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Synthesis of Diphenylmethane from Benzene and Paraformaldehyde Catalyzed by Acidic Ionic Liquids

Shuhan Cui · Bin Lu · Xue Xiao · Yuanyuan Han · Qinghai Cai

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Abstract Condensations of benzene or toluene, xylene and paraformaldehyde to diphenylmethane (DPM) or its derivatives were performed using acidic ionic liquids $Et_3NHCl–AlCl_3$, $Et_3NHCl–FeCl_3$, $Et_3NHCl–ZnCl_2$, $Et_3NHCl–CuCl_2$, $Et_3NHCl–CuCl$, $Et_3NHCl–SnCl_2$ as catalysts. The catalytic activity of $Et_3NHCl–AlCl_3$ proved to be superior to that of other catalysts for the condensation of benzene and paraformaldehyde, giving 92.4% conversion of HCHO and 76.1% selectivity to diphenylmethane at 80 °C and atmospheric pressure. The effect of various reaction conditions on the reaction and reaction kinetics of DPM synthesis were explored.

Keywords Diphenylmethane · Benzene · Paraformaldehyde · Ionic liquid

1 Introduction

As an important chemical for the production of spices, pharmaceutics and other fine chemicals, diphenylmethane (DPM) was commercially synthesized by Friedel–Crafts alkylation of benzene with benzyl chloride in liquid phase, using homogeneous acids such as $AlCl_3$, $FeCl_3$, BF_3 or H_2SO_4 [1] as catalysts. These homogeneous catalysts suffer from the inherent problems of corrosiveness, non-reusability, environmental hazard and waste control after the reaction. To overcome this unfavorable situation, great efforts have been made to replace these materials with environmentally benign solid catalysts, but the activities of these solid acids such as zeolite [2], heteropoly acid salts [3], sulfated ZrO_2 [4], clays [5], and Fe-containing MCM-41 [6] are reported to be insufficient. Hence, there is still a need to develop a new catalytic system and/or an easy-clean technology more suitable for the synthesis of DPM and its derivatives.

Synthesis of DPM by condensation of benzene with formaldehyde is one kind of new process, which is economic and environmentally benign since no organic chlorides are used and the only by-product of the reaction is water. It has already been reported that the synthesis of DPM from benzene and paraformaldehyde or formalin was carried out in gas or liquid phase over various solid acids like Aciplex-SiO_2, H-ZSM-5, HY zeolites etc. [7], giving 66.3% or 38.7% of yield at the reaction temperature of 140 °C or 200 °C, respectively. However, the catalytic reaction of benzene with paraformaldehyde to form DPM catalyzed by metal-chloride ionic liquids in liquid phase has not been reported.

Room temperature ionic liquids are being more and more regarded as relatively clean catalysts and solvents [8, 9]. Recently, many organic reactions like alkylation [10], olefin dimerization [11], Diels-Alder reaction [12] etc. have been reported to proceed in chloroaluminate room temperature ionic liquids with excellent yield and selectivity. In these reactions, the acidity of the ionic liquids is a key aspect. It was known that metal chloride-based ionic liquids can be Lewis acidic if the molar ratio of MCl_x:quaternary ammonium salt is >1.0 [13], and a superacid may be formed, when protons are further added into the Lewis acidic ionic liquid [14]. Here, we wish to report the synthesis of DPM from benzene and paraformaldehyde catalyzed by metal chloride-based ionic liquids such as $Et_3NHCl–AlCl_3$, $Et_3NHCl–FeCl_3$, $Et_3NHCl–ZnCl_2$, $Et_3NHCl–CuCl_2$, $Et_3NHCl–CuCl$, $Et_3NHCl–SnCl_2$ that are

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2 Experimental

The ionic liquids such as $Et_3NHCl–AlCl_3$, $Et_3NHCl–FeCl_3$, $Et_3NHCl–ZnCl_2$, $Et_3NHCl–CuCl_2$, $Et_3NHCl–CuCl$, $Et_3NHCl–SnCl_2$ used in this work were prepared as described previously [15]. Reactions were carried out in a glass reactor equipped with a condenser and magnetic stirrer. Before the experiment, benzene after dehydrated with anhydrous calcium chloride and paraformaldehyde were added into the reactor, and then new-made catalysts were charged into the reactor at constant stirring. The reactor was heated to a desired temperature and the mixtures were stirred at the temperature for 2–7 h. After completion of the reaction, the catalyst was separated out and the solution samples were analyzed by GC and GC-MS. The obtained product was identified by FT-IR and ^1H NMR spectroscopy. Its FT-IR data: 3056.4, 3026.0, 2915.7, 1602.7, 1492.3, 1452.3, 1078.1, 1028.5, 726.3, 695.9, 604.7 cm^{-1}; ^1H NMR: 7.37, 7.26, 7.22, 7.12, 3.99, 3.95 ppm.

3 Results and Discussion

3.1 Catalytic Performances of Various Ionic Liquids

The catalytic performances of various ionic liquids like $Et_3NHCl–AlCl_3$, $Et_3NHCl–FeCl_3$, $Et_3NHCl–ZnCl_2$, $Et_3NHCl–CuCl_2$, $Et_3NHCl–CuCl$, $Et_3NHCl–SnCl_2$ were evaluated for the condensations of benzene, toluene and xylene with formaldehyde at 80 °C and ambient pressure for 5 h. As can be seen from Table 1, $Et_3NHCl–AlCl_3$ exhibited a surprising high activity for the reaction, giving 92.4% conversion of HCHO with 76.1% selectivity to DPM (entry 1). The main by-products produced in the reactions were identified to be dibenzylbenzene, along with a small quantity of toluene by means of GC-MS analysis. Contrarily, $Et_3NHCl–FeCl_3$ was found to be extremely low activity with conversion of 12.5% (entry 2), and $Et_3NHCl–ZnCl_2$, $Et_3NHCl–CuCl_2$, $Et_3NHCl–CuCl$ and $Et_3NHCl–SnCl_2$ were almost inactive with <1.1% conversions of HCHO (entries 3–6). The catalytic activity differences between them might be explained on the basis of their acidities, including Lewis and Brönsted acidities. It was reported that the Lewis acidity of metal chloride ionic liquids increases in the order $CuCl < FeCl_3 < ZnCl_2 < AlCl_3$ [16]. Meanwhile, Brönsted acidity of them is generally produced by trace of water in the reaction mixture [17]. The catalytic activity order of the ionic liquids observed in Table 1 was likely ascribed to both their Lewis and Brönsted acidity.

As has been pointed out, the so-called superacidity of protons in ionic liquids is generated when a strong mineral acid such as HCl, H_2SO_4 etc. was dissolved in acidic chloroaluminate ionic liquid. The superacid properties of protons have been explained by reaction between the dissolved HCl and the acidic species in the melt, which release nude protons with extremely low solvation and therefore very high reactivity (Eq. 1) [17]. Thus, the strong Lewis acids, especially the superacid of protons, exist in the system, since the $Et_3NHCl–AlCl_3$, as well as $Et_3NHCl–FeCl_3$ can release HCl when it encounters with water solubilized in organic reactants or produced in the reaction.

$$HCl + Al_2Cl_7^- = [H^+]_{nonsolved} + 2AlCl_4^- \quad (1)$$

The presence of the nonsolvated H^+ greatly accelerates the reaction. On the other hand, the strong polarity and electrostatic field of the chloroaluminate ionic liquid used as catalyst and reaction medium may stabilize the intermediate of carbenium ion [18], which would make it possible that the carbon charged positively has enough time to attack the benzene ring to generate the product. This is also the reason that the reaction is effectively accelerated in the presence of the chloroaluminate ionic liquid.

When activated aromatic hydrocarbons such as toluene and xylene were used as alternatives of benzene, the

Table 1 Catalytic performance of various catalysts for the condensations

Entry	Catalysts	Arom.	Conv./%	Selec./%	Y/%
1	$(C_2H_5)_3NHCl–AlCl_3$	C_6H_6	92.4	76.1	70.3
2	$(C_2H_5)_3NHCl–FeCl_3$	C_6H_6	12.5	84.8	10.6
3	$(C_2H_5)_3NHCl–ZnCl_2$	C_6H_6	0.9	78.0	0.7
4	$(C_2H_5)_3NHCl–CuCl_2$	C_6H_6	0.1	100	0.1
5	$(C_2H_5)_3NHCl–CuCl$	C_6H_6	1.1	26.5	0.3
6	$(C_2H_5)_3NHCl–SnCl_2$	C_6H_6	0.5	43.9	0.2
7	$(C_2H_5)_3NHCl–AlCl_3$	$C_6H_5CH_3$	100	74.7	74.7
8	$(C_2H_5)_3NHCl–AlCl_3$	$C_6H_4(CH_3)_2$	91.7	78.8	72.3

Reaction conditions: catal. 2.5 g; molar ratio of arom./aldehyde 10:1; reacting temperature: 80 °C; time 5 h condensation reactions were also investigated in the presence of $Et_3NHCl–AlCl_3$ as catalyst. The conversion of HCHO with toluene as an alternative was found to be about 100% at the same conditions, and 74.7% of selectivity to corresponding products was achieved (entry 7). The higher activity of the condensation of toluene as compared to that of benzene is due to the presence of the $–CH_3$ group that is a electron donating group. The $–CH_3$ group enhances the condensation reaction because the transition state carboniums are stabilized by the electron donating group on the benzene ring. And for the xylene system, the conversion and selectivity were 91.7% and 78.8%, respectively (entry 8). This lower conversion for the system as compared to that using toluene as reactant may be relative to the steric effect of xylene.

3.2 Effect of Reaction Conditions

Figure 1 shows the influence of catalyst amount on the conversion of HCHO and selectivity of DPM in the condensation of benzene and paraformaldehyde. As can be seen from the figure, the reaction rate was linearly increased in the range of catalyst amount from 1.5 g to 2.0 g. Similarly, the conversion of formaldehyde increased with increase in the amount of the catalyst. When 2.5 g of the catalyst was used, the conversion of formaldehyde reached up to 92.4% and the selectivity to DPM was not significantly changed with increase in the amount of the catalyst in the range from 1.5 g to 3 g. This phenomenon implies that 2.5 g of catalyst in the catalytic system has enough acid strength and amount to effectively catalyze the reaction with 92.4% conversion and 76.1% selectivity to DPM, giving the yield of 70.3%. To our knowledge, it has been the highest conversion and yield for the condensation of benzene and formaldehyde to DPM.

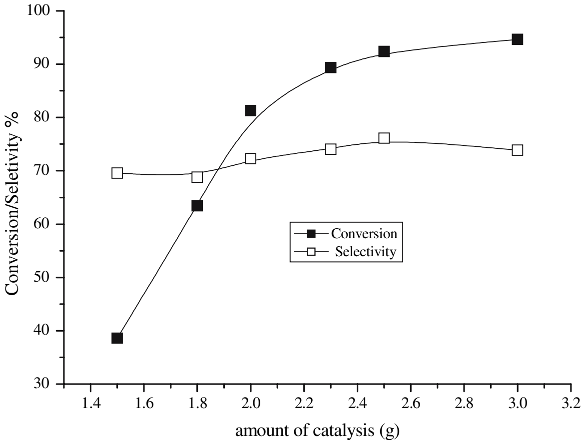


Fig. 1 Influence of catalyst amount on the reaction benzene/aldehyde = 10:1(mol ratio); T = 80 °C; t = 5 h

Figure 2 reveals dependence of the conversion and selectivity on benzene/formaldehyde molar ratio. As increase of benzene/formaldehyde molar ratio from 6:1 to 10:1, the conversion was greatly increased, and then it held almost constant at the ratios from 10:1 to 14:1. The selectivity was almost unchangeable in all the range of molar ratios.

Dependence of the conversion and selectivity of DPM on the reaction temperature was investigated in the temperature range of 50–100 °C using the chloroaluminated ionic liquid as the catalyst, as shown in Fig. 3. Both the conversion of formaldehyde and the selectivity to DPM were increased with the temperature from 50 °C to 80 °C, and then they evidently fell down above 80 °C. When at 100 °C, they are 49.5% and 61.9%, respectively. This finding is probably relative to characteristics of the reaction. For this synthesis reaction, the reaction heat is −185.5 kJ/mol, which is calculated from the formation

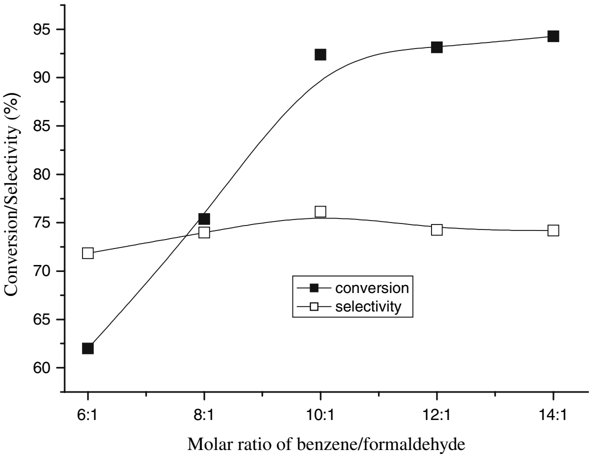


Fig. 2 Influence of benzene to aldehyde molar ratio on the reaction $W_{catalyst}$ = 2.5 g; T = 80 °C; t = 5 h

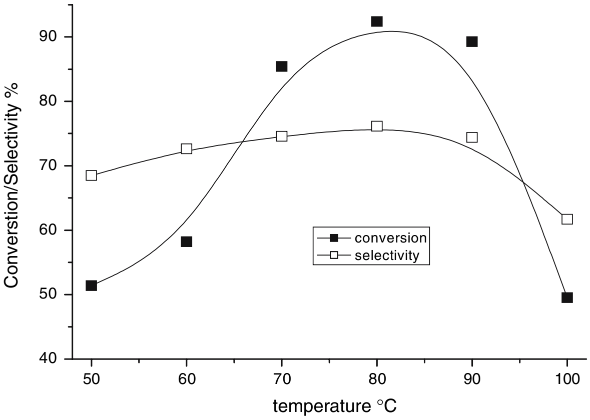


Fig. 3 Influence of reaction temperature on the reaction benzene/paraformaldehyde = 10:1(mol ratio) $W_{catalyst}$ = 2.5 g, t = 5 h

heats of various substances in the following reaction (Eq. 2):

$$2C_6H_6\,(l) + HCHO\,(g) = C_6H_5CH_2C_6H_5(l) + H_2O(l) \qquad (2)$$

This value suggests that the synthesis reaction is exothermic, and elevation of the reaction temperature is, therefore, of a great disadvantage to generation of DPM in terms of thermodynamics. However, the formaldehyde participating in the catalytic reaction comes from decomposition of paraformaldehyde in action of acidic catalyst. The great drop of the conversion was ascribed to increase in volatilization rate of the formaldehyde out of the reactor at high reacting temperature. Besides, the increase of the conversion in the range of 50–80 °C was attributed to reaction rate increase with the temperature in viewpoint of reaction kinetics, and the drops of the selectivity was due to further reaction of DPM to by-products at high temperatures.

Figure 4 depicts the conversion and the selectivity as a function of reaction time. The conversion increased with the reaction time up to 92.4% at 5 h, thereafter, the increase in the conversion was abated in the period from 5 h to 7 h, suggesting that the thermodynamic equilibrium was almost achieved at that time. Furthermore, the selectivity remained at about 75% in the range from 2 h to 5 h, and it dropped when the reacting time was prolonged, resulting from DPM further conversion into by-products at prolonged contact time of DPM with the catalyst.

It is worthy to note that the selectivity to DPM was almost unchanged at most of reaction conditions, which was probably ascribed to phase behavior of the reaction system and interaction between reactant and the catalyst. Since chloroaluminate ionic liquid is easily immiscible with benzene, and the product DPM is completely miscible with it. As a result, DPM rapidly diffuses into abounding benzene bulk once it is formed on the interface between benzene and the catalyst, which reduces probability of interaction between DPM and the catalyst to further react to generate by-products. On the other hand, benzene can interact with chloroaluminate ionic liquid to generate π-complexation of Lewis acid sites with the π-cloud of the aromatic ring [19], likely resulting in modification of electronic properties of Lewis acid sites. Such a complexation process is presumably beneficial for the condensation because it inhibits side reactions, further resulting in obvious improvement in the product composition. In addition, it is formation of the biphase system, organic benzene and catalyst phase in the process of the reaction, that make the reaction equilibrium greatly shift to the direction of right hand side of the Eq. 2, which is advantages to DPM generation in terms of reaction thermodynamics. Consequently, acceleration of the reaction and the selectivity unchanged with the conversion are attributed to associated action of the reaction thermodynamics and kinetics.

3.3 Reaction Kinetics

Figure 5 is a plot of HCHO and DPM concentrations in the process of the reaction versus time at different temperatures. It appears that the DPM is the kinetically favored product. It was the predominant product until HCHO conversion reached 92.4% in the case at 80 °C. By-products such as dibenzylbenzene and toluene appear to be thermodynamically favored products. At higher temperatures and given enough reaction time, the DPM could further be converted to dibenzylbenzene or its derivatives, as shown in Fig. 4. According to the experimental data as shown in Fig. 5, a plot of ln (C/C_0) versus time at different temperatures was obtained (Fig. 6), where C and C_0 are the

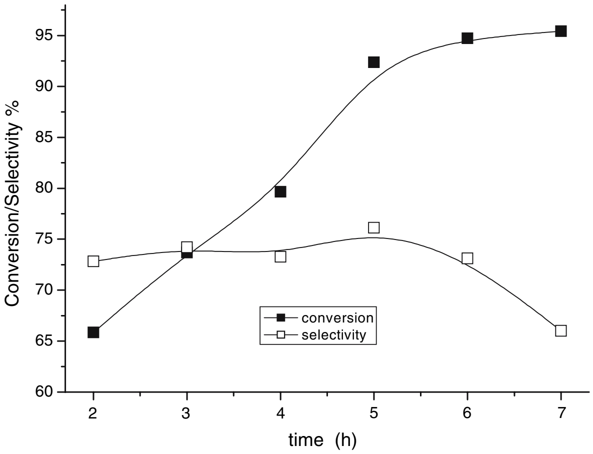


Fig. 4 Influence of reaction time on the reaction benzene/paraformaldehyde = 10:1(mol ratio) $W_{catalyst}$ = 2.5 g, T = 80 °C

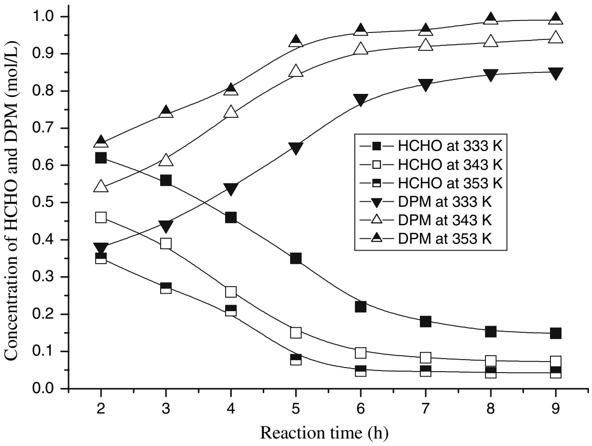


Fig. 5 HCHO and DPM concentrations as a function of reaction time at different temperatures

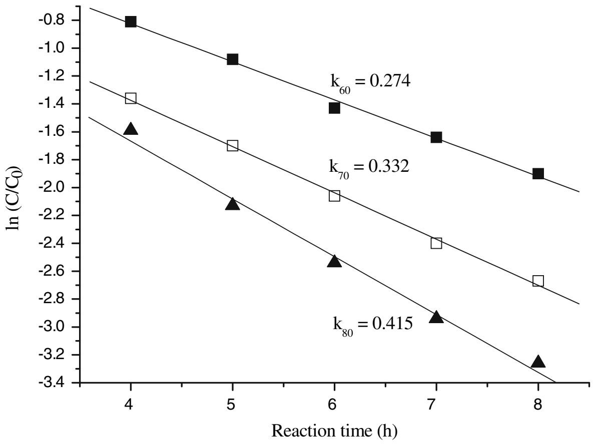
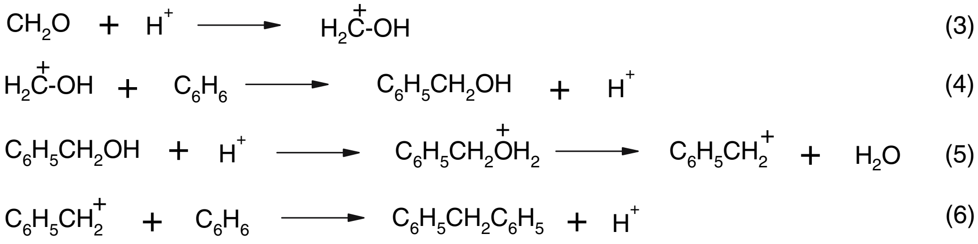


Fig. 6 Plots of ln (C/C_0) versus reaction time at different temperatures

HCHO concentration at time *t* and the time zero, respectively. This plot shows good linearity, suggesting the reaction is clearly quasi-first order in HCHO at the temperatures of 60, 70 and 80 °C. First order rate constants calculated from the plots are $k_{60} = 0.274\ h^{-1}$ at 60 °C, $k_{70} = 0.332\ h^{-1}$ at 70 °C and $k_{80} = 0.415\ h^{-1}$ at 80 °C, respectively. Similarly, a plot of ln k versus 1/T (K) also shows a good linearity (Fig. 7). The activation energy of the reaction was calculated by the linear slope, $E_a = 20.1$ kJ/mol, also showing the high activity of the ionic liquid catalyst for the condensation reaction.

It was known from above discussion that the ionic liquids exhibit high catalytic activity for the condensation due to its superacidity. Thus, the reaction mechanism of DPM synthesis from benzene and HCHO catalyzed by the chloroaluminated ionic liquid is shown in Scheme 1 on the basis of previous report [7]. In this network, HCHO firstly accepts a nonsolvated H^+ produced from Eq. 1 on the carbonyl oxygen atom to form a methylol cation (H_2C^+OH) (Eq. 3). Then the cation attacks the benzene ring to produce an intermediate product, benzyl alcohol (Eq. 4). This alcohol can be activated to be converted into benzyl carbenium (Eq. 5). Finally, the benzyl carbenium reacts with another benzene molecule to generate DPM (Eq. 6). In our case, the intermediate product, benzyl alcohol was not detected in the final products, indicating that the reaction rate of the Eq. 5 was so fast that the alcohol was rapidly activated by nonsolvated H^+ to give benzyl carbenium once it was generated. Apart from the Eq. 5, the Eqs. 4 and 6 are also faster than the Eq. 3 due to the highly activated particles H_2C^+OH and $C_6H_5CH_2^+$ participating in these reactions. In other words, the Eq. 3 is the rate-determining step of the synthesis reaction. Therefore, it exhibits first order reaction in HCHO, which further validated the kinetic experimental results as above.

Scheme 1 Reaction mechanism



$$CH_2O + H^+ \longrightarrow H_2\overset{+}{C}\text{-}OH \quad (3)$$

$$H_2\overset{+}{C}\text{-}OH + C_6H_6 \longrightarrow C_6H_5CH_2OH + H^+ \quad (4)$$

$$C_6H_5CH_2OH + H^+ \longrightarrow C_6H_5CH_2\overset{+}{O}H_2 \longrightarrow C_6H_5CH_2^{+} + H_2O \quad (5)$$

$$C_6H_5CH_2^{+} + C_6H_6 \longrightarrow C_6H_5CH_2C_6H_5 + H^+ \quad (6)$$

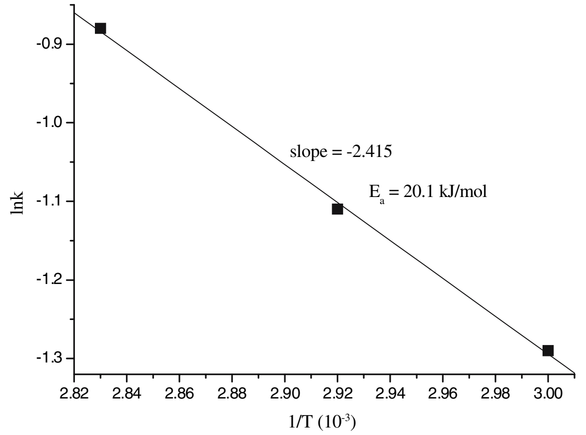


Fig. 7 Plot of ln k versus 1/T

4 Conclusions

The ionic liquid $Et_3NHCl–AlCl_3$ was the best catalyst for synthesis of DPM via benzene and paraformaldehyde condensation among six kinds of ionic liquids, such as $Et_3NHCl–AlCl_3$, $Et_3NHCl–FeCl_3$, $Et_3NHCl–ZnCl_2$, $Et_3NHCl–CuCl_2$, $Et_3NHCl–CuCl$, $Et_3NHCl–SnCl_2$, and gave DPM in higher yield and selectivity. The high activity of the catalyst was mainly enhanced by formation of the superacidic protons in the acidic chloroaluminated ionic liquid. The investigations on the reaction kinetics showed that the reaction is clearly quasi-first order in HCHO and the activation energy of the reaction was obtained to be 20.08 kJ/mol. This also suggested high activity of the ionic liquid catalyst for the condensation reaction. The higher selectivity to diphenylmethane was mainly due to biphase nature of the reaction system and the interaction of aromatics with Lewis acid sites reducing acidity.

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