RSC Advances

Graphic abstract

Highlights

Temperature-dependent biphasic system of IL-phenol-water was developed.

The system was applied in the hydroxyalkylation of phenol with formaldehyde to bisphenol F.

The catalytic activity was dependent on both the acidity and the alkyl chain length of IL.

[C$_6$MIM][HSO$_4$] gave high yield of 80.5% and selectivity of 96.9% for bisphenol F.

The recovered [C$_6$MIM][HSO$_4$] retained the original activity after six recycling-uses.

ARTICLE TYPE

The efficient hydroxyalkylation of phenol with formaldehyde to bisphenol F over a thermoregulated phase-separable reaction system containing water-soluble Brønsted acidic ionic liquid

Qing Wang,[a] Zhi Min Wu*, Yongfei Li, Ying Tan, Ning Liu, Yuejin Liu*

The efficient hydroxyalkylation of phenol with formaldehyde to bisphenol F over a thermoregulated phase-separable reaction system containing water-soluble Brønsted acidic ionic liquid was studied. The reaction system containing water-soluble IL showed the thermoregulated biphasic behavior with change 10 of the alkyl chain length of IL, temperature and water amount. Four types of imidazolium-, ammonium-, phosphonium- and pyridinium-based water-soluble ionic liquids with different anions of dihydrogen phosphate $[H_2PO_4]^-$, acetate $[CH_3COO]^-$ and hydrogen sulfate $[HSO_4]^-$ were used as both Brønsted acidic catalysts and thermoregulated solvents. Among them, $[C_6MIM][HSO_4]$ gave high yield of 80.5% and selectivity of 96.9% for bisphenol F, and the optimal reaction conditions were stirring speed 450 rpm, 15 phenol/formaldehyde ratio 6:1, IL catalyst molar concentration 12.5%, reaction temperature 90 °C and reaction time1 h. $[C_6MIM][HSO_4]$ could be recovered by simple decantation and could retain the original activity even after six recycling-uses $[C_nMIM][HSO_4]$ with the alkyl chain length n=6 was found to be the most suitable for the synthesis of bisphenol F because of both the forming of thermoregulated monophasic reaction system at 90 °C to enhance the reaction efficiency and as a thermoregulated phase-20 transition solvent to facilitate its recovery from reaction system.

Key words: hydroxyalkylation; bisphenol F; thermoregulated phase-separable; acidic ionic liquid

1 Introduction

Bisphenol F is an important raw material used for the production 25 of bisphenol F epoxy resin which has higher resistance to wear and tear, lower viscosity than bisphenol A epoxy resin,[1] and also used for the production of phenolic and polycarbonate resins.[2] These products derived from bisphenol F have gained tremendous interest in a wide range of application such as adhesive, coating, 30 liquid-injection molding compound, reinforced plastic and large wind turbine blade material.[3]

Bisphenol F is generally synthesized from phenol with formaldehyde through acid-catalyzed hydroxyalkylation reaction. The conventional catalysts for the synthesis of bisphenol F are 35 mainly liquid protonic acids such as oxalic acid, phosphoric acid and hydrochloric acid.[4-6] These traditional inorganic acids have some disadvantages of equipment corrosion, environmental pollution with acidic wastewater, and inconvenient purification procedure. Some researchers focused on solid acid catalysts that 40 can avoid the corrosion problem and facilitate the separation of catalysts.[7-10] Although solid acid catalysts are environmentally benign, they also have shortcomings of the restricted accessibility of acid sites and the sudden deactivation by coke formation.[8, 11] Also, when formalin is used as the source of formaldehyde, the 45 active sites of solid acids are easily blocked by polar water molecules.[10, 12] Thereof, it remains an important challenge to develop a more environmentally friendly route for the synthesis of bisphenol F.

Ionic liquid (IL), a kind of green catalyst and solvent, has become

School of Chemical Engineering, Xiangtan University, Xiangtan 411105, P.R. China. Tel: +86-18973211676; E-mail: xdwuzm@163.com.

School of Chemical Engineering, Xiangtan University, Xiangtan 411105, P.R. China. Tel: +86-13574069061; E-mail: xdlyj@163.com.

increasingly attractive for a range of organic reactions due to their tunable physical and chemical properties.[13-17] Recently, the versatility of IL has been further enhanced in a thermoregulated system where both reagents and a thermoregulated phase-transition solvent are coupled together.[18-21] The reaction performs actually in a homogeneous system under heated, and upon cooled to room temperature, a homogeneous reaction system becomes into a biphasic system that enabling easier IL catalyst recovery from reaction system. Such a novel process combines the advantages of both homogenous and heterogeneous catalyses, i.e., highly catalytic efficiency and good recyclability.[16] The thermoregulated method will be a viable alternative route to develop modern chemical industry, especially for the increasing environmental concerns. The Brønsted acidic IL can be efficiently used as catalyst for the hydroxyalkylation of phenol with carbonyl compounds such as levulinic acid,[22] acetone[23] and tert-butyl alcohol.[24] However, to our knowledge, research on the hydroxyalkylation of phenol with formaldehyde catalyzed by IL in thermoregulated reaction system hasn't been reported yet.

Herein, we adopted a series of water-soluble Brønsted acidic ILs (Scheme 1) that can form a thermoregulated reaction system with phenol and formaldehyde for the synthesis of bisphenol F. Through the research on the thermoregulated phase behaviour of reaction system and the relationship of structure of IL with acidity and catalytic activity, both high activity and high selectivity for bisphenol F were obtained and the recycling-use of IL catalyst was also realized.
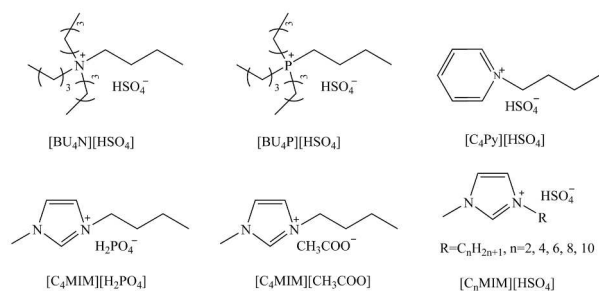
Scheme 1. The structures of water-soluble Brønsted ILs used for the synthesis of bisphenol F

2. Experimental

2.1 Materials

Tetrabutylammonium hydrogen sulfate ([BU$_4$N][HSO$_4$], 98%), tetrabutyl phosphonium hydrogen sulfate ([BU$_4$P][HSO$_4$], 98%), N-butylpyridinium hydrogen sulphate ([C$_4$Py][HSO$_4$], 98%) were purchased from Shanghai Cheng Jie Chemical Co. Ltd, Shanghai, China. 4-Nitroaniline and the standard of bisphenol F (99%) were purchased from Alfa Aesar. N-methylimidazole and alkyl halides were from Aladdin Chemicals. All chemicals were used as

received.

2.2 The synthesis of imidazolium-based ILs with different length of alkyl chain

The imidazolium-based ILs with different length of alkyl chain (n) were synthesized according to previously reported procedures.[25,26] The first step was the synthesis of 1-alkyl-3-methylimidazolium bromide [C$_n$MIM][Br]: N-Methylimidazole was dissolved in toluene and the resultant solution was cooled to 0 °C; after the dropwise addition of bromoalkane into the resultant solution at 0 °C, the reaction mixture was continuously stirred for 8 h at 0 °C and then was heated to 70 °C keeping for 24 h; after the removal of solvent, washed and dried in vacuo, [C$_n$MIM][Br] was obtained. The second step comprised an anion exchange of Br$^-$ with another one existed in such salts as NaHSO$_4$, NaH$_2$PO$_4$ or CH$_3$COONa·3H$_2$O. As an example, the 1-hexyl-3-methylimidazolium hydrogen sulfate of [C$_6$MIM][HSO$_4$] was synthesized through addition of an equimolar amount of NaHSO$_4$ into an anhydrous acetone solution of [C$_6$MIM][Br]. After the reaction mixture being stirred at room temperature for 24 h, [C$_6$MIM][HSO$_4$] was obtained via filtration, ether washing and drying in vacuum.

The chemical structures of the synthesized imidazolium-based ILs were determined by ^{1}H NMR spectroscopy using a Bruker ARX400 spectrometer at room temperature with deuterated water (D$_2$O) as the solvent. The detailed ^{1}H NMR spectra of the synthesized imidazolium-based ILs shown in Figs. S1-S7 (see Supporting Information) was in agreement with the designed structures.

2.3 The acidity measurement

The Brønsted acid scales of the synthesized imidazolium-based ILs were determined using a Cary 5000 UV-vis spectrophotometer with a basic indicator according to the previously reported Hammett method.[27, 28] The Brønsted acidity was measured by evaluating the extent of protonation of the basic indicator (termed as "I") in ILs via the measurable ratio of [I]/[IH$^+$]. The Hammett function (H$_0$), which presents the relative acidity of ILs, is defined as follows:

$$H_0 = pK(I)aq + \log([I]/[IH^+]) \tag{1}$$

Where $pK(I)aq$ is the pKa value of the basic indicator in aqueous solution, and [I] and [IH$^+$] are the molar concentrations of the unprotonated and protonated forms of the indicator in solution, respectively. 4-Nitroaniline (5 mg/L, $pK(I)aq = 0.99$) was chosen as the basic indicator in water, and the concentration of each IL was 27 mmol/L. The H$_0$ values of the synthesized imidazolium-based ILs were determined from the difference in the measured absorbance after the addition of IL in water. As the acidity of IL increases, i.e., the decrease in H$_0$, the absorbance of the unprotonated form of the indicator decreases. The detailed absorbances of the unprotonated form of the indicator with different IL in water were shown in Figs. S8 and S9 (see Supporting Information).

2.4 The determination of phase behavior of phenol- IL-water system

Phenol and IL with 6:1 of mole ratio were mixed with different mole fractions of water to form a serial of phenol-IL-water systems which were cooled down to 0 °C and then heated gradually to a serial of given temperatures. During the process, phase behaviors were visually observed and a serial of critical miscibility temperatures (T_m) at which the phase-transfer took place from biphase to monophase were recorded reproducibly within ± 0.5 °C.

2.5 The measurement of optical microscopy

A serial of suspensions containing a known mole fraction of IL catalyst were prepared by dispersing IL catalyst in a blank solution consisting of phenol and formaldehyde. The mole ratio of phenol/formaldehyde/IL was 6:1:1. Samples were obtained from the suspensions both immediately after stopping stirring and 24 h later, and a drop of each sample was placed on a glass slide to settle. The morphologies of samples were examined at a magnification level of ×1000 under a polarized optical microscope (POM; Leica DM-LM/P) equipped with a Mettler-Toledo hot stage (FP82HT).

2.6 The synthesis of bisphenol F

The hydroxyalkylation of phenol with formaldehyde to bisphenol F was performed in a 100 mL three-necked round-bottom flask equipped with a condenser under nitrogen atmosphere. Firstly, a certain amount of phenol and the synthesized IL catalysts were mixed and stirred at a given reaction temperature for 20 min, and then 37% aqueous formaldehyde 4.05 g (0.05 mol) was slowly added into them. After the reaction completed, the reaction system was cooled to room temperature and washed three times with water. The upper organic phase was separated from the lower aqueous phase by decantation, and then immediately analyzed by gas chromatography. Each sample was obtained from an individual batch run at a specific reaction time, and each point represented the average of three replicates.

2.7 The determination of yield and selectivity for bisphenol F

The activities of various IL catalysts under different reaction conditions were evaluated by the yield and selectivity for bisphenol F, which are defined as follows:

$$\text{Yield (\%)} = \frac{\text{Actual moles of formed Bisphenol F}}{\text{Theoretical moles of Bisphenol F based on consumed formaldehyde}} \times 100$$

(2)

$$\text{Selectivity (\%)} = \frac{\text{Moles of formed Bisphenol F}}{\Sigma \text{ Moles of all products}} \times 100$$

(3)

The composition of the product was quantified by Gas chromatography (GC) with the external standard method. The test solution for GC analysis was prepared by diluting 0.1 g of sample in 10 mL of ethanol. The GC analysis was conducted using an Agilent 7890A GC equipped with an HP-5 capillary column (30

m*0.25 mm, 0.25 m film thickness) using the following temperature program: at initial temperature of 50 °C hold for 3 min; then ramp to 120 °C at 10 °C/min and hold for 5 min; and then ramp to 270 °C at 15 °C/min and hold for 5 min. The injector temperature was set at 280 °C. Helium was used as carrier gas with 1.0 mL/min of flow rate through the column. The GC-MS analysis of bisphenol F were shown in Fig. S10 (see Supporting Information).

2.8 The recycling-use of IL catalyst

After the reaction completed, the reaction system was cooled to room temperature and washed three times with water. The upper organic phase was separated from the lower aqueous phase by decantation. Bisphenol F product was obtained by the distillation of phenol in organic phase under a reduced pressure. The IL catalyst was recovered by evaporating water in aqueous phase, then purified by washing with diethyl ether and dried in vacuum before being reused.

3. Results and discussion

3.1 The thermoregulated phase-transition property of reaction system

In this work, based on the solubility of IL both in phenol and in water, the thermoregulated ionic liquid biphasic system for the synthesis of bisphenol F was firstly chosen to be composed of water-soluble imidazolium-based IL, water and organic substrates phenol. The phase diagram for the system of IL-water-phenol is shown in Fig. 1. The critical miscibility temperature (T_m) means the temperature at which all the components become completely miscible in one another phase, which is strongly dependent on the alkyl chain length of IL.[29] As shown in Fig. 1a, with an increase in the hydrophobic alkyl chain length of water-soluble IL, the T_m of the IL-phenol-water system increases significantly. Thereof phase behaviour of the thermoregulated phase-separable system can be exactly customized depending on the required reaction temperature. In addition, the increasing of water amount would affect the T_m during the synthesis process of bisphenol F. As shown in Fig. 1b，the T_m of the IL-phenol-water system obviously increases with the increase of water amount. However, further increasing of water amount over 97% results in the decreasing of T_m value, which is probably by the shift of IL-phenol-water from a biphasic system to a aqueous phase. The system composed of different composition of IL-phenol-water may be changed from a biphasic to a monophasic phase with the increasing of temperature and vice versa.
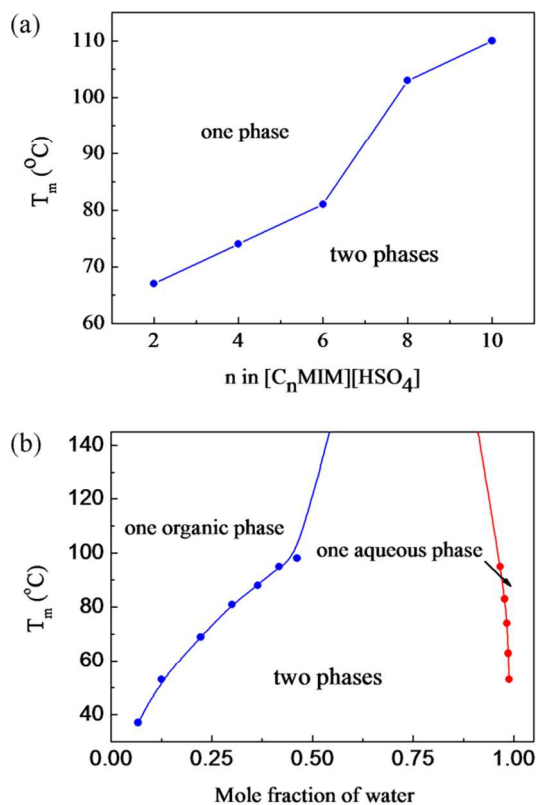
Fig. 1. The phase diagram of phenol-[C$_n$MIM][HSO$_4$]-water system with different: (a) alkyl chain length and (b) water amount

As shown in Fig. 2, the [C$_6$MIM][HSO$_4$] as water-soluble IL was
5 firstly chosen to investigate the thermoregulated phase-transition property of the reaction system. At room temperature, the aqueous ionic liquid phase is immiscible with the mixture of phenol and formaldehyde with 6:1 of molar ratio (Fig. 2a), and small aqueous droplets exist with a size of approximately 2
10 microns in diameter (Fig. 2d). When the temperature is elevated gradually to over 88 °C (the T$_m$ range of reaction system is 81-88 °C), the biphasic system becomes into a clear transparent homogeneous system where the hydroxyalkylation reaction take place (Fig. 2b). After reaction completes, the reaction system is
15 cooled to room temperature and the clear transparent homogeneous reaction system becomes again into a biphasic system with the forming of an aqueous phase having a size of approximately 2.5 microns (Fig. 2c). By simple water extraction, the IL catalyst can be separated from the organic phase composed
20 of phenol and bisphenol F, and be reused in subsequent reaction runs. Here, [C$_6$MIM][HSO$_4$] acts not only as a homogenous catalyst to enhance the reaction efficiency but also as a thermoregulated phase-transition solvent to facilitate its separation from reaction system. This thermoregulated phase-
25 transition reaction and separation process will provide a simple and high efficiency environmentally benign way for the synthesis of bisphenol F.
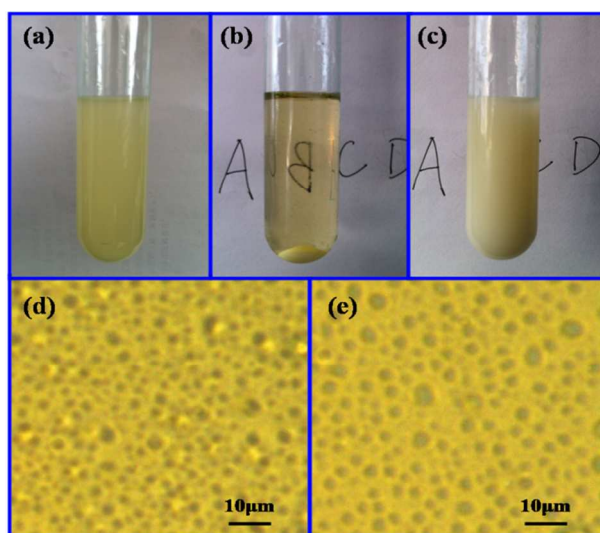

Fig. 2. The thermoregulated phase-transition process of reaction system

30 **3.2 Catalytic activities of various water-soluble ILs for the synthesis of bisphenol F**

Four types of water-soluble ammonium-, phosphonium-, pyridinium- and imidazolium-based ILs were screened for being used in the thermoregulated system for the synthesis of bisphenol
35 F, and their catalytic activities were summarized in Fig. 3. The types of both cations and anions of ILs have a remarkable influence on their catalytic activities. Among these ILs, [C$_6$MIM][HSO$_4$] exhibits the best catalytic activity with 80.5% of yield and 96.9% of selectivity which are higher than those
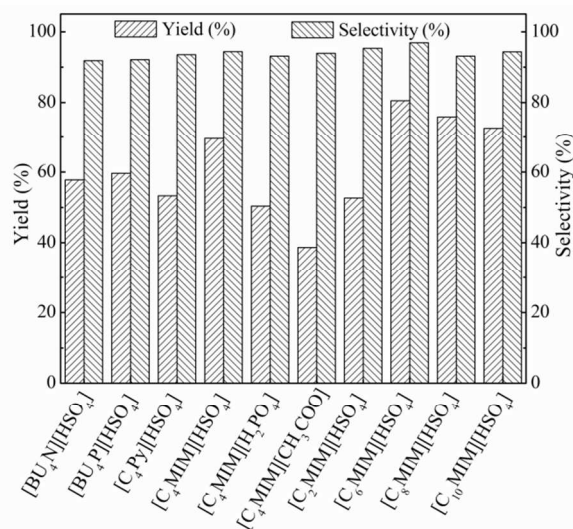40 obtained by solid acid catalysts.[7-10]

Fig. 3 The comparison of various ILs catalytic activities for bisphenol F. Reaction conditions: stirring speed 450 rpm, phenol/formaldehyde ratio 6:1, IL catalyst molar concentration 12.5%, reaction temperature 90 °C
45 and reaction time 1 h

3.3 The relationship of structure and acidity of IL with catalytic activity

It is known that the nature of anion influences the catalytic activity of IL in the hydroxyalkylation of phenol.[22-24] The acidity-

activity relationships of ILs with different anions for the synthesis of bisphenol F were shown in Fig. 4. Here, $[C_4MIM][HSO_4]$ gives higher yield of bisphenol F than $[C_4MIM][H_2PO_4]$ and $[C_4MIM][CH_3COO]$, while their Brønsted acidities follow the following order: $[C_4MIM][HSO_4]$ > $[C_4MIM][H_2PO_4]$ > $[C_4MIM][CH_3COO]$. So it means that the hdroxyalkylation of phenol to bisphenol F is closely associated with the acidity strength of IL.

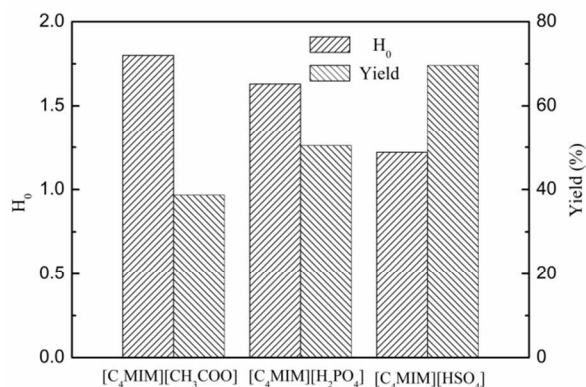Fig. 4. The effect of anion $[X]^-$ on the acidity and catalytic activity of $[C_4MIM][X]$

The effects of cations in the imidazolium-based ILs on the activity in the hydroxyalkylation of phenol were studied, and the acidity-activity relationships of ILs with different alkyl chain length were shown in Fig. 5. Both the catalytic activity and the acidity of IL increase with the increasing of alkyl chain length from C_2 to C_6. However, further increasing in the alkyl chain length over C_6 leads to the decreasing of catalytic activity with a drop of 8% in yield of bisphenol F, although at this time the acidity strength keeps increasing slightly. This is because that when the alkyl chain length of ILs is over six, its phase-miscible temperature is higher than the given reaction temperature and forms a biphasic reaction system (see Fig. 1a) which results the decreasing of catalytic activity due to mass transfer resistance between organic and aqueous phases. The results demonstrate that both the acidity and the structure of the ILs play an important role in the thermoregulated catalytic reaction system for the synthesis of bisphenol F. Therefore, it can explain the result that $[C_6MIM][HSO_4]$ exhibits the best catalytic activity among the water-soluble ILs listed in Fig 3.
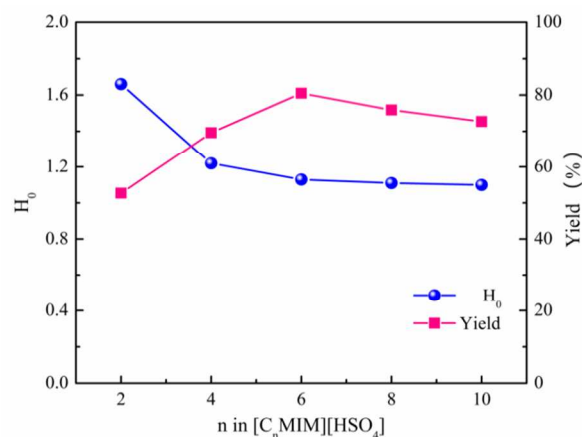

Fig. 5. The effect of the alkyl chain length n on the acidity and catalytic activity of $[C_nMIM][HSO_4]$

3.4 The influence of reaction conditions on the catalytic activity

The effect of stirring speed on the hydroxyalkylation activity of IL catalyst $[C_6MIM][HSO_4]$ was illustrated in Fig. 6 within 150, 300, 450 and 600 rpm, and the reaction conditions were as follows: 6:1 of phenol/formaldehyde ratio, 12.5% of catalyst molar concentration, 90 °C of reaction temperature. In the initial reaction 10 min, the reaction occurs very fast and the yield of bisphenol F can reach over 50%. After 10 min of reaction time, the yield of bisphenol F increases to 65%-80% slowly with the increasing of stirring speed from 150 to 450 rpm. When the stirring speed increases to 600 rpm, no improvement in yield of bisphenol F is obtained during the whole reaction period. At this time, the mass transfer resistance in reaction system is eliminated and the reaction rate is intrinsically-controlled. Thus, the optimum stirring speed is 450 rpm.
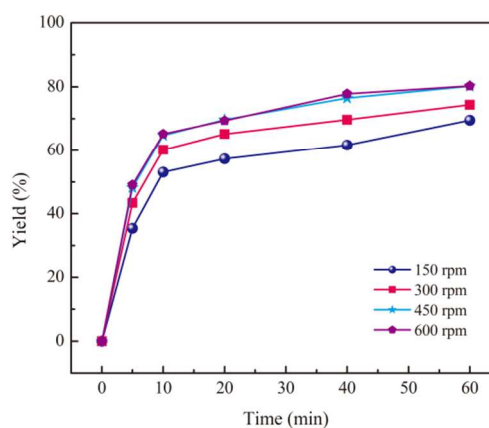

Fig. 6. The effect of stirring speed on the yield of bisphenol F

The effect of reaction time on the hydroxyalkylation activity of IL catalyst $[C_6MIM][HSO_4]$ was illustrated in Fig. 7a. Both the yield and selectivity for bisphenol F increases with the reaction time up to 1 h, but decrease beyond 1 h. This is because that there are some further reactions of bisphenol F with formaldehyde and phenol, such as the formation reactions of trimers or higher oligomers.[30] Thus, the optimum reaction time is 1 h.
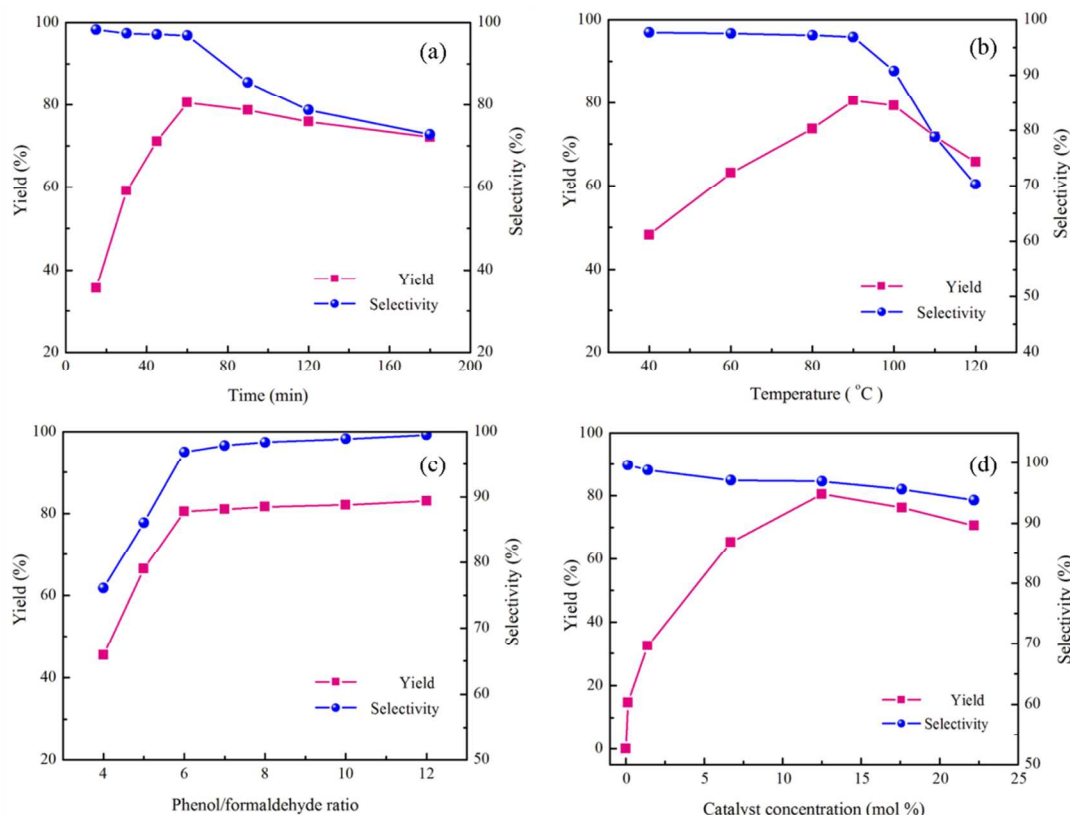
Journal Name

ARTICLE TYPE

Fig. 7. The effect of (a) reaction time, (b) reaction temperature, (c) phenol/ formaldehyde ratio and (d) concentration of [C$_6$MIM][HSO$_4$] on the yield and selectivity for bisphenol F. Reaction conditions: stirring speed, 450 rpm; reaction time, 0.25-3 h; reaction temperature, 40-120 °C; phenol/formaldehyde ratio, 4:1-12:1; IL catalyst molar concentration, 0-22.5%

5 The effect of reaction temperature on the hydroxyalkylation activity of [C$_6$MIM][HSO$_4$] was illustrated in Fig. 7b. With the increasing of reaction temperature from 40°C to 90 °C, the yield of bisphenol F increases significantly from 47% to 80.2% with over 96% of high selectivity for bisphenol F. But, when reaction 10 temperature further increases over 90 °C, both the yield and the selectivity for bisphenol F begin to decline rapidly. This is because that with the increasing of reaction temperature, more and more formaldehyde will escape from the reaction system where the low-boiling azeotropic temperature is 97 °C.[31] Thus, 15 the optimum reaction temperature is 90 °C.

The effect of phenol/formaldehyde ratio on the hydroxyalkylation activity of IL catalyst [C$_6$MIM][HSO$_4$] was illustrated in Fig. 7c. Both the yield and the selectivity for bisphenol F significantly increase from 45.4% to 80.5% and 62% to 94%, respectively, 20 with the increasing of phenol/formaldehyde ratio from 4:1 to 6:1. However, when the phenol/formaldehyde ratio is over 6:1, the concentration of IL catalyst becomes diluted, which limits the further increasing in its catalytic activity. Thus, the optimum phenol/formaldehyde ratio is 6:1.

25 The effect of IL catalyst concentration on its hydroxyalkylation activity of [C$_6$MIM][HSO$_4$] was illustrated in Fig. 7d. The yield of bisphenol F increases sharply to 80% with the increasing of IL catalyst concentration up to 12.5 mol%. This is because that the increased amount of IL catalyst provides more Brønsted acid 30 which facilitates the formation of bisphenol F. However, when IL catalyst molar concentration is over 12.5 %, a higher Brønsted acidic environment is formed, which may increase the forming chance of trimers, thus resulting in the decreasing in both yield and selectivity for bisphenol F. Thus, the optimum IL catalyst 35 molar concentration is 12.5 mol%.

As a result of the process described above, optimized reaction conditions had a stirring speed 450 rpm, phenol/formaldehyde ratio 6:1, [C$_6$MIM][HSO$_4$] molar concentration 12.5 mol%, reaction temperature 90 °C and reaction time 1 h. The yield and 40 selectivity for bisphenol F were 80.5% and 96.9%, respectively.

3.5 The recycling-use of IL catalyst [C$_6$MIM][HSO$_4$]

After the reaction completed, the reaction system was cooled to

room temperature and two phases were formed, thus enabling easier recovery of IL catalyst [C$_6$MIM][HSO$_4$] by simple decantation. After extracting the IL catalyst from reaction system with water for 3 times at 20 °C, there was only less than 4% of IL

5 catalyst loss. Under the optimum reaction conditions, the recycling-use results of [C$_6$MIM][HSO$_4$] were shown in Fig. 8. The recovered [C$_6$MIM][HSO$_4$] IL catalyst can retain the original activity even after the sixth recycling-use, and both the yield and selectivity for bisphenol F remain nearly unchanged at 80% and
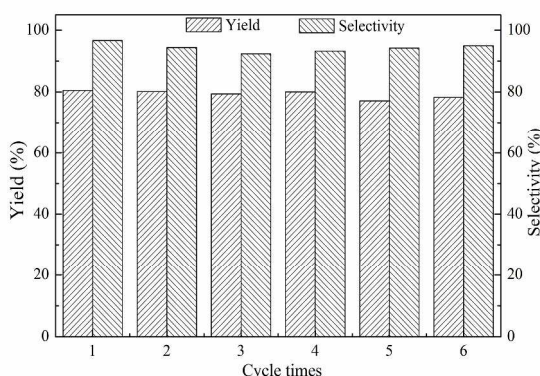
10 96%, respectively.

Fig. 8. The recycling-use of IL catalyst [C$_6$MIM][HSO$_4$]

3.6 The plausible mechanistic pathway for the synthesis of bisphenol F

15 The synthesis of bisphenol F involves a number of complex reactions, and the acid-catalyzed mechanism was presented in the literature.[10,32] It is widely accepted that phenol reacts with aldehydes through the protonation of aldehyde followed by the electrophilic aromatic substitution of phenol.[33] Here, a plausible

20 parallel-consecutive reaction mechanism for the synthesis of bisphenol F using Brønsted acidic IL catalyst is presented in Scheme 2.
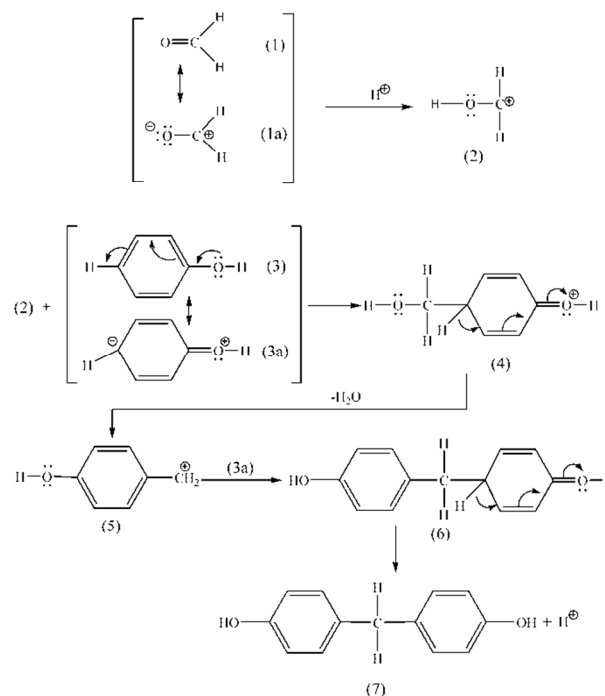
Scheme 2. The plausible mechanistic pathway for the synthesis of
25 bisphenol F

The protonation reaction of formaldehyde with IL catalyst occurs to form the hydroxymethyl carbocation CH$_2$OH$^+$ (2). Then, the hydroxymethyl carbocation CH$_2$OH $^+$ attacks the carbon atom of phenol with a larger electron cloud density, resulting in the

30 electrophilic substitution reaction: the positive charge transfers to the oxygen atom of the hydroxymethyl to form the hydroxyl oxygen cation (4) which isn't stable and is easy to take off a molecular of water with generating the benzyl methyl carbocation HO(C$_6$H$_4$)C$^+$ (5). The benzyl methyl carbocation continues to

35 attack another carbon atom of phenol with a larger electron cloud density, generating the unstable intermediate (6) which at once takes off the proton, thus the stable bisphenol F product is finally formed.

Conclusions

40 The water-soluble imidazolium-, ammonium-, phosphonium- and pyridinium-based Brønsted acidic ILs were used as catalysts for the synthesis of bisphenol F from phenol with formaldehyde, and it was found that the imidazolium-based ILs had better catalytic activity. The results showed the catalytic activity increased with

45 the acidity of ILs, and for the same acidity, the catalytic activity was affected with the alkyl chain length of ILs. Based on the further research on the thermoregulated phase behavior of reaction system containing phenol-[C$_6$MIM][HSO$_4$]-water, it was revealed that the hydroxyalkylation reaction temperature 90 °C

50 was just between the highest miscible temperature 88 °C of reaction system and the azeotropic point 97 °C of formaldehyde/water. Thus, the combination of high efficiency homogenous catalytic reaction and thermoregulated phase-transition recovery of IL catalyst from reaction system was

55 realized. [C$_6$MIM][HSO$_4$] gave higher yield of 80.5% and selectivity of 96.9% for bisphenol F under the optimal reaction

conditions of stirring speed 450 rpm, phenol/formaldehyde ratio 6:1, of IL catalyst molar concentration 12.5 mol%, reaction temperature 90 °C and reaction time 1 h. Furthermore, the recovered IL catalyst [C$_6$MIM][HSO$_4$] in the thermoregulated reaction system by simple decantation could retain the original activity even after six recycling-uses with only 4% of loss.

Acknowledgements

References

1 T. Ueki, S. Nishijima and Y. Izumi, *Cryogenics*, 2005, **45**, 141.

2 M. Granda, C. Blanco, P. Alvarez, J. W. Patrick and R. Menéndez, *Chem. Rev.* , 2013.

3 L. Pilato, *Phenolic resins: a century of progress*, Springer Berlin Heidelberg, 2010.

4 M. Okihama and Y. Kunitake, 1996, **JP08198790**.

5 M. Okihama and Y. Kunitake, 1996, **JP08268943**.

6 M. Okihama and Y. Kunitake, 1997, **JP09067287**.

7 S. K. Jana, T. Kugita and S. Namba, *Catal. Lett.* , 2003, **90**, 143.

8 S. K. Jana, T. Kugita and S. Namba, *Appl. Catal. A*, 2004, **266**, 245.

9 S. K.Jana, T. Okamoto, T. Kugita and S. Namba, *Appl. Catal. A*, 2005, **288**, 80.

10   A. Garade and V. Kshirsagar, C. Rode, *Appl. Catal. A*, 2009, **354**, 176.

11 A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes and J. H. Davis, *J. Am. Chem. Soc.* , 2002, **124**, 5962.

12 Z. Hou and T. Okuhara, *J. Mol. Catal. A: Chem.* , 2003, **206**, 121.

13 Z. S. Qureshi, K. M. Deshmukh, K. P. Dhake and B. M. Bhanage, *RSC Adv.* , 2011, **1**, 1106.

14 Q. Zhang, S. Zhang and Y. Deng, *Green Chem.* , 2011, **13**, 2619.

15 R. Hayes, S. Imberti, G. G. Warr and R. Atkin, *Angew. Chem. Int. Ed*. , 2013, **52**, 4623.

16 H. Olivier-Bourbigou, L. Magna and D. Morvan, *Appl. Catal. A*, 2010, **373**, 1.

17 X. Wang, M. Sternberg, F. T. Kohler, B. U. Melcher, P. Wasserscheid and K. Meyer, *RSC Adv.* , 2014, **4**, 12476.

18 W. S. Zhu, P.W. Wu, L. Yang, Y. H. Chang, Y. H. Chao, H. M. Li, Y. Q. Jiang, W. Jiang and S. H. Xun, *Chem. Eng. J.* , 2013, **229**, 250.

19 Y. Wang, H. Zhi and J. Luo, *J. Mol. Catal. A: Chem.* , 2013, **379**, 46.

20 Y. Xu, Y. Wang, Y. Zeng, J. Jiang and Z. Jin, *Catal. Lett.* , 2012, **142**, 914.

21 A. Behr, G. Henze and R. Schomaecker, *Adv. Synth. Catal.* , 2006, **348**, 1485.

22 H. F. Liu, F. X. Zeng, L. Deng, B. Liao, H. Pang and Q. X. Guo, *Green Chem.* , 2013, **15**, 81.

23 L. J. Jia, C. Y. Hua, L. Y. Dai and Y. K. Shan, *React. Kinet. Catal. Lett.* , 2004, **81**, 235.

24 P. Elavarasan, K. Kondamudi and S. Upadhyayula, *Chem. Eng. J.* , 2011, **166**, 340.

25 J. Fraga-Dubreuil, K. Bourahla, M. Rahmouni, J. P. Bazureau and J. Hamelin, *Catal. Commun.* , 2002, **3**, 185.

26 F. M. Maia, O. Rodríguez and E. A. Macedo, *J. Chem. Thermodyn.* , 2011, **48**, 221.

27 C. Thomazeau, H. Olivier-Bourbigou, L. Magna, S. Luts and B. Gilbert, *J. Am. Chem. Soc.* , 2003, **125**, 5264.

28 R. Kore and R. Srivastava, *Catal. Commun.* , 2011, **12**, 1420.

29 B. Tan, J. Jiang, Y. Wang, L. Wei, D. Chen and Z. Jin, *Appl. Organomet. Chem.* , 2008, **22**, 620.

30 A. Garade, V. Kshirsagar, R. Mane, A. Ghalwadkar, U. Joshi and C. Rode, *Appl. Clay Sci.* , 2010, **48**, 164.

31 M. Ott, H. Schoenmakers and H. Hasse, *Chem. Eng. Process.* , 2005, **44**, 687.

32 H. Malhotra, *J. Appl. Polym. Sci.* , 1976, **20**, 2461.

33 S. Udayakumar, S. Ajaikumar and A. Pandurangan, *Catal. Commun.* , 2007, **8**, 366.