess  $[\text{AlCl}_7^-]$  and  $[\text{AlCl}_{10}^-]$  anions over  $\text{Cl}^-$  [Chauvin and Oliver-Bourbigou, 1995]. The benzylation reaction results above confirmed the acidic property of ionic liquids at  $\text{AlCl}_3/\text{BMIC}>1$  and it was catalyzed by Lewis acid sites of the ionic liquid.

An alkyl group of variable chain length in the cation constituting the ionic liquids can be used to adjust the properties of the ionic liquid [Huddleston et al., 1998; Bonhote et al., 1996]. Thus, 3-propyl-1-methylimidazolium tetrachloroaluminate ionic liquid (PMIC- $\text{AlCl}_3$ ) was also prepared by using 1-chloropropane instead of 1-chlorobutane in the synthesis, and its benzylation activity was measured. PMIC- $\text{AlCl}_3$  produced ca. 92% benzyl chloride conversion and 89% diphenylmethane selectivity after 4 h reaction; about 6% less conversion accompanied by 7% decrease in diphenyl methane selectivity compared with the performance of BMIC- $\text{AlCl}_3$ . More pronounced difference in catalytic activity was measured after 2 h reaction, indicating the superior performance of BMIC- $\text{AlCl}_3$  with butyl group in its cationic composition. Steric hindrance of longer

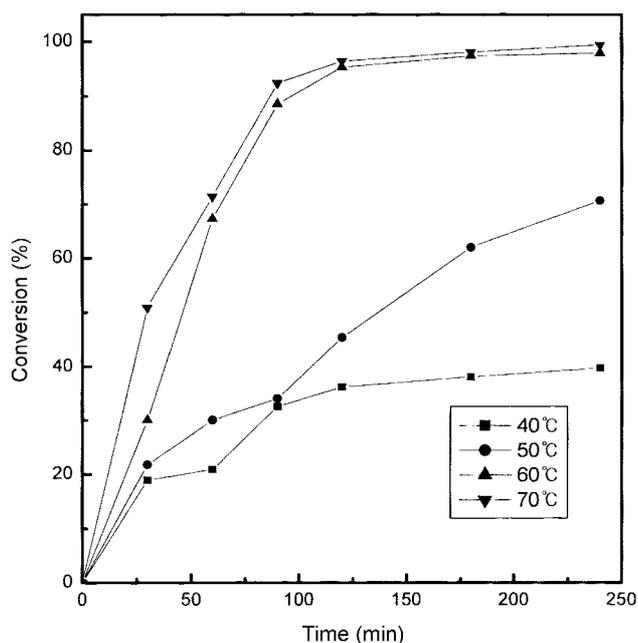


Fig. 2. The conversion of benzyl chloride in benzylation of benzene at different reaction temperatures.

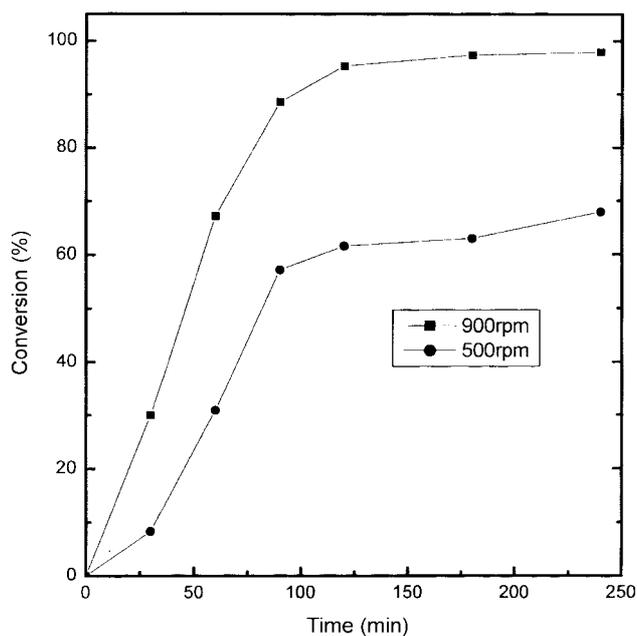


Fig. 3. The conversion profiles of benzyl chloride in benzylation of benzene at different stirring speeds.

butyl group in BMIC- $\text{AlCl}_3$  may be involved in inhibiting the poly-alkylated by-product formation.

The effects of reaction temperature and stirring speed on benzylation activity of the BMIC- $\text{AlCl}_3$  ionic liquid were studied by varying the temperature between 40-70 °C under the standard reaction conditions of Table 1, and conducting the reaction at the stirring speed to 200 rpm, 500 rpm, and 900 rpm at 60 °C. The conversion profiles of benzyl chloride in each case are shown in Figs. 2 and 3. Conversion after 4 h reaction increased steadily from 39.7 to 99.4% accompanied by slight decrease in diphenylmethane selectivity from 100 to 96% as the reaction temperature was changed from 40 to 70 °C. Above 60 °C, little improvement in catalytic performance was observed upon further temperature increase, and the reaction rate is believed to be mass transfer-limited. Stirring speed had a major impact on catalytic activity of the BMIC- $\text{AlCl}_3$  ionic liquid. As shown in Fig. 3, benzyl chloride conversion decreased substantially from 98 to 68% as the stirring speed was reduced from 900 to 500 rpm, and eventually no reaction took place at 200 rpm. At 200 rpm, the dense BMIC- $\text{AlCl}_3$  ionic liquid would sink to the bottom of the reactor, and no intimate contact between ionic liquid and reactants was expected to take place to promote the catalytic reaction. Apparently, the reaction rates depend critically on the interfacial area between the catalyst and the feed, and mixing of the reactants with ionic liquid will be a critical factor [Freemantle, 1998].

Dependence of diphenylmethane selectivity on the reactant ratios in the BMIC- $\text{AlCl}_3$  ionic liquid system was examined by varying the benzene/benzyl chloride ratio to 17 : 1, 10 : 1, 5 : 1 and the results are shown in Table 3. Conversions of benzyl chloride higher than 90% with corresponding selectivities to diphenylmethane above 80% were obtained in all cases after 4 h reaction. However, at benzene/benzyl chloride=5, selectivity to diphenylmethane decreased from 98.3% (2 h) to 80.5% (4 h) and, at benzene/benzyl chloride=10, it decreased from 90.8% (2 h) to 88.3% (4 h). The highest se-

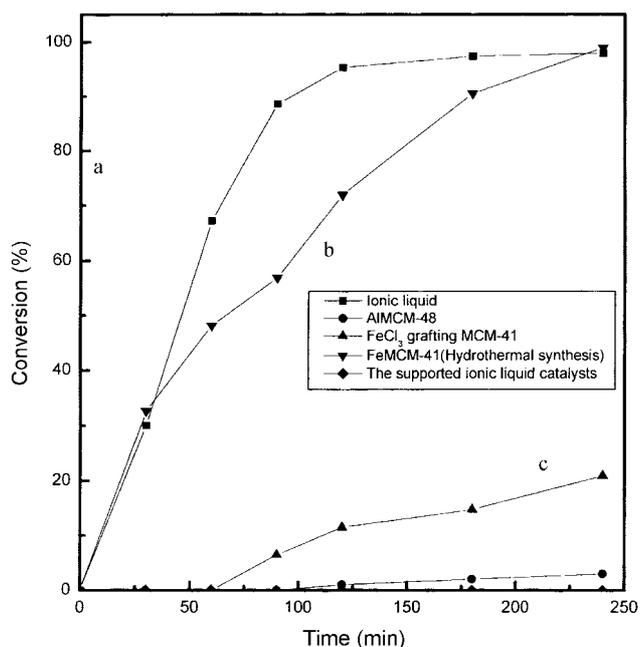
**Table 3. The conversion of benzyl chloride and selectivity to diphenylmethane at different mole ratio of benzene to benzyl chloride**

Mole ratio <sup>a</sup> (B : BC)	Conversion of benzyl chloride (%)		Selectivity to diphenylmethane (%)	
	2 h	4 h	2 h	4 h
5 : 1	88.4	98.3	98.3	80.5
10 : 1	65.6	91.9	90.8	88.3
17 : 1	95.3	97.9	96.1	96.1

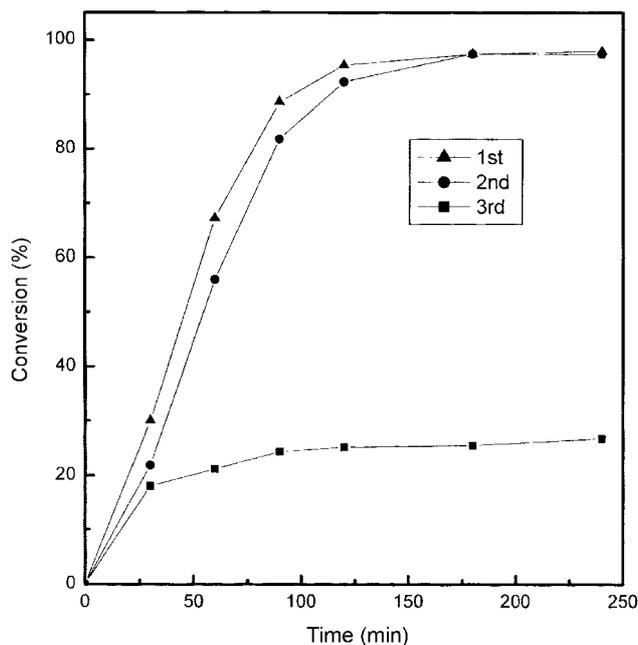
<sup>a</sup>Mole ratio of benzene to benzyl chloride (B : BC).

lectivity of 96.1% to diphenylmethane was obtained at benzene/benzyl chloride=17 and remained virtually constant after 2 h reaction. Thus, the higher the concentration of alkylating agent, the higher was the level of selectivity to monoalkylated product obtained [Gondos and Kapocsi, 1996].

The catalytic activity of the 3-butyl-1-methylimidazolium tetrachloroaluminate ionic liquid (BMIC-AlCl<sub>3</sub>) was also compared with that of the Fe-containing mesoporous solid acid catalysts, which was recently reported to be very active for the benzylation of benzene [He et al., 1998]. For this purpose, MCM-41 impregnated with Fe(III)Cl<sub>3</sub> (Fe-MCM-41(IM)) and FeMCM-41 by direct hydrothermal synthesis method (Fe-MCM-41(D)) were prepared following the literature recipes [He et al., 1998], and the benzylation reaction was carried out at the standard reaction conditions of Table 1. Characterization work of XRD, N<sub>2</sub>-adsorption, and TEM confirmed the high quality of the mesoporous materials used in the reaction. The conversion profiles of benzyl chloride in each case are shown in Fig. 4, and selected results are summarized in Table 2. As is shown in Fig. 4, BMIC-AlCl<sub>3</sub> ionic liquid showed the best catalytic performance among the three catalysts tested despite a small drop in



**Fig. 4. Conversion profiles of benzyl chloride in benzylation of benzene for ionic liquid and transition metal incorporated mesoporous catalysts.**



**Fig. 5. The conversion profile of benzyl chloride for benzylation of benzene using a recycled ionic liquid catalyst.**

selectivity than Fe-MCM-41(D) after 4 h. Fe-MCM-41(D) was also very active with >98% conversion and 100% selectivity to diphenylmethane after 4 h reaction, even though the benzyl chloride conversion profile developed more slowly than that of ionic liquid, reflecting lower activity of the former on equal weight basis. The high activity of Fe-MCM-41(D) was reported as a consequence of highly dispersed octahedral Fe oxide species formed on the channel walls of mesoporous MCM-41 after calcinations. The dependence of catalytic activity of Fe containing MCM-41 on the preparation method was also in accordance with the report by He et al. [1998] For Fe-MCM-41(IM), dispersion of Fe oxide is expected to be substantially lower than Fe-MCM-41(D), and was far less active than either BMIC-AlCl<sub>3</sub> or Fe-MCM-41(D) with only 20.9% conversion (4 h).

Stability of BMIC-AlCl<sub>3</sub> was tested by repeating the catalytic runs using the recycled ionic liquid catalyst, and the result is shown in Fig. 5. The ionic liquid could be recovered easily after phase separation, which was completed 2-3 min after stopping the reaction. The performance of BMIC-AlCl<sub>3</sub> ionic liquid was maintained after the second run with 97.4% conversion and 95.6% selectivity, but substantial drop in activity was observed after the third run with only 26.8% conversion. The color of the pale reaction mixture changed to yellow during the third run, signaling the decomposition of BMIC-AlCl<sub>3</sub>. It is not clear whether this degradation is a consequence of the reaction product, HCl, or due to air exposure during the catalyst recovery step. Successful recycle of ionic liquid up to 5 times was reported for ionic liquid comprising AlCl<sub>3</sub> and trimethylamine hydrochloride in benzene alkylation with dodecene in a patent literature [Shbrir, 1999].

## CONCLUSIONS

Organochloroaluminate ionic liquid was applied as Lewis acid

catalyst to prepare diphenylmethane by benzene alkylation using benzyl chloride and the following conclusions were obtained.

1. Catalytic activity of ionic liquid was strongly affected by its composition such as aluminum trichloride ( $\text{AlCl}_3$ ) to 3-butyl-1-methylimidazolium chloride (BMIC) mole ratios, and alkyl group in methylimidazolium chloride. Optimum  $\text{AlCl}_3$ /BMIC ratio of the ionic liquid for the benzylation reaction was 2, and the butyl group attached to methylimidazolium chloride produced the enhanced selectivity to diphenylmethane more than the propyl group.

2. Benzene alkylation using ionic liquid was strongly affected by temperature, substrate mole ratio, and stirring. Conversion increased steadily from 40 to 99% and diphenylmethane selectivity decreased slightly from 100 to 96% using ionic liquid catalyst. The higher the benzyl chloride/benzene ratio, the higher was the selectivity to diphenylmethane. Benzyl chloride conversion decreased substantially from 98 to 68% as the stirring speed was reduced from 900 to 500 rpm, and eventually no reaction proceeded at 200 rpm.

3. The catalytic activity of the 3-butyl-1-methylimidazolium tetrachloroaluminate ionic liquid (BMIC- $\text{AlCl}_3$ ) was higher than Fe-containing mesoporous solid acid catalysts—recently reported to be very active for the benzylation of benzene. However, the former deactivated after 3 catalytic runs; change of alkylating agent and improved air/water stability may be necessary.

#### ACKNOWLEDGMENT

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