



Cite this: DOI: 10.1039/c8nj01175c

Ionic liquid-mediated solvothermal synthesis of 4,4'-methylenediphenyl diisocyanate (MDI): an efficient and environment-friendly process†

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4,4'-Methylenediphenyl diisocyanate (4,4'-MDI) is an immensely important intermediate employed in the manufacturing of polyurethanes. Many synthetic routes have been developed over the decades for the synthesis of 4,4'-MDI compounds on a large scale; these compounds are highly toxic and hazardous in nature. In this study, an environment-friendly route is proposed for the synthesis of 4,4'-MDI using 4,4'-diaminodiphenylmethane and dimethyl carbonate (DMC) as starting materials, which are nontoxic in nature. The synthesis of ionic liquids (ILs) and their utilization in the decomposition reaction are systematically investigated. Imidazole-functionalized ionic liquids were prepared for the synthesis of 4,4'-MDI, and their thermal performances were evaluated by TGA. We found that in comparison with other imidazole-functionalized ionic liquids, 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate ([EAmim]BF₄) exhibited preferable thermal activity for the decomposition of 4,4'-methylenediphenyl dimethylcarbamate (4,4'-MDC). Moreover, these ILs were more effective when they were combined with zinc as a catalyst, which enhanced the decomposition of MDC. Under optimal conditions, the yield of MDI compared to that of Zn(OAc)₂-[EAmim]BF₄ catalyst increased up to 96%. The mechanism of the enhanced performance of ionic liquids by catalytic activity of zinc acetate was also investigated.

Received 13th March 2018,
Accepted 14th June 2018

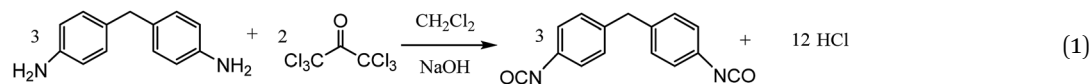
DOI: 10.1039/c8nj01175c

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Introduction

Diisocyanates such as toluene diisocyanate (TDI) and methylene-diphenyl diisocyanate (MDI) are considered important raw materials in the manufacture of polyurethanes, pesticides and herbicides.^{1,2} 4,4'-MDI is one of the most important isocyanates widely used in polyurethane production as it is a non-volatile material, which is safe for handling.^{3,4} Thus, MDI has emerged as an alternative to conventional pure TDI, and it has been developed to produce elastomers and flexible polyurethane foams.⁵

In a simple way, 4,4'-MDI can be synthesized by the reaction of phosgene with methylene dianiline in dichloromethane as a solvent (eqn (1)). However, this conventional method for producing isocyanates is an extremely hazardous process because of the high toxicity of phosgene and corrosive nature of the co-product HCl.^{6–8} There have been persistent efforts for developing alternative processes avoiding phosgene such as the reductive carbonylation of nitrobenzene,^{9–11} oxidative carbonylation of aniline, and aminolysis of dimethyl carbonate (DMC).^{12–16}



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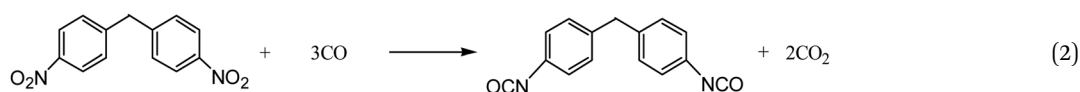
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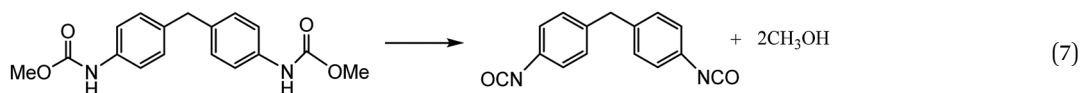
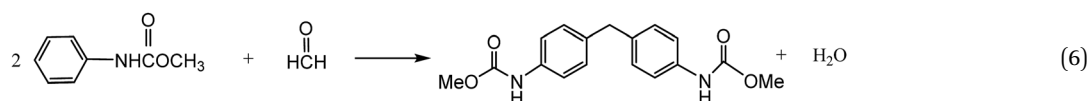
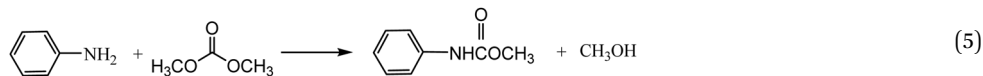
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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8nj01175c

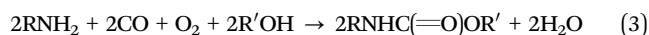
In 1996, Tafesh demonstrated synthesis of 4,4'-MDI utilizing 4,4'-dinitrodiphenylmethane and carbon monoxide (CO) as reagents and palladium metal as the catalyst (eqn (2)),⁹ but there are a few shortcomings of this method: it cannot be applied at room temperature due to the low thermal energy associated with this process, which is not sufficient for this reaction as it requires high activation energy. Even at elevated temperatures of 160–210 °C, the required pressure for reductive carbonylation of dinitrodiphenylmethane is at least 29 MPa.^{10,11} It is apparent from eqn (2) that only one-third of CO can be used effectively, and recycling of unreacted CO mixed with the co-product CO₂ can increase the production cost. Although the palladium metal exhibits excellent catalytic activity during the synthesis of MDI, it is not cost-effective as the process for recycling the catalyst is complicated. Therefore, this process is never adopted for the commercial production of MDI.



Another method developed by several groups for the synthesis of MDI is the catalytic oxidative carbonylation of aniline with CO and O₂ in the presence of an alcohol and appropriate catalyst, followed by decomposition of the resultant carbamate, as delineated in eqn (3) and (4).^{12–16} Kim demonstrated that by adding SeO₂/K₂CO₃ to the reaction system, 49% selectivity could be achieved for carbamate.¹² In the process, oxidative carbonylation of aniline was performed even at a high pressure of 6.8 MPa. It was reported later by Chen *et al.*¹³ that the yield of carbamate could reach 43.5% when



the reaction was performed at a reduced pressure of 3.8 MPa over CuCl₂-NaI during 1 h of batch reaction at 438 K. However, several problems were observed for the above-mentioned process such as the hazards associated with reaction conditions and low selectivity of the intermediate for manufacturing MDI.



Recently, a greener approach has been adopted for the synthesis of MDI, as shown in eqn (5)–(7).¹⁷ It has been documented that dimethyl carbonate (DMC) is an environmentally benign reagent,

which does not produce any toxic byproducts other than methanol and water. In the oxidative carbonylation process, the aminolysis of DMC can be completed under mild conditions, and DMC can also be reproduced by the oxidative carbonylation of methanol, which increases the overall efficiency of the process and lowers the cost of the production of DMC. This non-phosgene route uses nontoxic reagents and produces non-polluting co-products and therefore, this process has been explored to a great extent;^{18–20} the aminolysis of methylene diphenyl dicarbamate (MDC) is believed to be one of the most efficient processes for thermal decomposition by the removal of low-boiling alcohols.^{21–23} It was demonstrated by Chen *et al.*²¹ that the yield of MDI could be 52% with thermal decomposition of 3% MDC in dibutyl phthalate at 260 °C. Guan reported that the yield could be increased to 67% in the presence of ZnO/Zn catalyst.²² When Zn was used as the catalyst and

nitrobenzene-tetrahydrofuran as the solvent during thermal decomposition, the yield of MDI increased to 87%. Although this method can reduce polymerization of MDI to give higher yield, the removal of large amounts of solvents to concentrate the product may pose technical challenges and create hindrance to the large-scale production of MDI. Therefore, our focus is to explore a better method for synthesizing MDI by the decomposition of MDC in low amount of solvents, which can improve the product concentration process.

Ionic liquids (ILs) have emerged as environment friendly media, and they can be used as alternatives to traditional volatile organic solvents due to their nonflammability, low volatility, low toxicity and high thermal and chemical stabilities.^{24,25} Therefore, ILs are widely used in various capacities: they are used as solvents, catalysts in chemical reactions, and in separation and manufacturing processes,^{26–30} especially as heat transfer fluids^{31–33} and in fuel cells.^{34–36} In the past few years, a large number of ionic liquids have been reported.³⁷ The most common ones are imidazole-based ionic liquids such as 1-butyl-3-methylimidazolium ([bmim]) and 1-allyl-3-methylimidazolium ([amim]) ferric chloride, which are used for the study of thermo-chemical and other

thermodynamic properties.^{38–46} The decomposition temperatures of these ILs are in the range of 360 °C to 424 °C.^{43–46} Thus, there is growing interest regarding their application for the reactions that require high temperatures. An example is imidazole-based ionic liquid, which is used as a thermal fluid in chemical reactions performed at high temperatures. It is important to find an ionic liquid with extended thermal stability because these reactions are usually carried out at elevated temperatures. Qu *et al.* reported the syntheses and thermochemical properties of 1-butyl-3-methylimidazolium tetrafluoroborate and 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate;^{47,48} the results demonstrated that these ILs with BF₄ anions possessed long-term stabilities and excellent thermo-durabilities.^{47,48} These imidazole-functionalized ionic liquids were used for the synthesis of MDI; it is well-known that an organic cation, an inorganic anion and the length of the alkyl chain in the cation can influence its properties such as melting point, density, viscosity and thermostability.^{49–51} To study the decomposition of MDC, three kinds of imidazole-functionalized ionic liquids were synthesized and investigated systemically. Imidazole-functionalized ionic liquids are also used as catalysts in many reactions. For example, Zhang *et al.*⁵² prepared an acid–base bifunctional ionic liquid, 1-(2-(1-piperidinyl)ethyl)-3-methylimidazolium trichlorolead ([PEmim]PbCl₃), and they used it successfully as a catalyst for the synthesis of MPC. It was also demonstrated by Wang⁵³ that a mixture of [bmim]BF₄ and tetramethyl guanidine (TMG) can be used as a catalyst in the synthesis of MPC. For the synthesis of MDI from methylene diphenyl dicarbamate, Zn(OAc)₂ and Zn(OAc)₂/acetate have been used as catalysts.^{22,54,55} The above-mentioned catalysts can be easily dissolved in the reaction medium, which accelerates the reaction rate and improves the product yield. Ionic liquids can effectively assist zinc catalysts to improve the reaction rate, and they can be successfully separated from the catalysts after completion of the reaction; moreover, due to their low volatility, they are more stable at higher temperatures. Three kinds of imidazole-functionalized ionic liquids were synthesized and employed for the decomposition of 4,4'-MDC. After complete decomposition of MDC, the recovery and reuse of catalysts and ILs were investigated systemically.

Experimental section

Materials and reagents

N-Methylimidazole (99%) was obtained from Sinopharm Chemical Reagent Co., Ltd. Bromobutane, bromooctane, ethylchloroacetate and sodium tetrafluoroborate (NaBF₄) were obtained from Tianjin Kermel Chemical Reagent Co. Zn(OAc)₂, ZnO, zinc phenylacetate and silver nitrate were purchased from Tianjin Damao Chemical Co. All other chemicals used in the experiment were obtained commercially and used without further purification.

Preparation of ionic liquids

The purity of ionic liquids is very important, and it has a significant impact on thermal decomposition. Ionic liquids such as 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim]BF₄) and 1-octyl-3-methylimidazolium tetrafluoroborate ([C₈mim]BF₄)

were synthesized according to previously reported methods.^{56,57} 1-alkyl-3-methylimidazolium bromides ([C_{*n*}mim]Br) were prepared by the reaction of *N*-methylimidazole and bromobutane or *N*-methylimidazole and bromooctane. A white precipitate of NaBr appeared immediately when [C_{*n*}mim]Br was added to NaBF₄ solution. The mixture was filtered after stirring for 4 h, and the filtrate was removed by vacuum distillation at 393 K after 4 h. Finally, the resultant neutral ionic liquid [C_{*n*}mim]BF₄ was dried in a vacuum dryer. The completion of anion exchange was monitored with silver nitrate. Both the products were liquid with yields of 90% and 92%. 1-Ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate ([EAmim]BF₄) was synthesized following a two-step method reported by Qu *et al.*^{47,58} The first step was nucleophilic substitution by *N*-methylimidazole on ethylchloroacetate to obtain a 1-ethoxycarbonylmethyl-3-methylimidazole-containing halide salt ([EAmim]Cl). The second step involved sodium tetrafluoroborate-mediated anion exchange reaction with the intermediate chloride salt to produce the final product 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate ([EAmim]BF₄). Anion exchange was monitored as [C_{*n*}mim]BF₄ was formed, and the yield of the product was 90%. Handling of materials and tests were conducted in an argon-filled glove box to ensure accuracy of measurements for determining the thermal behaviour and temperatures, which allowed correct and safe application. The argon-filled glove box was free of oxygen contamination and water vapor with levels controlled at less than 5 and 2 ppm, respectively. More details about the synthesis and characterization of ionic liquids can be seen in the ESI.†

Reaction apparatus and operation

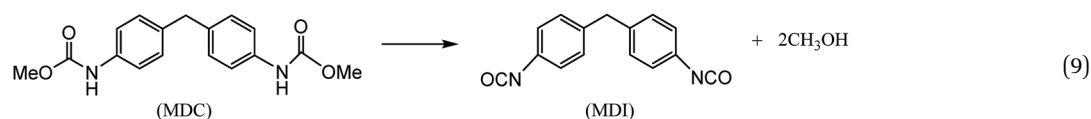
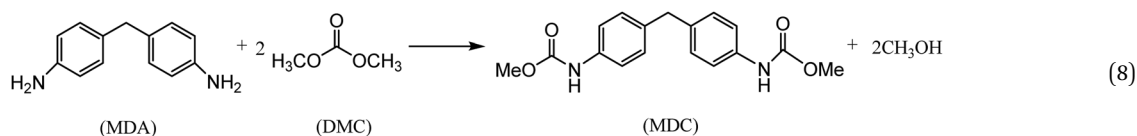
The reaction of diaminodiphenylmethane and DMC was carried out in a 500 mL stainless steel autoclave fitted with a magnetic stirrer bar. A typical operation for MDC synthesis is as follows: aniline (20 g), Zn(OAc)₂ (0.7 g), and DMC (200 g) were charged and then stirred at 140–180 °C for 3 h. After the reaction was complete, the intermediate was cooled to room temperature, and the remaining DMC was recycled. MDI was prepared by thermal decomposition of 4,4'-MDC by adding certain amounts of 4,4'-MDC (5 g), 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate (20 g) and catalysts such as Zn(OAc)₂, ZnO, zinc and phenylacetate in a three-neck bottle. Before the decomposition process started, a continuous flow of nitrogen gas at a rate of 10 mL min⁻¹ was purged into the reaction system. The operational procedure included the introduction of a heat carrier into the reactor to raise the temperature, and the pressure was adjusted for the vacuum system. The pressure was maintained at 0.5 kPa during the whole decomposition process. As the temperature increased rapidly from 25 to 230 °C, the product MDI was formed, and it flowed into the receiving flask rapidly. The reaction was completed in 15 min, and the corresponding reactions are shown in eqn (8) and (9). Finally, the product MDI was weighed and analyzed by IR and ¹H-NMR. It is well-known that the –NCO group in MDI is highly moisture-sensitive and therefore, it had to be stored in an argon-filled glove box before application and testing. After complete decomposition of MDC, the by-product

methanol was removed under reduced pressure to obtain the product MDI in the receiving flask. The reaction mixture containing $\text{Zn}(\text{OAc})_2$ -[EAmim] BF_4 , methanol and [EAmim] BF_4 was filtered under vacuum and then, non-toxic dimethyl carbonate having a small amount of activated charcoal was added to the filtrate. Finally, the filtrate was distilled at 90 °C under reduced pressure and subsequently dried in a vacuum dryer at 120 °C for 4 h to afford [EAmim] BF_4 . It should be noted that an infrared vortex-evaporator connected to the PoleStar Coldtrap System was used for drying the ionic liquids under vacuum.

Results and discussion

Preparation of MDC

The reactions of diaminodiphenylmethane and DMC for the synthesis of 4,4'-MDC over various zinc catalysts were conducted at different temperatures, and the results are shown in Fig. 1. When no catalyst was added to the system, the yield of 4,4'-MDC was low, around 54% at 145 °C, which indicated that there was scope for improvement by employing a suitable catalyst in terms of yield and reaction time. Among the catalysts



Analysis and characterization of the product

Fourier transform infrared spectroscopy (FT-IR) was carried out on a Nicolet 380 FT-IR spectrometer. The FT-IR spectra of reagents, MDC and the ILs were recorded on a Vector 22 infrared spectroscope at frequency ranges of 400–4000 and 400–2000 cm^{-1} . The intermediate MDC and product MDI were identified by Mercury 300 nuclear magnetic resonance (^1H -NMR) at 293 K in CDCl_3 solvent. The yields of MDC and MDI were calculated based on stoichiometric MDC or MDI. The equation is as follows:

$$\begin{aligned}
 &\text{Yield of MDC or MDI} \\
 &= \frac{\text{moles of MDC or MDI formed}}{\text{stoichiometric MDC or MDI}} \times 100\%
 \end{aligned}$$

After the reaction of diaminodiphenylmethane and DMC was complete, the reaction system was cooled to room temperature. The intermediate MDC, which was precipitated from the solvent of DMC, was weighed using an electronic balance. Based on the theoretical yield of methoxycarbonylation between diaminodiphenylmethane and DMC as well as the above-mentioned results, the yield of MDC was calculated. The yield of MDI was calculated based on the same method. The pressure was fixed at 0.5 kPa during the whole decomposition process. As the temperature was increased rapidly from room temperature to 190 °C, the product MDI started forming and flowed into the receiving flask rapidly. After complete decomposition, the product MDI was obtained in the receiving flask, and it was washed with methanol and weighed using an electronic balance. Finally, the yield of MDC was calculated according to the theoretical yield of the decomposition of MDC and the amount of MDI that was formed.

mentioned in Fig. 1, $\text{Zn}(\text{OAc})_2$ exhibited excellent catalytic activity during 4,4'-MDC synthesis. In comparison with ZnO and zinc, phenylacetate and $\text{Zn}(\text{OAc})_2$ produced 4,4'-MDC in 88% yield at 145 °C. The catalytic activity of $\text{Zn}(\text{OAc})_2$ for methoxycarbonylation of diaminodiphenylmethane with DMC was investigated by Baba;⁵⁹ $\text{Zn}(\text{OAc})_2$ was dissolved in DMC to achieve a homogenous reaction system. The transformation of $\text{Zn}(\text{OAc})_2$ catalyst in methoxycarbonylation was supported by the formation of methyl acetate, which was presumably produced by the reaction of acetate anions coordinated to Zn^{2+} with DMC (or methanol formed by the decomposition of DMC). The effect of various temperatures on the reaction of methoxycarbonylation for diaminodiphenylmethane was also studied (Fig. 1). Fig. 1 shows that the conversion of diaminodiphenylmethane increased with the increase in temperature from 150 to 180 °C, whereas the yield of MDC increased below 160 °C and then decreased dramatically with further increase

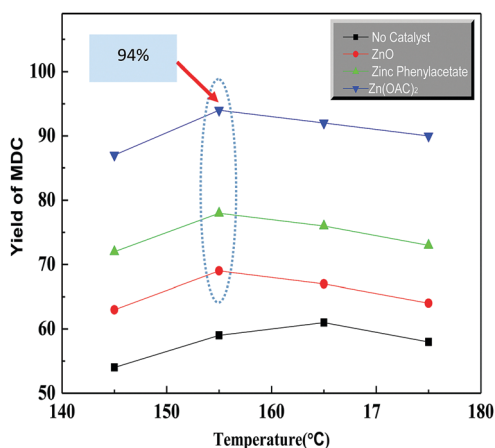


Fig. 1 Influence of temperature and catalyst on the reaction for MDC synthesis.

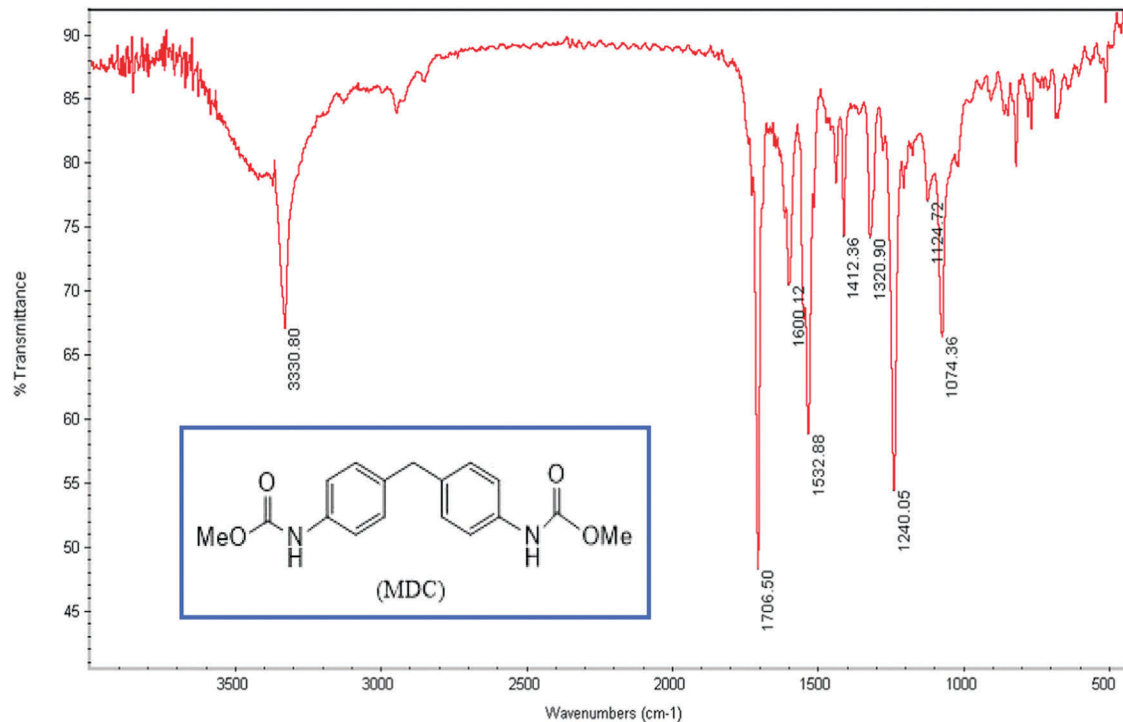


Fig. 2 IR spectrum of MDC, which was synthesized at 155 °C with $\text{Zn}(\text{OAc})_2$ catalyst.

in the temperature. For MDC, the maximum yield was 94% at 155 °C. This observation corroborated the findings of Guan, who mentioned that higher temperature did not facilitate the production of MDC.²² The decrease in the yield of MDC above 160 °C was due to the effect of higher temperature, which favored the production of a trimer or tetramer of MDC.

A freshly prepared MDC sample was analyzed by FT-IR and $^1\text{H-NMR}$, and the results are shown in Fig. 2 and 3, respectively. The spectral data agreed with the values of the standard, indicating that the intermediate was MDC. In the IR spectrum, the peaks centered at 3330 cm^{-1} and 2950 cm^{-1} were assigned to the stretching vibrations of N-H and C-H bonds, respectively. The peaks centered at 1710, 1240 and 1070 cm^{-1} were assigned to the stretching vibration of C=O bond in the ester group. The peaks at around 1600, 1540, 1450 and <1000 cm^{-1} corresponded to the benzene ring. The $^1\text{H-NMR}$ spectrum of MDC was consistent with a strong singlet peak centered at around 3.78 ppm, corresponding to 3H in OCH_3 group. Fig. 3 also shows that nine moderate peaks were observed around 7.07–7.40 ppm in the spectrum, which corresponded to 5H in the benzene ring. The moderate broad singlet peak at around 6.66 ppm corresponded to 1H in NH group. The peaks at around 3.89 ppm and 3.79 ppm were assigned to Hs in $-\text{CH}_2$ and $-\text{OCH}_3$, respectively. Based on the above-mentioned analysis, it was concluded that pure MDC was formed with molecular formula of $\text{C}_{17}\text{H}_{18}\text{O}_4\text{N}_2$. Therefore, this result can be used as an indicator for the completion of methoxycarbonylation.

Synthesis of ionic liquids used for decomposition of MDC

To study the effect on the decomposition of MDC, the thermodynamic activities of different imidazole-functionalized ionic

liquids were systemically investigated by TGA. As shown in Fig. 4, the TGA curve of $[\text{C}_4\text{mim}]\text{BF}_4$ declined from 368 °C (this value was obtained from TGA as identified by T_{decomp} ; T_{decomp} was calculated using a thermal analysis software, which provided the translation of the intercept of two linear functions: the baseline of zero weight loss and tangent of weight vs. temperature upon decomposition), indicating that these ILs were suitable for MDC decomposition. These results agreed with the results provided by Erdmenger, who proved that conventional ionic liquids such as $[\text{C}_4\text{mim}]\text{BF}_4$ start decomposing at a temperature of about 380 °C.^{60–62} However, it should be noted that the actual degradation starts before at a lower temperature than T_{decomp} .⁶³ Valkenburg demonstrated that $[\text{C}_2\text{mim}]\text{BF}_4$ has a T_{decomp} value of 455 °C, but at least 1.37 wt% is decomposed at 200 °C.⁴⁶ Hence, the maximum operating temperature was set considerably lower than T_{decomp} . It can also be seen in Fig. 4 that the T_{decomp} value of $[\text{C}_8\text{mim}]\text{BF}_4$ was 322 °C, which was slightly lower than the value for $[\text{C}_4\text{mim}]\text{BF}_4$. It is known that the length of the alkyl chain of the cation affects the thermal stability of ionic liquids. Kosmulski⁶⁴ demonstrated that the thermal stabilities of ionic liquids decrease with the increase in the length of alkyl chain, especially for imidazolium ionic liquids with basic $[\text{Cl}]$ and coordinating $[\text{BF}_4]$ and $[\text{PF}_6]$ anions. Thus, $[\text{C}_8\text{mim}]\text{BF}_4$ was found to have lower thermal stability than $[\text{C}_4\text{mim}]\text{BF}_4$.^{60,65} In comparison with the decomposition temperature of $[\text{C}_n\text{mim}]\text{BF}_4$, it was worth noting that the decomposition temperature of 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate occurred at 425 °C, which was higher than the decomposition temperature of $[\text{C}_n\text{mim}]\text{BF}_4$. Due to over-estimation and limitations posed by the non-isothermal TGA

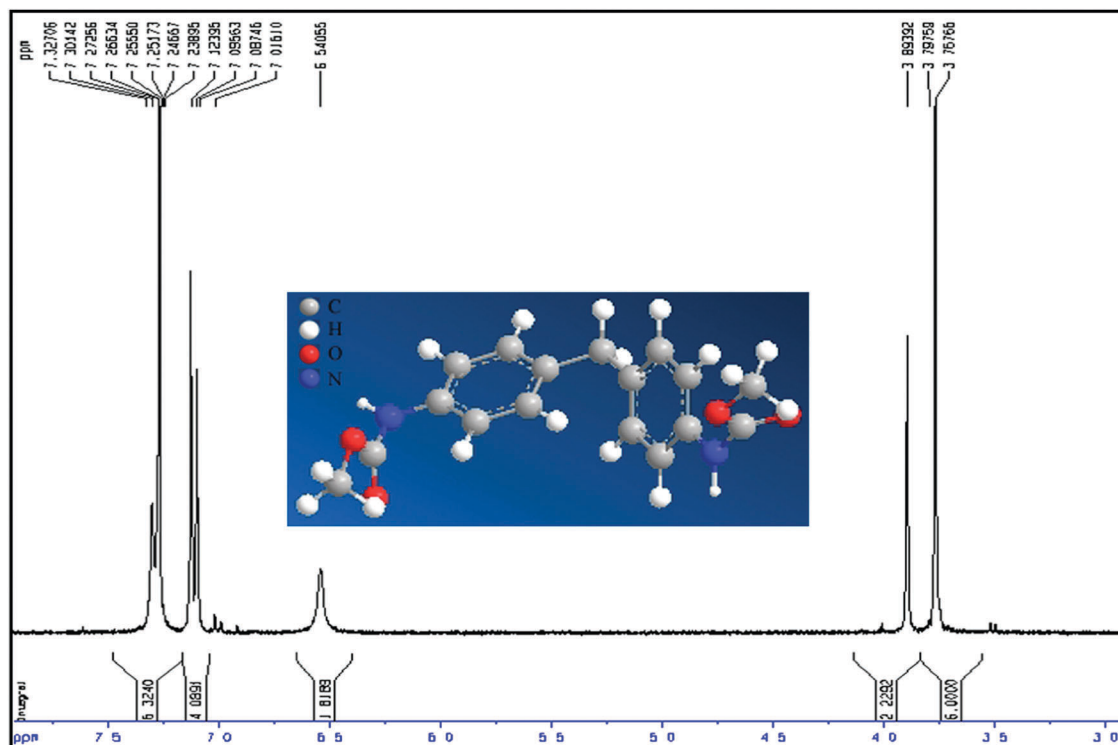


Fig. 3 $^1\text{H-NMR}$ of MDC, which was synthesized at $155\text{ }^\circ\text{C}$ with $\text{Zn}(\text{OAc})_2$ catalyst.

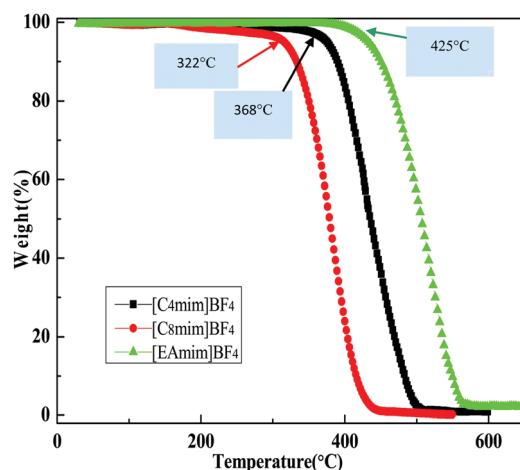


Fig. 4 TGA curves of various ionic liquids between $30\text{ }^\circ\text{C}$ and $650\text{ }^\circ\text{C}$.

method, it was necessary to perform long-term isothermal (static) TGA measurements for a prolonged period of time; moreover, compared with normal TGA, it could provide more information on stability at higher temperatures. Isothermal analyses showed that in 120 min, just 1% was lost at $230\text{ }^\circ\text{C}$ (Fig. S1, ESI†). As the temperature was raised to $430\text{ }^\circ\text{C}$, the weight loss of 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate was only 4.8% after heating for the same time. This suggested that 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate, which showed excellent thermostability at higher temperatures, can be used as the solvent in the applications of MDC decomposition.

Based on the above-mentioned analysis, 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate ($[\text{EAmim}]\text{BF}_4$) was selected and applied for the decomposition of MDC for synthesizing MDI.

Fig. 5 shows the FT-IR spectra of 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate ($[\text{EAmim}]\text{BF}_4$) in the range of $4000\text{--}400\text{ cm}^{-1}$. The bands at 1440 cm^{-1} and 1580 cm^{-1} were assigned to hydrogen-bonded imidazole. The characteristic peaks centered at 3127 and 3166 cm^{-1} were assigned to the stretching vibration of C-H bond of sp^2 -hybridized carbon. The band at 1751 cm^{-1} was due to the presence of carbonyl group. The peaks centered at 1440 and 1377 cm^{-1} were assigned to C-H bending in CH_3 group. The characteristic peak of BF_4 appeared at 1054 cm^{-1} . To determine the structure of 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate accurately, $[\text{EAmim}]\text{BF}_4$ was analysed using $^1\text{H-NMR}$, and the results are presented in Fig. 6. $^1\text{H-NMR}$ analysis was performed after drying the sample under high vacuum for a long time. The $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) data of $\delta = 9.03$ (s, 1H), 7.69 (t, 2H), 5.21 (s, 2H), 4.21 (m, 2H), 3.96 (s, 3H), 2.49 (t, 1H) and 1.23 (m, 3H) corresponded to the hydrogen atoms marked as 1, 2, 3, 4, 5, 6 and 7 in Scheme 1, which inserts in Fig. 6.

Decomposition of MDC

Chen found that by utilizing ultrafine ZnO as a catalyst, the yield of MDI can be increased to 52% at $260\text{ }^\circ\text{C}$.²¹ Wang *et al.* reported a method that gave high yield of MDI at $300\text{ }^\circ\text{C}$ without adding any solvent.⁶⁶ It was clear that the solvent method can reduce side reactions such as polymerization to

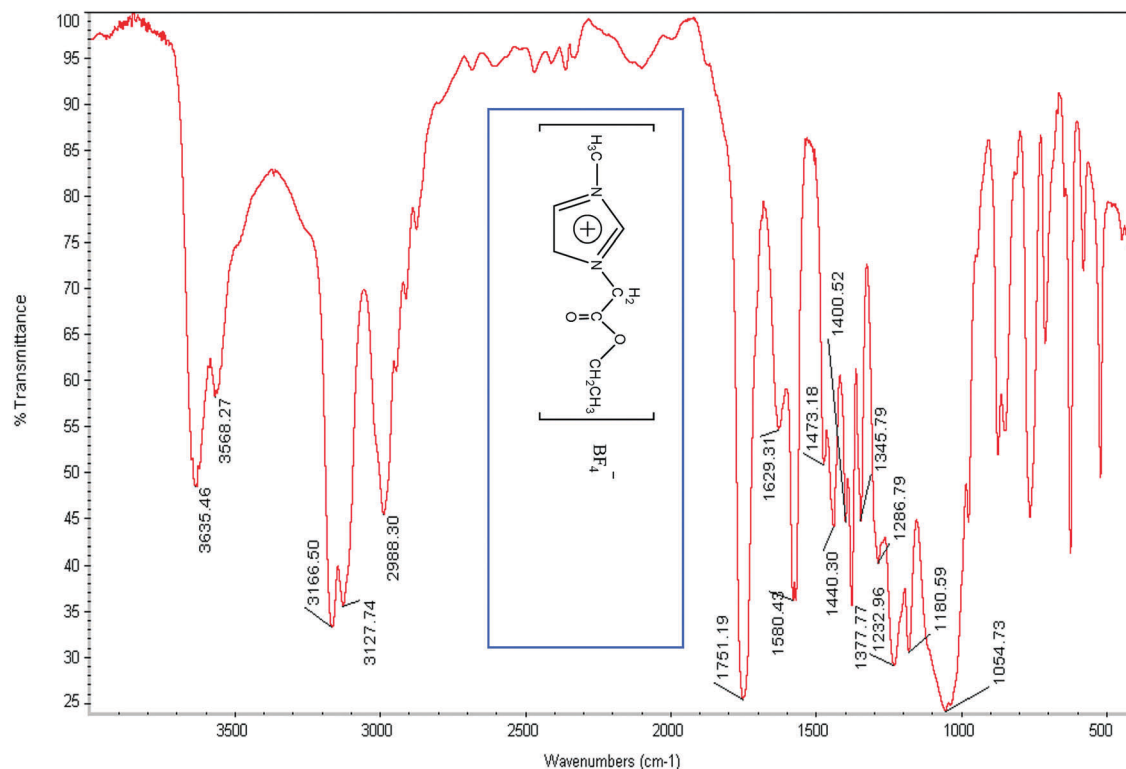


Fig. 5 FT-IR spectra of 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate in the range of 4000–400 cm^{-1} .

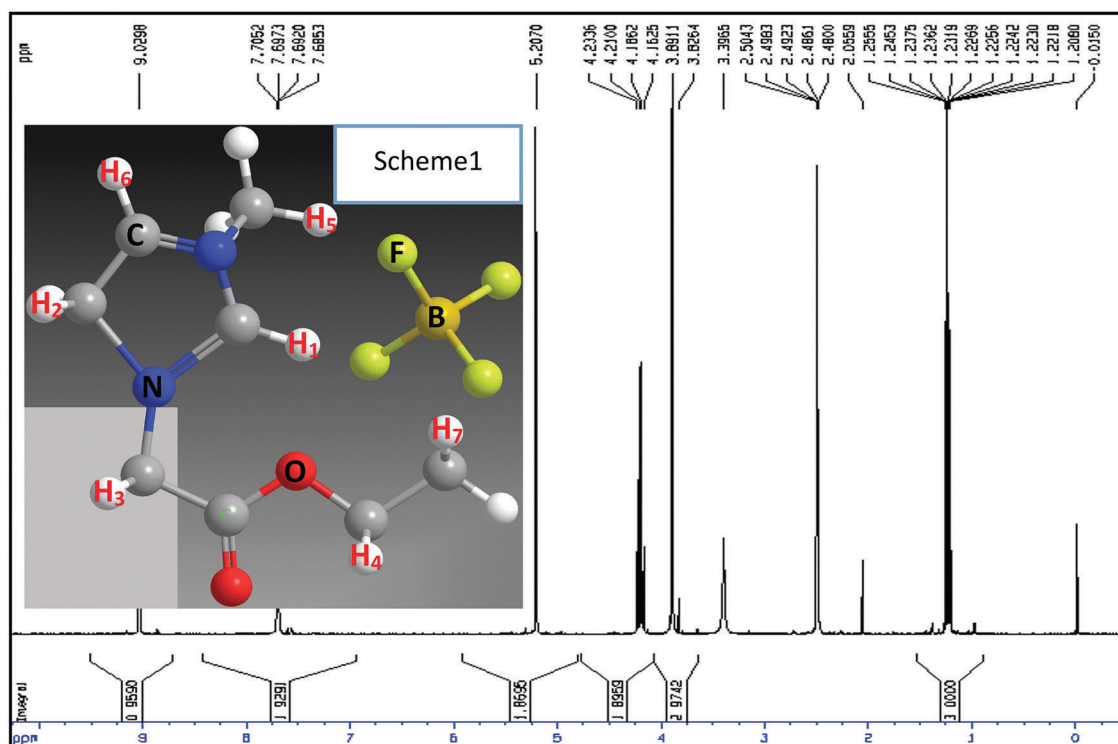


Fig. 6 ^1H -NMR spectra of 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate.

give high yield. In addition, it was reported by Chen *et al.*^{21,67} due to its thermosensitivity. Based on the analysis, the optimum temperature was favorable for polymerization of MDI that high temperature was favorable for polymerization of MDI optimum temperature for decomposition was found to be 230 $^{\circ}\text{C}$.

Table 1 Influence of different catalysts on decomposition of MDC at 230 °C in liquid paraffin and [EAmim]BF₄ solvents

Temperature (°C)	Cat	Solvent	Yield of MDI (%)
230	—	Liquid paraffin	37
230	Zn(OAc) ₂	Liquid paraffin	88
230	Zinc phenylacetate	Liquid paraffin	58
230	ZnO	Liquid paraffin	43
230	—	[EAmim]BF ₄	37
230	Zinc phenylacetate	[EAmim]BF ₄	69
230	ZnO	[EAmim]BF ₄	52
230	Zn(OAc) ₂	[EAmim]BF ₄	96

To obtain high yield of MDI, various zinc-related catalysts were tested. The activities of various catalysts for the decomposition of MDC are shown in Table 1. As shown in Table 1, liquid paraffin and [EAmim]BF₄ without the addition of any catalyst exhibited very low activity for MDI synthesis, and the yield obtained was only 37%. It is believed that the behavior of [EAmim]BF₄ is similar to that of a normal solvent, and it was only used as the thermal medium in the decomposition. After loading the zinc species as catalysts at 230 °C for 15 min, the catalytic activity increased sharply, and the yield of MDI enhanced several fold. Among these above-mentioned catalysts, Zn(OAc)₂ produced better MDI yield than other zinc catalysts. The yields of MDI reached the highest values of 88% and 96% in the presence of Zn(OAc)₂ in the solvents liquid paraffin and [EAmim]BF₄, respectively.

MDI prepared by this process was characterized by both FT-IR and ¹H-NMR spectroscopies. In the FT-IR spectra of MDI (Fig. 7), the absence of absorption bands at about 2290–2250 cm⁻¹ (identified by NCO groups) confirmed the existence of MDI. It was also observed that narrow bands that appeared at 3290–3320 cm⁻¹ were due to the presence of N–H stretching vibration. It appeared that MDI was

hydrolyzed during the process of analysis. Moreover, the absorption peaks that appeared at 1721–1725 cm⁻¹, 1640–1646 cm⁻¹ and 1533–1545 cm⁻¹ corresponded to C=O bending, C=N stretching, and C–H bending in Ar–H, indicating the formation of MDI.

To establish the structure and purity of the product conclusively, ¹H-NMR spectra (Fig. 8) were obtained, which confirmed the structure of MDI. As expected, –CH₂ protons appeared at 3.91 ppm, and the peaks that appeared between 7.11 and 6.99 ppm corresponded to the C–H protons of the benzene ring, which was consistent with MDI structures. It is known that the solvent peak from CDCl₃ appears at 7.26 ppm, and the low-intensity peak around at 3.76 ppm is associated with the residual methanol. Based on IR and ¹H-NMR analyses, the final product was identified as MDI, which was the result of the decomposition of MDC.

Catalytic activity and mechanism of Zn(OAc)₂–[EAmim]BF₄

Based on the above-mentioned analysis, it was apparent that there were differences in the yields of MDI when Zn(OAc)₂ was added to liquid paraffin or [EAmim]BF₄ separately. Zn(OAc)₂ with water-soluble ionic liquids such as [EAmim]BF₄ showed excellent catalytic activity. It was concluded that the integration of Zn(OAc)₂ and [EAmim]BF₄ occurred during the decomposition, which facilitated the formation of MDI. To study the catalytic performance of Zn(OAc)₂–[EAmim]BF₄ more systematically, efficacy tests of the reaction regarding temperature and amount of the catalyst were conducted, and the results are listed in Tables 2 and 3. Table 2 shows the effect of reaction temperature on the catalytic performance of Zn(OAc)₂–[EAmim]BF₄. It was clear that the yield of MDI decreased with the decrease in reaction temperature from 230 to 190 °C. When the temperature was maintained at

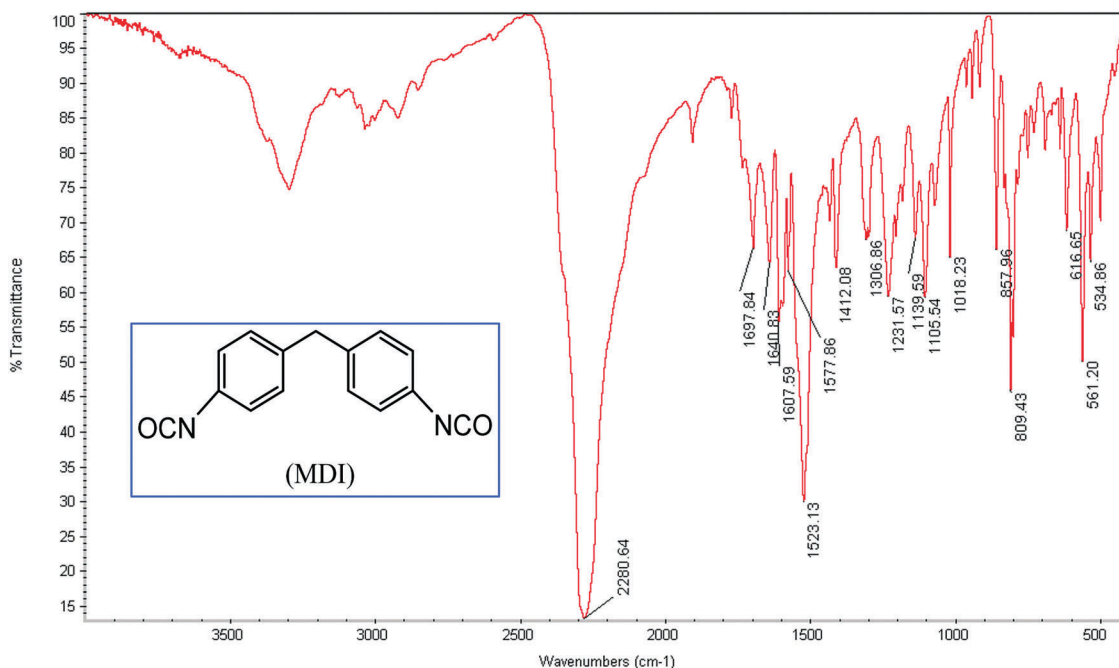


Fig. 7 IR spectrum of MDI that was synthesized at 230 °C with Zn(OAc)₂–[EAmim]BF₄ catalyst.

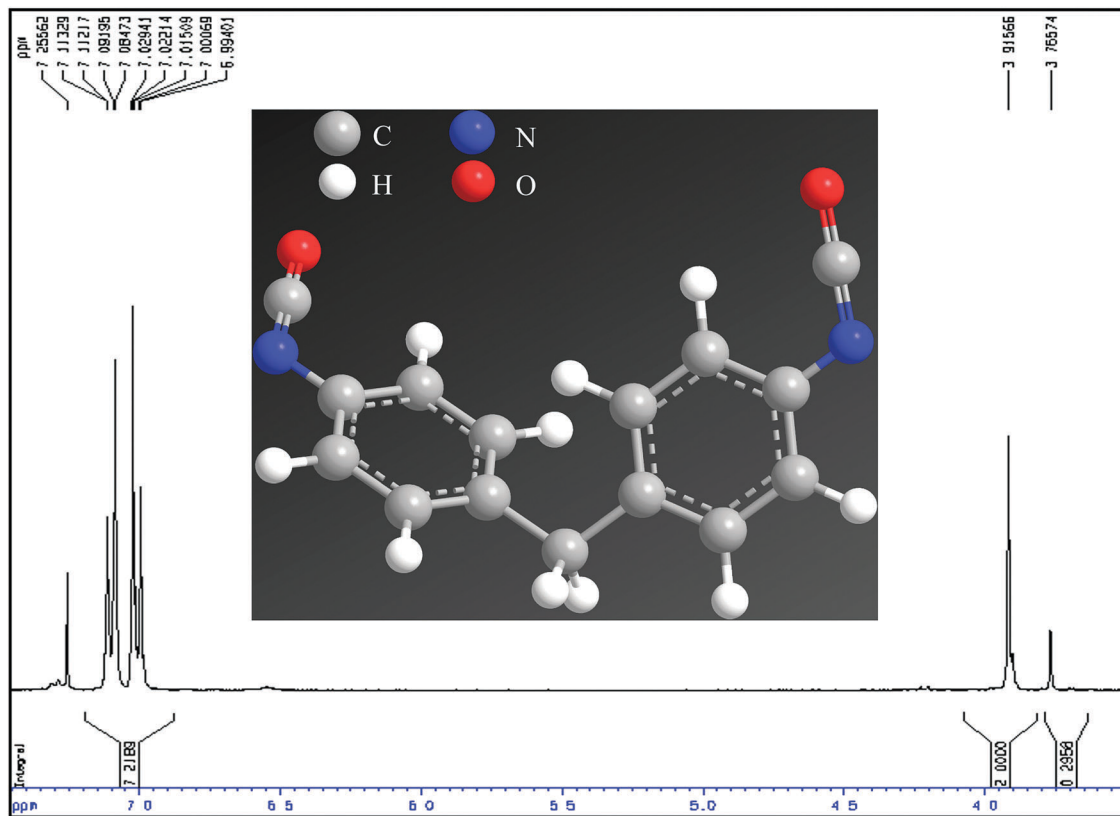


Fig. 8 $^1\text{H-NMR}$ of MDI, which was synthesized at $230\text{ }^\circ\text{C}$ with $\text{Zn}(\text{OAc})_2\text{-[EAmim]BF}_4$ catalyst.

Table 2 The effect of reaction temperature on the catalytic performance of $\text{Zn}(\text{OAc})_2\text{-[EAmim]BF}_4$ utilized in the decomposition of MDC in $[\text{EAmim]BF}_4$

Temperature ($^\circ\text{C}$)	Cat	Solvent	Yield of MDI (%)
190	—	$[\text{EAmim]BF}_4$	—
190	$\text{Zn}(\text{OAc})_2$	$[\text{EAmim]BF}_4$	43
210	$\text{Zn}(\text{OAc})_2$	$[\text{EAmim]BF}_4$	74
230	$\text{Zn}(\text{OAc})_2$	$[\text{EAmim]BF}_4$	96

Table 3 The effect of catalyst amount on the catalytic performance of $\text{Zn}(\text{OAc})_2\text{-[EAmim]BF}_4$ utilized in the decomposition of MDC at $230\text{ }^\circ\text{C}$ in solvent of $[\text{EAmim]BF}_4$

Temperature ($^\circ\text{C}$)	Cat amount (%)	Solvent	Yield of MDI (%)
230	—	$[\text{EAmim]BF}_4$	37
230	1	$[\text{EAmim]BF}_4$	78
230	5	$[\text{EAmim]BF}_4$	96
230	10	$[\text{EAmim]BF}_4$	82

$210\text{ }^\circ\text{C}$, the yield of MDI reduced by 22%. As the temperature further declined from 210 to $190\text{ }^\circ\text{C}$, the yield was merely 43%. It is well-known that temperature plays a significant role in the decomposition reaction.²² It was concluded that the activity of $\text{Zn}(\text{OAc})_2\text{-[EAmim]BF}_4$ decreased dramatically with further decrease in the temperature. It was observed that without the addition of the catalyst to the reaction system, the product MDI could not be formed at $190\text{ }^\circ\text{C}$. It was apparent that thermal energy alone was not

sufficient for the reaction to cross the barrier of activation energy. Thus, the maximum yield of 4,4'-MDI was found to be 96% at a temperature of $230\text{ }^\circ\text{C}$. The effect of the amount of the catalyst on the synthesis of MDI was also studied (Table 3). It is shown in Table 3 that the yield of MDI increased with the increase in weight percentage of $\text{Zn}(\text{OAc})_2\text{-[EAmim]BF}_4$, and a maximum yield of 96% was achieved by employing 5 wt% ($\text{Zn}(\text{OAc})_2\text{-[EAmim]BF}_4/[\text{EAmim]BF}_4$). Further increase in the amount of the catalyst eventually decreased the yield of MDI to 82%. Based on this observation, it was concluded that the optimum catalyst amount for the decomposition of MDC was 5 wt%.

The catalytic mechanism of $\text{Zn}(\text{OAc})_2\text{-[EAmim]BF}_4$ was investigated for the decomposition of MDC, and the result is shown in Fig. 9. Schreiner⁶⁸ investigated the effect of ionic liquids on the Diels-Alder reaction between cyclopentadiene and methacrylate, and it was found that a hydrogen bond can be formed between the carbonyl oxygen of methacrylate and C-H-C on the imidazolium ring of the ionic liquids, which is a crucial factor for facilitating the reaction. The strongest hydrogen bond is observed in ionic liquids that have the strongest hydrogen-donating cations coupled with the weakest hydrogen-accepting anions.⁶⁹ Ionic liquids with $[\text{mim}]$ cations can form strong hydrogen bonds. In addition, the BF_4^- anions are weaker than hydrogen-bond acceptors.²⁴ Thus, the hydrogen bond between C-H-C on an imidazolium ring of ILs and the carbonyl oxygen atom of zinc acetate is strong. Thus, strong hydrogen bonding between ILs and zinc acetate was formed,

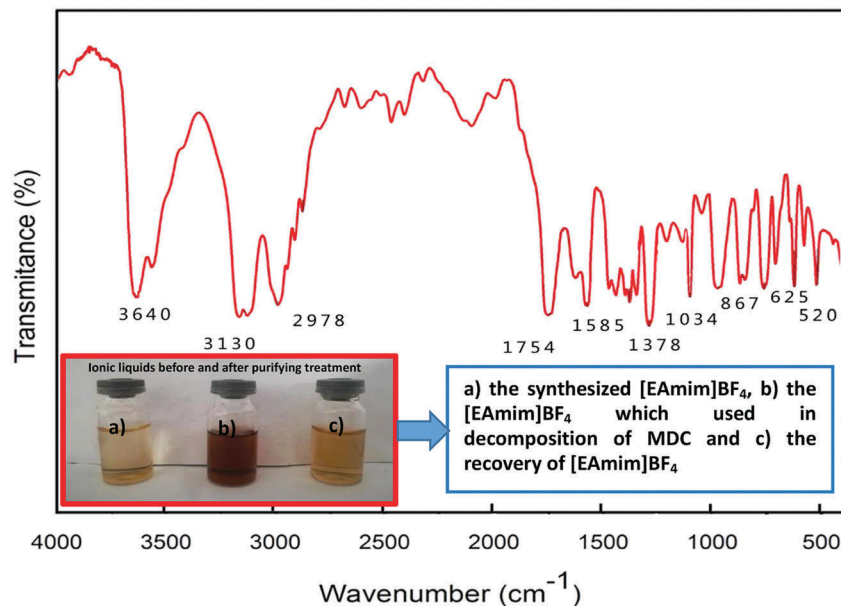


Fig. 11 IR spectra of the recovered [EAmim]BF₄; the inset is the picture of [EAmim]BF₄ before and after purification.

Recycling of the catalyst and ILs

It is a fact that ionic liquids as solvents darken quickly when heated to high temperatures, which can be regenerated with additional purification processes. After complete decomposition of the reagent MDC, a large amount of methanol was produced as a byproduct, and it was removed under reduced pressure to afford the product MDI in excellent yield. It was demonstrated by Zhang⁷² that extractive distillation is an efficient method for the separation of methanol, dimethyl carbonate and imidazole-functionalized ionic liquids from the reaction mixture. To isolate the catalyst and residual methanol in [EAmim]BF₄, the reaction system containing Zn(OAc)₂-[EAmim]BF₄ and [EAmim]BF₄ was filtered, and the filtrate was added to nontoxic dimethyl carbonate having a small amount of activated charcoal. The mixtures were distilled at 90 °C under reduced pressure and subsequently dried in a vacuum drier at 120 °C for 4 h to afford [EAmim]BF₄. [EAmim]BF₄ was transformed into a pale-yellow liquid, and it was similar to crude [EAmim]BF₄ obtained after re-purification, as shown in the inset of Fig. 11. By this process, the recovery of [EAmim]BF₄ was 86%. The recovered [EAmim]BF₄ sample was also characterized by IR, and the result from Fig. 11 shows that the structure of the recovered [EAmim]BF₄ had not changed (the corresponding characterization of the recovered ionic liquids is given in ESI[†]). To study the purity of recycled [EAmim]BF₄, ¹H-NMR analysis was conducted, and the results are presented in Fig. S2 (ESI[†]). Based on IR and ¹H-NMR analyses, the recovered ionic liquids were identified as [EAmim]BF₄ with a higher purity of 99%.

The catalytic performance of the recycled Zn(OAc)₂-[EAmim]BF₄ sample for the decomposition of MDC was also studied. Results in Table 4 indicate that the yield of MDI decreased slightly with the increase in the number of recycling processes. After five purifications, the yield of MDI was 92.4%. This result corroborated the observation of Zhao,⁷⁰ who found that Zn(OAc)₂-[bmim]PF₆ utilized

Table 4 The catalytic performance of recovered Zn(OAc)₂-[EAmim]BF₄ for the decomposition of MDC at 230 °C in [EAmim]BF₄ solvent

Temperature (°C)	Recovery times	Solvent	Yield of MDI (%)
230	1	[EAmim]BF ₄	96
230	2	[EAmim]BF ₄	94.5
230	3	[EAmim]BF ₄	93
230	4	[EAmim]BF ₄	92.6
230	5	[EAmim]BF ₄	92.4

in the synthesis of MPC could be recycled up to 5 times and even then, the catalytic performance was excellent. Based on the analysis shown in Table 4, no significant loss in the catalytic activity of Zn(OAc)₂-[EAmim]BF₄ was observed during the decomposition process. Therefore, it was considered that the recovered Zn(OAc)₂-[EAmim]BF₄ can be recycled at least thrice.

Conclusions

Conventional methods for synthesizing MDI involve the application of unsuitable organic solvents. Thus, 4,4'-methylenediphenyl diisocyanate (MDI) was synthesized by the reaction of 4,4'-diaminodiphenylmethane and non-toxic dimethyl carbonate (DMC) and subsequently, the decomposition of MDC was completed in ionic liquids. It was found that at a fixed temperature of 230 °C, the highest yield of 96% of MDI was obtained in the presence of Zn(OAc)₂ as a catalyst and 1-ethoxycarbonylmethyl-3-methylimidazolium tetrafluoroborate as a solvent. Compared with other catalysts, Zn(OAc)₂-[EAmim]BF₄ showed excellent catalytic performance for the decomposition of MDC, and its catalytic mechanism was investigated systemically. After complete decomposition, a maximum recovery of 86% was achieved for [EAmim]BF₄ through re-purification. The catalyst Zn(OAc)₂-[EAmim]BF₄ retained

its activity even after recycling five times, and the yield of MDI achieved was 92.4%. Thus, a greener method has been developed, which can be useful for large-scale production of MDI.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The present work was supported financially by the Natural Science Foundation of Hebei Province (Grant E2018502054). This work was also supported financially by the Fundamental Research Funds for the Central Universities (Grant 2017MS141), the National Nature Science Foundation of China (Grant 21506043), and the National Major Science and Technology Program for Water Pollution Control and Treatment (Grant 2017ZX07101-001-007).

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