

The structure of acidified ionic liquid [emim]BF₄ and its catalytic performance in the reaction for 4,4'-MDC synthesis

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Abstract

Acidified ionic liquid [emim]BF₄ (H⁺[emim]BF₄) was prepared and its structure was ascertained using ¹H NMR analysis and experimental verification. It was found that the cation of H⁺[emim]BF₄ is composed of a central imidazole molecule surrounded by a water layer in which excessive HBF₄ molecules are dissolved. H⁺[emim]BF₄ showed high catalytic performance in the condensation of methyl *N*-phenyl carbamate (MPC) and formaldehyde (HCHO) to methylene diphenyl dimethylcarbamate (4,4'-MDC). Under the suitable reaction conditions of 70 °C, molar ratio of MPC to HCHO = 4, weight ratio of H⁺[emim]BF₄ to MPC = 4, and reaction time 1.5 h, the yield and selectivity of 4,4'-MDC attained 71.7% and 71.9%, respectively. Besides, H⁺[emim]BF₄ could be reused for 4 runs after being treated by ultrasonic extraction with CHCl₃ and no significant catalytic activity loss was observed after the second run.

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Keywords: [emim]BF₄ ionic liquid; Structure; Methyl *N*-phenyl carbamate; Formaldehyde; Methylene diphenyl dimethylcarbamate

1. Introduction

Ionic liquids (ILs), due to their favorable properties like low volatility, non-inflammability, high thermal and chemical stability, have received much more attention as environmentally benign solvents in catalysis and organic synthesis reactions. In all kinds of ILs, acidic ILs are extremely important because they can be used as both catalyst and solvent in acid-catalysed reactions. Some research work has indicated that the acidity and catalytic activity of the ionic liquid would be significantly enhanced by adding some kind of protonic acid to a neutral ionic liquid [1]. However, the structures of the acidified ILs have not been studied and the reason for their catalysis has not been analyzed in the literature so far.

Diphenylmethane diisocyanate (MDI) is an important monomer for the manufacture of polyurethanes. There are three isomers of MDI: 4,4'-MDI, 2,4'-MDI and 2,2'-MDI. Among them, 4,4'-MDI is the most important one. At present, there are two methods for synthesis of MDI: one is phosgene route

and the other is non-phosgene route. The phosgene route is currently used for the production of MDI in industry. However it is not environmentally friendly due to using toxic phosgene as raw material, and generating highly corrosive hydrochloride as a byproduct, and producing MDI with residual chlorine anion. For the purpose of eliminating all these drawbacks, several non-phosgene routes [2] have been developing. Among them, dimethyl carbonate (DMC) route is the most competitive one, which comprises the synthesis of methyl *N*-phenyl carbamate (MPC) from aniline and DMC, condensation of MPC with formaldehyde (HCHO) to diphenylmethane dicarbamate (MDC), and then the thermal decomposition of MDC to MDI. Up to now, much more research work has been done on the first and third step and great progress has been made [3,4]. The second step, i.e. the condensation of MPC with HCHO, needs much more attention because of its lower product yield, selectivity and environmental problems. The catalysts used in this reaction include liquid acids (such as HCl, H₂SO₄, H₃PO₄, CF₃SO₃H, mixed acid) [2,5] and solid acids (such as SbCl₅, ZnCl₂, BF₃, ion-exchange resin, zeolites) [6–9]. The liquid acid catalysts cause corrosion to the equipment and result in environmental pollution while the solid acid catalysts not only deactivate rapidly but also need organic solvents in the reaction. Therefore,

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it is necessary to develop a novel environmentally friendly and highly active catalyst for the condensation reaction of MPC with HCHO to MDC.

In this work, the structure of the ionic liquid [emim]BF₄ with excess of 20% HBF₄ was ascertained by ¹H NMR analysis and experimental verification, and its catalytic performance in the reaction for 4,4'-MDC synthesis was evaluated.

2. Experimental

2.1. Materials and reagents

N-methylimidazole was purchased from Acros. Tetrafluoroboric acid (HBF₄) and lead monoxide were obtained from Tianjin Kermel Chemical Reagent Co. Bromic ethane and formaldehyde were purchased from Tianjin Damao Chemical Co. MPC was prepared from phenyl isocyanate and methanol and was characterized by means of IR. All other chemicals used in the experiment were obtained commercially and used without further purification unless otherwise stated.

2.2. Preparation of ionic liquids

Preparation of acidified ionic liquid H⁺[emim]BF₄ [10]: ① 1-ethyl-3-methylimidazolium bromide ([emim]Br) was prepared by the reaction of *N*-methylimidazole and bromic ethane. ② Lead monoxide (0.1 mol) and water were charged into a three-necked flask equipped with a mechanical stirrer, and tetrafluoroboric acid (excessive) was slowly added under strong agitation, resulting in a colorless Pb(BF₄)₂ aqueous solution. ③ [emim]Br (0.2 mol, diluted by water) was added into the Pb(BF₄)₂ solution, and white PbBr₂ precipitate immediately appeared. The reaction mixture was filtrated after stirring for 1.5 h and the remaining water in the filtrate was removed by vacuum distillation at 80 °C. Finally, the resultant ionic liquid H⁺[emim]BF₄ was dried in vacuum.

Preparation of neutral ionic liquid [emim]BF₄ [11] was almost the same except NaBF₄ was used to replace Pb(BF₄)₂ (avoid using HBF₄) and acetone was used as the solvent in the step ②.

2.3. Condensation reaction

In the condensation reaction, MPC, ILs and HCHO were charged into a 100 mL round-bottom flask immersed in a water bath and fitted with a reflux condenser. The mixture was stirred at a certain temperature for a period of time. When the reaction finished, the product was obtained by filtration, and H⁺[emim]BF₄ could be reused after purified by ultrasonic extraction with CHCl₃.

2.4. Characterization procedures

The FT-IR spectra of MPC, MDC and the ILs were recorded on a Vector22 infrared spectroscopy (KBr pellets/film) in a frequency range of 400–4000 cm⁻¹. On compared with the standard spectrum in the literature [12], the reaction product MDC

was identified as cis-4,4'-MDC. The structure of H⁺[emim]BF₄ was also identified by a Mercury300 nuclear magnetic resonance (NMR) at 300 K with CD₃COCD₃ as the solvent. 4,4'-MDC was quantitatively analyzed by Waters 515 HPLC with a Nova-Pak C18 (3.9 mm × 150 mm) column, methanol–water (3/2 by volume) as the mobile phase at a flow of 0.6 mL/min and 254 nm UV detector.

In this work, the yield of MDC was calculated based on HCHO added, while the selectivity of MDC was calculated with MPC as the basis because the concentration of HCHO after reaction was difficult to determine.

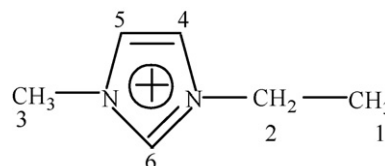
3. Results and discussion

3.1. Structure of H⁺[emim]BF₄

3.1.1. ¹H NMR analysis

In order to ascertain the structure of H⁺[emim]BF₄, ¹H NMR analysis of H⁺[emim]BF₄ was made. The configuration of the cation of H⁺[emim]BF₄ is illustrated in Scheme 1, and the ¹H NMR spectra of [emim]BF₄ and H⁺[emim]BF₄ are shown in Figs. 1 and 2, respectively.

As for [emim]BF₄, the ¹H NMR (CD₃COCD₃, 300 MHz) data of δ = 1.540 (m, 3H), 4.388 (t, 2H), 4.024 (s, 3H), 7.757 (t, 1H), 7.683 (t, 1H), and 9.065 (t, 1H) correspond separately to the hydrogen atom marked by 1, 2, 3, 4, 5 and 6 in Scheme 1. The resonance signals δ = 2.051 and 2.999 are caused by CD₃COCD₃ and trace water. The ¹H NMR data of H⁺[emim]BF₄ are almost the same as [emim]BF₄'s except the wide resonance signals δ = 4.651 and 4.838. We preliminarily considered that one of the wide signals in the ¹H NMR spectrum of H⁺[emim]BF₄ was



Scheme 1. Configuration of the ionic liquid cation.

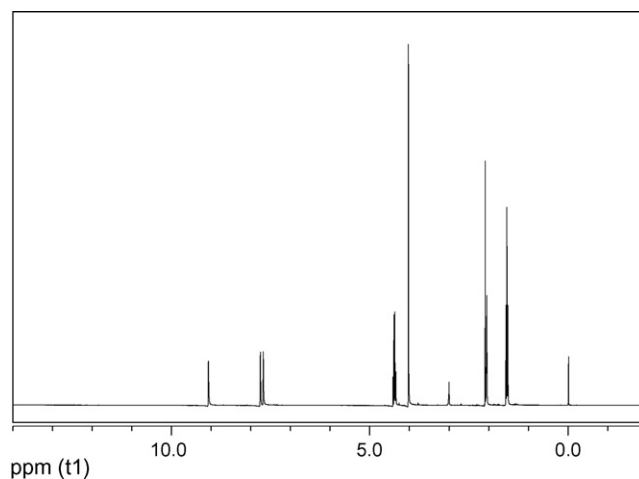


Fig. 1. ¹H-NMR spectra of [emim]BF₄.

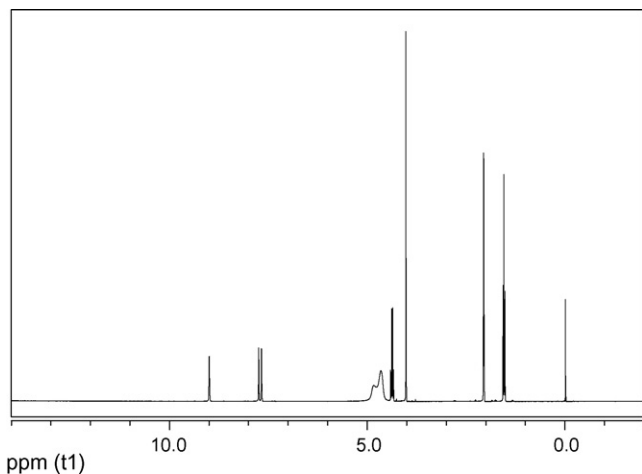


Fig. 2. ^1H -NMR spectra of $\text{H}^+[\text{emim}]\text{BF}_4$.

attributed to the chemical shift of water, and the other might be caused by the chemical action between HBF_4 and the cation. Tiny changes of the chemical shifts about the three hydrogen atoms (marked 4, 5 and 6 in Scheme 1) proved that the inference was right.

In order to analyze the structure of $\text{H}^+[\text{emim}]\text{BF}_4$ further research was done. ^1H NMR analysis was made after $[\text{emim}]\text{BF}_4$ and $\text{H}^+[\text{emim}]\text{BF}_4$ were dried under high vacuum for a long time (<0.01 MPa, 80°C , 48 h). The ^1H NMR spectra of $[\text{emim}]\text{BF}_4$ had no change before or after the treatment. However, the two wide resonance signals in the ^1H NMR spectra of $\text{H}^+[\text{emim}]\text{BF}_4$ before it was dried decreased to only one wide resonance signal (associated with methylene in $\delta = 4.408$) after the treatment (Fig. 3), which suggested that one impurity in $\text{H}^+[\text{emim}]\text{BF}_4$ had been eliminated in the drying treatment.

3.1.2. Experimental verification

Based on the ^1H NMR analytic results, a series of experiments were arranged to analyze the structure of $\text{H}^+[\text{emim}]\text{BF}_4$. $\text{H}^+[\text{emim}]\text{BF}_4$ (after drying treatment) was used as both the catalyst and the solvent in 4,4'-MDC synthesis reaction, and result showed that its catalytic activity did not decrease. However, even

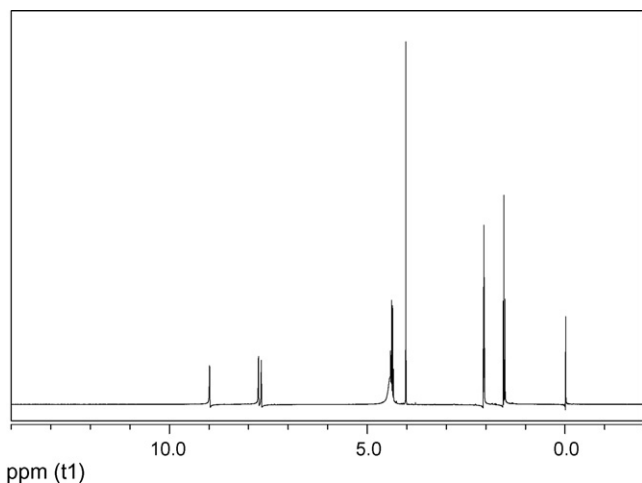
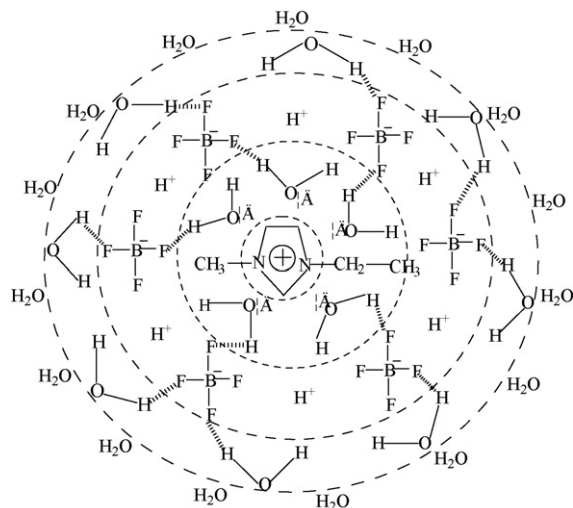


Fig. 3. ^1H -NMR spectra of $\text{H}^+[\text{emim}]\text{BF}_4$ after drying.



Scheme 2. Hypothetic model of $\text{H}^+[\text{emim}]\text{BF}_4$ cation.

if some water was added to $[\text{emim}]\text{BF}_4$, the mixture had no catalytic activity. The results obtained above indicated that HBF_4 , as the catalytic centre, existed in $\text{H}^+[\text{emim}]\text{BF}_4$ whatever before or after it was dried. Considering that HBF_4 can only exist in the water solution, the existence of water in $\text{H}^+[\text{emim}]\text{BF}_4$ (before or after it was dried) was confirmed. Because imidazolium cation has positive charge and the oxygen in a water molecule has some negative charge for its high electronegativity, the cation and water can be bonded by electrostatic attraction. Moreover, hydrogen bond is easily formed between water molecule and HBF_4 molecule.

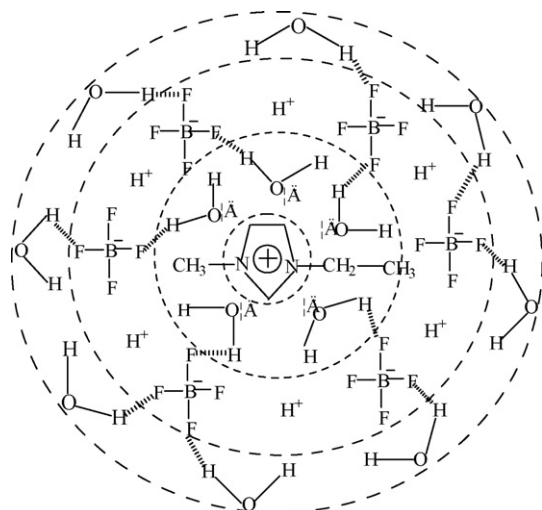
3.1.3. Structure of $\text{H}^+[\text{emim}]\text{BF}_4$

Based on the results obtained above, the structure of $\text{H}^+[\text{emim}]\text{BF}_4$ cation is illustrated in Scheme 2, i.e. an acidic compound system that is composed of a central imidazole molecule surrounded by a water layer in which excessive HBF_4 molecules are dissolved. There are two kinds of water existing in the compound system: one is bonded with imidazole molecule by electrostatic attraction and is connected with HBF_4 molecule by hydrogen bonds, and the other is in a dissociation form existing in the outer layer of the cation. Scheme 3 shows the structure of $\text{H}^+[\text{emim}]\text{BF}_4$ after undergoing drying treatment; the dissociative water has been removed by vacuum drying. However, the first kind of water and HBF_4 are too difficult to be removed for their chemical actions. That is the reason why $\text{H}^+[\text{emim}]\text{BF}_4$ still has good catalytic activity after being dried and its ^1H NMR spectra has only one wide resonance signal left.

Because of the chemical bonds in the acidic compound system, $\text{H}^+[\text{emim}]\text{BF}_4$ is expected to possess high catalytic activity and stability. Further investigation on the catalytic performance of $\text{H}^+[\text{emim}]\text{BF}_4$ in the 4,4'-MDC synthesis reaction was made below.

3.2. Effect of different excessive degree of HBF_4

Table 1 shows the effect of different excessive degree of HBF_4 in $\text{H}^+[\text{emim}]\text{BF}_4$ on the condensation reaction of MPC

Scheme 3. Hypothetic model of $\text{H}^+[\text{emim}]\text{BF}_4$ cation after drying treatment.

with HCHO. The acidity of the ionic liquids has great influence on its catalytic activity and the neutral ionic liquid $[\text{emim}]\text{BF}_4$ even had no activity for the condensation reaction. When the excessive degree of HBF_4 in $\text{H}^+[\text{emim}]\text{BF}_4$ is low, the acidity and reactive activity of $\text{H}^+[\text{emim}]\text{BF}_4$ are promoted with the increasing of the content of HBF_4 . However, when the excess of HBF_4 surpasses 20%, the catalytic activity has no obvious changes. Consequently, we choose $\text{H}^+[\text{emim}]\text{BF}_4$ with the excess of HBF_4 of 20% as both the catalyst and the solvent for the condensation reaction.

3.3. Catalytic performance of $\text{H}^+[\text{emim}]\text{BF}_4$

3.3.1. Effect of reaction temperature

The effect of reaction temperature on the condensation reaction was studied. As shown in Fig. 4, the conversion of MPC increases with the rising of the reaction temperature. Both the yield and selectivity of MDC monotonously increase at low temperature and separately reach the highest value of 71.7% and 71.9% at 70 °C. However, when the temperature surpasses 70 °C they decrease due to the formation of dinuclear, trinuclear or other polynuclear compounds with methylene-amino bond [5,13].

Table 1
Catalytic activity of ionic liquids with different excessive degree of HBF_4

The excess of HBF_4 %	Yield of MDC (%)	Conversion of MPC (%)	Selectivity of MDC to MPC (%)
0	2.8	12.7	11.1
10	56.3	50.5	55.4
20	64.8	51.6	62.5
30	62.2	51.5	59.9
40	63.9	51.9	61.2

Reaction conditions: 10 mL $\text{H}^+[\text{emim}]\text{BF}_4$; 20 mmol MPC; molar ratio of MPC to HCHO 4:1; 80 °C; 3 h.

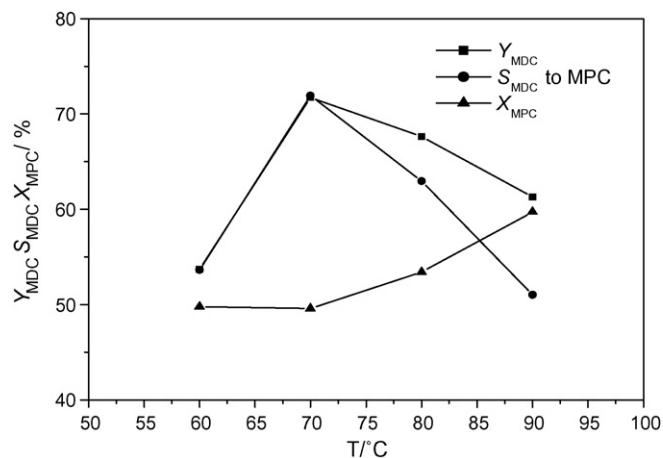


Fig. 4. Effect of reaction temperature on the condensation reaction. Reaction conditions: 10 mL $\text{H}^+[\text{emim}]\text{BF}_4$; mass ratio of $\text{H}^+[\text{emim}]\text{BF}_4$ to MPC 4:1; molar ratio of MPC to HCHO 4:1; 1.5 h.

3.3.2. Effect of the molar ratio of MPC to HCHO

Fig. 5 shows the effect of the molar ratio of MPC to HCHO ($n(\text{MPC})/n(\text{HCHO})$) on the condensation reaction. As $n(\text{MPC})/n(\text{HCHO})$ increases, the conversion of MPC decreases monotonously while the yield of MDC passes a maximum of 86.6% at 6/1 and the selectivity gets a maximum of 71.9% at 4/1. When $n(\text{MPC})/n(\text{HCHO})$ is lower than 4/1, the by-products of polycondensation reactions are easily formed because of the higher concentration of HCHO. When $n(\text{MPC})/n(\text{HCHO})$ surpasses 6/1, the lower concentration of HCHO slows down the reaction rate, so the yield and selectivity of MDC both decrease. The optimal molar ratio of $n(\text{MPC})/n(\text{HCHO})$ is 4/1 from the standpoint of selectivity.

3.3.3. Effect of the amount of $\text{H}^+[\text{emim}]\text{BF}_4$

The effect of the weight ratio of $\text{H}^+[\text{emim}]\text{BF}_4$ to MPC ($\text{wt}(\text{ILs})/\text{wt}(\text{MPC})$) on the condensation reaction was studied by varying $\text{wt}(\text{ILs})/\text{wt}(\text{MPC})$ from 3/1 to 5/1. As shown in Fig. 6, when $\text{wt}(\text{ILs})/\text{wt}(\text{MPC}) = 4/1$, the yield and selectivity of MDC reach 71.7% and 71.9%, respectively. When $\text{wt}(\text{ILs})/\text{wt}(\text{MPC})$

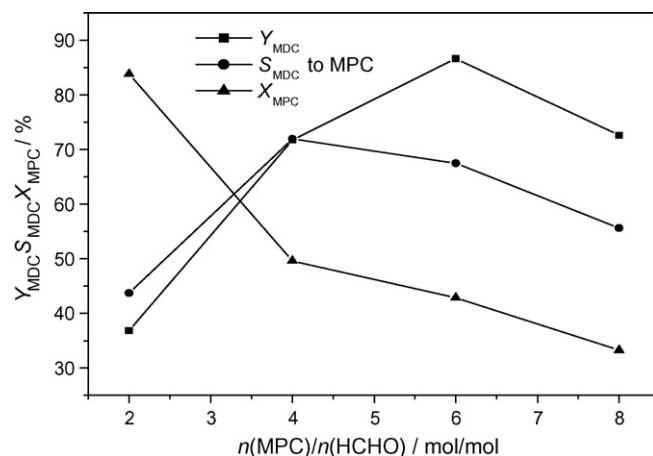


Fig. 5. Effect of molar ratio of MPC to HCHO on the condensation reaction. Reaction conditions: 10 mL $\text{H}^+[\text{emim}]\text{BF}_4$; mass ratio of $\text{H}^+[\text{emim}]\text{BF}_4$ to MPC 4:1; 70 °C; 1.5 h.

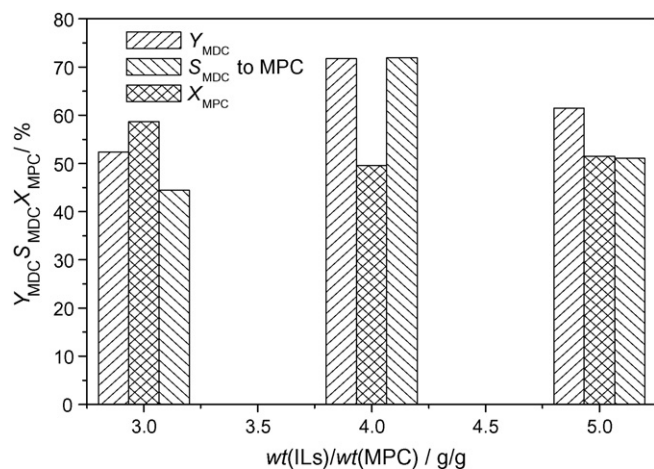


Fig. 6. Effect of the amount of ionic liquid on the condensation reaction. Reaction conditions: 10 mL H⁺[emim]BF₄; molar ratio of MPC to HCHO 4:1; 70 °C; 1.5 h.

is below 4, polynuclear compounds are easily formed as the by-products, and the yield and selectivity of MDC decrease. When wt(ILs)/wt(MPC) is above 4/1, lower concentrations of the reactants slow down the reaction rate. Therefore, the optimal ionic liquid amount is wt(ILs)/wt(MPC) = 4/1.

3.3.4. Effect of reaction time

Fig. 7 shows the effect of reaction time on the condensation reaction. The conversion of MPC increases with the prolonging of the reaction time, while the yield of MDC increases in the early stage of the reaction and reaches 71.7% at 1.5 h, then decreases. No significant changes can be observed after 2.5 h because the reaction approaches to the chemical balance.

3.3.5. Recycle of H⁺[emim]BF₄

H⁺[emim]BF₄ was purified by ultrasonic extraction with CHCl₃ (*V*(ILs)/*V*(CHCl₃) = 1/1, and ultrasonic time 2 min) for 3 times at room temperature. Under the suitable condensation reaction conditions, the purified H⁺[emim]BF₄ was reused and

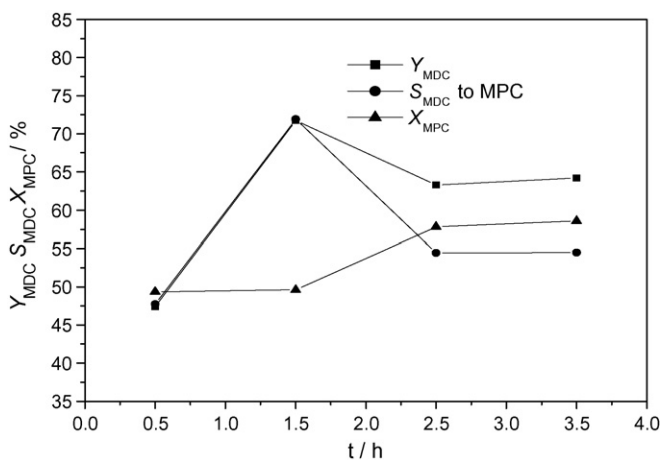


Fig. 7. Effect of reaction time on the condensation reaction. Reaction conditions: 10 mL H⁺[emim]BF₄; mass ratio of H⁺[emim]BF₄ to MPC 4:1; molar ratio of MPC to HCHO 4:1; 70 °C.

Table 2
Reuse of ionic liquid in the condensation reaction

Run time	Yield of MDC (%)	Conversion of MPC (%)	Selectivity of MDC to MPC (%)
1	71.7	49.6	71.9
2	60.7	52.2	55.8
3	60.3	51.2	57.5
4	61.7	51.9	57.0
5	59.3	48.1	57.7

Reaction conditions: 10 mL H⁺[emim]BF₄; mass ratio of H⁺[emim]BF₄ to MPC 4:1; molar ratio of MPC to HCHO 4:1; 70 °C; 1.5 h.

the results are listed in Table 2. It could be seen that no significant loss in catalytic activity was observed after the second run. Therefore, H⁺[emim]BF₄ has good stability, which is in a good agreement with the result of its structure analysis.

4. Conclusions

The acidified ionic liquid H⁺[emim]BF₄ was prepared and its structure was first ascertained using ¹H NMR analysis and experimental verification. The cation of H⁺[emim]BF₄ is composed of a central imidazole molecule surrounded by a water layer in which excessive HBF₄ molecules are dissolved. H⁺[emim]BF₄ has all of the advantages of acid ionic liquids and can be used as both the catalyst and the solvent in the condensation reaction of MPC with HCHO. Under the suitable reaction conditions of 70 °C, molar ratio of MPC to HCHO = 4/1, weight ratio of H⁺[emim]BF₄ to MPC = 4/1, and reaction time 1.5 h, the yield and selectivity of 4,4'-MDC attain 71.7% and 71.9%, respectively. Besides, H⁺[emim]BF₄ can be reused for 4 runs after being treated by ultrasonic extraction with CHCl₃ and no significant catalytic activity loss is observed after the second run.

Acknowledgments

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