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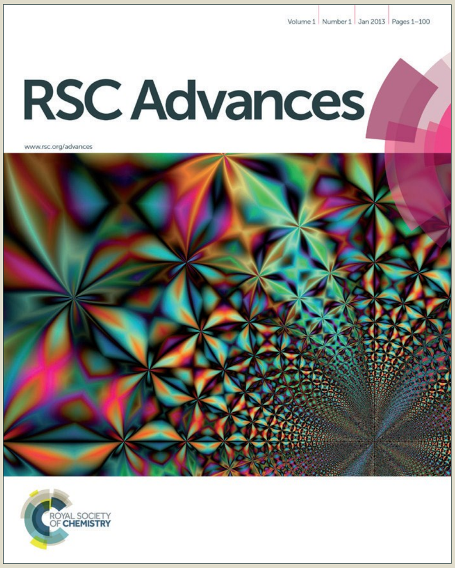

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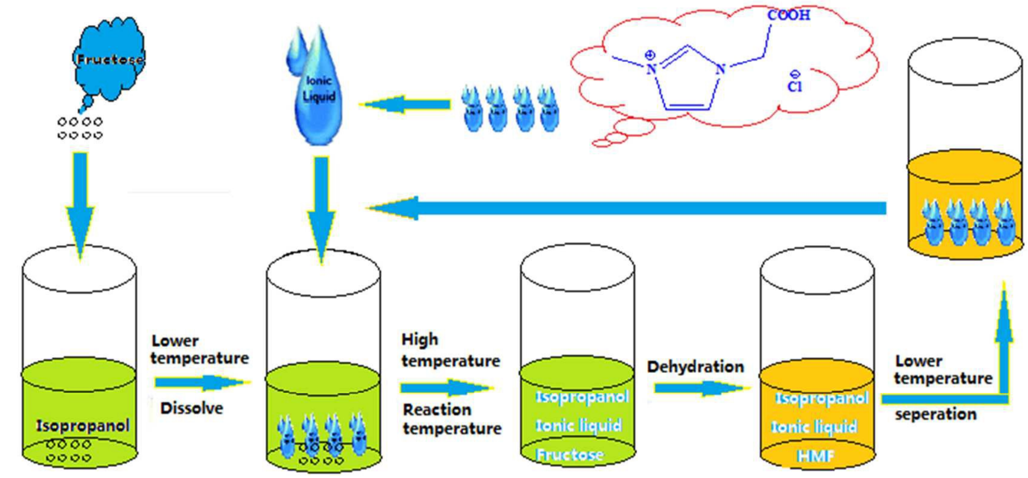

Highlights

A thermo-regulated recyclable ionic liquid catalyst bearing acidic functional group for fructose dehydration to produce HMF in 91.2% yield.

Production of 5-Hydroxymethylfurfural from Fructose by a Thermo-regulated and Recyclable Brønsted Acidic Ionic Liquid Catalyst

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Abstract

In this work, a thermo-regulated recyclable catalytic system using ionic liquid, [HO_2CMMIm]Cl as the catalyst and isopropanol as the solvent has been demonstrated to be effective for the dehydration of fructose to synthesize 5-hydroxymethylfurfural(HMF). The solubility of [HO_2CMMIm]Cl ionic liquid in isopropanol is temperature-dependent, being miscible with isopropanol at temperature range suitable for fructose dehydration (*e.g.*, above 80 ℃) while not soluble at lower temperature such as room temperature. Temperature-responsive solubilization/precipitation of [HO_2CMMIm]Cl in isopropanol renders the acidic ionic liquid an appealing thermo-regulated phase-switchable catalyst. Furthermore, the effects of various parameters including catalyst loading, fructose concentration, reaction time and temperature on the catalytic performance of fructose dehydration have been studied systematically. Under optimized reaction conditions, up to 91.2 mol% HMF yield could be obtained. Additionally, when the ionic liquid catalyst precipitated out after the reaction, the solvent can be simply decanted and [HO_2CMMIm]Cl could be directly reused for the next run with freshly added solvent and substrate. It was found that [HO_2CMMIm]Cl could be reused at least five times without considerable lose of activity. Furthermore, a kinetic analysis was carried out, indicating the activation energy for the reaction to be 62.1 kJ mol^{-1}. This catalytic system can be envisioned to find applications in a wide range of acid-catalyzed reactions with facile, thermo-regulated catalyst recovery features.

Keywords: Ionic liquid, Fructose, 5-Hydroxymethylfurfural, Dehydration, Thermo-regulated

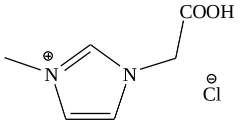
1. Introduction

Continuing and accelerating depletion of fossil-derived carbon resources has increasingly represented a challenge that has to be dealt with urgently to meet the goal of achieving a sustainable development of the society. In this regard, carbohydrates provide an attractive alternative to fossil resource, since they account for almost 75% of biomass feedstock in nature. Consequently, recent years have witnessed an extensive research effort aiming to develop technologies that have the potential to be implemented in order to convert carbohydrates to useful chemical intermediates economically and practically. One such carbohydrate-based model molecule is 5-hydroxymethyl furfural (HMF), which has been proposed by US Department of Energy to be one of the top 12 platform chemicals. When produced economically, HMF can be envisioned to serve as a building block molecule, having the potential to be derivatized to synthesize furanic-based polyamides, polyesters, and polyurethanes analogous to petroleum-based terephthalic acid[1-6].

HMF can be synthesized from C6 carbohydrates (glucose and fructose) via a triple dehydration reaction, generally catalyzed by acids[7]. Extensive research efforts have studied the production of HMF using fructose as feedstock, with excellent HMF yields being reported[8-10]. A variety of solvent have been exploited to carry out this dehydration reaction, namely water[11], organic solvents (*e.g.*, DMSO)[12-14], organic/aqueous binary mixtures[11, 15, 16], ionic liquids[17-26]. A multitude of catalyst systems have been developed for this reaction[10, 27-32] ,such as homogeneous mineral acids including H_2SO_4, HCl, H_3PO_4, and oxalic acid[4, 5, 33, 34], or heterogeneous solid acids H-formzeolites[35-37], strong acid cation exchange resins[21, 38, 39], and most recently, acidic ionic liquids[12, 13, 24, 27, 40-43]. Because of its unique and tunable properties, strategies utilizing ionic liquids (ILs) as solvent or using acidic ionic liquids as catalysts for sugar dehydration to produce HMF have grown rapidly. For example, Bao et al reported that both the Lewis acidic and Brønsted acidic ionic liquids could effectively catalyze the dehydration of fructose under microwave irradiation., obtaining good HMF yields.[40] In addition, systems consisting of IL, 1-H-3-methyl imidazolium chloride and choline chloride/citric acid as catalysts, could lead to good HMF yields.[24, 27] Tong et al. reported that a 72.3% HMF yield (87.2% selectivity) using fructose as feedstock can be obtained for 2 h at 90 ^oC in the presence of Brønsted-Acidic ionic liquid $[NMP]^+[CH_3SO_3]^-$ catalyst in DMSO[12], later the same group reported a 74.8% HMF yield achieved over protic ionic liquid catalyst $[NMM]^+[CH_3SO_3]^-$ using an N,N-dimethylformamide-lithium bromide (DMF-LiBr) mixed solvent system[13]. Liu et al. reported that a 95.7% HMF yield could be obtained with fructose as the feedstock, using [CMIm]Cl as the catalyst in DMSO[42]. Although good results using ionic liquid for fructose dehydration have been obtained, development of efficient catalytic systems with superior catalytic performance and recyclability is still high desirable.

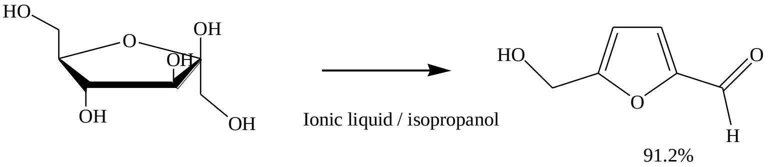
1-carboxymethyl-3-methylimidazolium chloride, $[HO_2CMMIm]Cl$ (Scheme 1) is an acidic ionic liquid with a carboxylic acid group tethered to the core of the imidazolium ring, which could be envisioned to be effective in converting fructose to HMF. In general, $[HO_2CMMIm]Cl$ is in the solid form with a melting temperature of 190^{o}C. In order to test the catalytic activity of $[HO_2CMMIm]Cl$ for fructose dehydration, screening experiments of $[HO_2CMMIm]Cl$ in various commonly used organic solvent for fructose dehydration were first carried out. Interestingly, to our surprise, it was found that $[HO_2CMMIm]Cl$ had a temperature-dependent solubility in isopropanol. It is completely insoluble in isopropanol at the room temperature, whereas it is miscible in isopropanol when the solution is heated to temperatures higher than 80^{o}C. Cooling the solution down to room temperature resulted in the precipitation of the ionic liquid out of isopropanol and the solubilization/precipitation cycle can be performed repeatedly. Inspired by this observation, we set out to devise a thermo-regulated recyclable catalytic system consisting of

[HO_2CMMIm]Cl as acidic ionic liquid catalyst and isopropanol as solvent for HMF production from fructose. To the best of our knowledge, ionic liquid catalytic system simultaneously having both catalytic activity and facile, thermo-regulated catalyst recyclability features for carbohydrate dehydration reaction is yet to be reported.



Scheme 1 Molecular structure of [HO_2CMMIm]Cl

Herein, we report selective dehydration of fructose to HMF using a [HO2CMMIm]Cl/isopropanol system, shown in Scheme 2. In addition to its facile thermo-regulated recyclability, [HO2CMMIm]Cl also showed high activity for fructose dehydration reaction, producing HMF at a yield of 91.2% under optimized reaction conditions. It is desirable to take advantage of the convenient catalyst recyclability of the present catalytic system to avoid extra separation processing step in practice.



Scheme 2. Conversion of fructose into HMF catalyzed by [HO_2CMMIm]Cl IL in isopropanol

2. Experimental section

2.1 Materials

The ionic liquid (IL) 1-carboxymethyl-3-methylimidazolium chloride ([HO_2CMMIm]Cl) was supplied by Lanzhou Greenchem ILS, LIPC, CAS (Lanzhou, China). Fructose and isopropanol were purchased from Alfa Aesar. HMF standard sample was purchased from Aldrich sigma. All the materials were of analytic or higher grad and used as received without further purification.

2.2 Reaction testing

All the reactions were carried out in 10 ml thick-walled glass reactors (Alltech). An oil bath was used to heat the reactor rapidly to the desired reaction temperature, with temperature and stirring being controlled by an Isotemp digital stirring hot plate (Fisher Scientific). In a typical experiment, desired amounts of fructose, desired amounts of [HO_2CMMIm]Cl and 3.0 g isopropanol were added to the Alltech reactor. A triangular stir bar (Fisher Scientific) was also added to allow for adequate agitation. The reactor was then sealed with PTFE liner covered caps (Fisher Scientific) and immersed in the oil bath at desired reaction temperature and stirred at 350 rpm. At specified time, the reactors were removed from the oil bath and then cooled rapidly in an ice bath to quench the reaction. For all the reactions, significant amounts of soluble and insoluble brownish humins were formed, of which the production rate was difficult to quantify. The humin formation precluded a closed carbon balance analysis and thus the only product analyzed was HMF. Each reaction was repeated at least three times, and the average yield was reported. In the catalyst recyclability experiment, the mother liquid was decanted after the solution was cooled down and the remaining [HO_2CMMIm]Cl solid catalyst was directly used for the next run by adding fresh fructose and isopropanol.

2.3 Sample analysis

After each reaction, the liquid sample was filtered and then analyzed by an HPLC equipped with UV and refractive index detectors. HPLC analysis was performed using a Shimadzu LC-20A system equipped with a SPD-20A UV detector at 280 nm and a refractive index (RI-20A) detector maintained at 333 K. The samples were analyzed using an Aminex HPX-87H Column at 333 K with 5 mM H_2SO_4 at a flow rate of 0.6 ml min^{-1} as the mobile phase. The amount of HMF was analyzed by HPLC with a Shimadzu UV-Vis SPD-20A detector at 280.0 nm, and a InterSustain C18 column at 313 K, with a methanol: 5 mM H_2SO_4 (8:2 v/v) binary solvent as the mobile phase at a flow rate of 0.7 ml min^{-1}. The conversion/selectivity being used in this manuscript are defined as below: the conversion of fructose is defined as the moles of fructose reacted divided by the moles of initial fructose added, the selectivity of HMF is defined as the moles of HMF produced divided by the moles of fructose reacted, and the yield of HMF is defined as the fructose conversion multiplied by the HMF selectivity**.**

3. Results & discussion

3.1 Rationale

As shown in Fig. 1, a thermo-regulated catalytic system comprising of [HO_2CMMIm]Cl and isopropanol is designed for fructose dehydration reaction. At low temperature, fructose and

[HO_2CMMIm]Cl are not soluble in isopropanol. Increasing the temperature resulted in the solubilization of fructose and [HO_2CMMIm]Cl, while at the same time, the acid functionality on [HO_2CMMIm]Cl can catalyze fructose dehydration to produce HMF. When the reaction is complete, isopropanol solution was cooled down, precipitating out the [HO_2CMMIm]Cl catalyst, which can be recycled and used for the subsequent reactions. It can be speculated that because of the reversible solubilization/precipitation of [HO_2CMMIm]Cl in a thermo-regulated manner, the catalytic system can be recycled for multiple times.

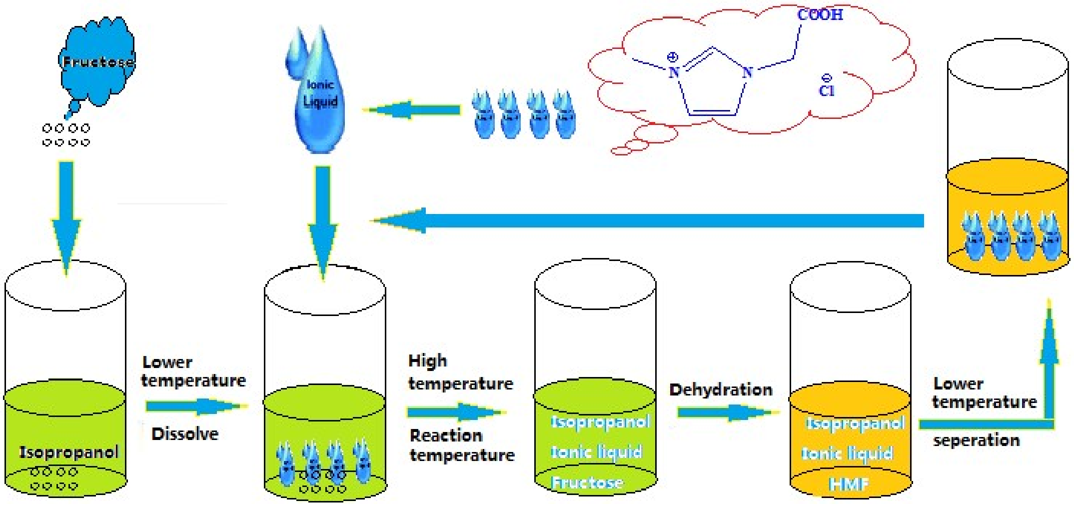


Fig. 1 Designing principle of thermo-regulated recyclable catalytic system.

3.2 Effect of reaction temperature

The effect of reaction temperature on the dehydration of fructose to HMF in isopropanol with [HO_2CMMIm]Cl as the catalyst (reaction time of 3 h) was examined, and the results are shown in Fig.2. When the temperature increased from 80 ℃ to 110 ℃, both fructose conversion and HMF yield increased gradually, reaching 100% and 90.8%, respectively at 110 ℃. HMF yield decreased to 71% when the reaction temperature was further increased to 120 ℃ although at 100% fructose conversion. It is concluded that the dehydration of fructose was accelerated by increasing the reaction temperature while an optimized temperature would be preferred since side reactions, such as polymerization and rehydration of HMF[44] can also readily take place at high temperature. Based on the results above, the reaction temperature of 110 ^{o}C was used for further reaction condition optimization of fructose dehydration.

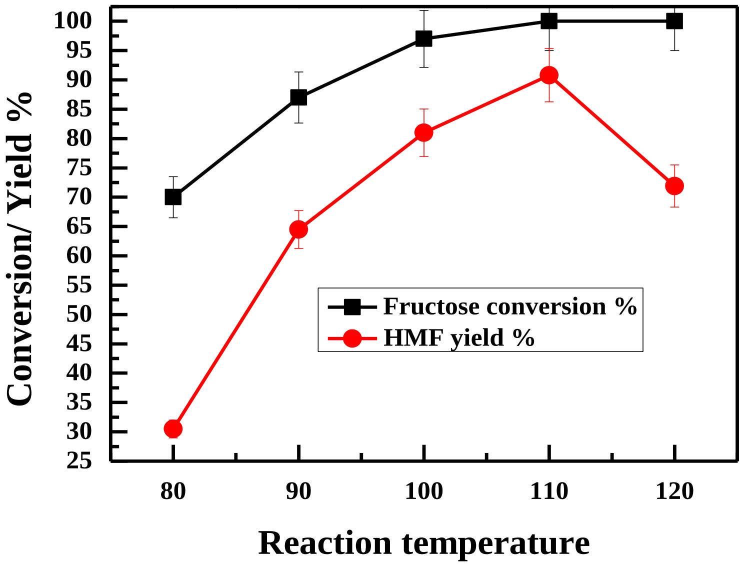


Fig. 2 Effect of reaction temperature on the catalytic conversion of fructose to HMF. Experimental conditions: 0.1 g [HO_2CMMIm]Cl, 0.1 g fructose, 3.0 g isopropanol, reaction time of 3 h.

3.3 Effect of reaction time

The influence of reaction time on the conversion of fructose and the yield of HMF was also examined, and the data are summarized in Fig. 3. It can be seen that the conversion of fructose and the HMF yield increased readily with time. At the reaction time of 3 h, fructose conversion and HMF yield were ~100% and 90.8% respectively, indicating under studied condition, full conversion of fructose can be obtained within 3 h. Prolonging the reaction time to 4h, however, resulted in a slightly decreased HMF yield of 89% at 100% fructose conversion.

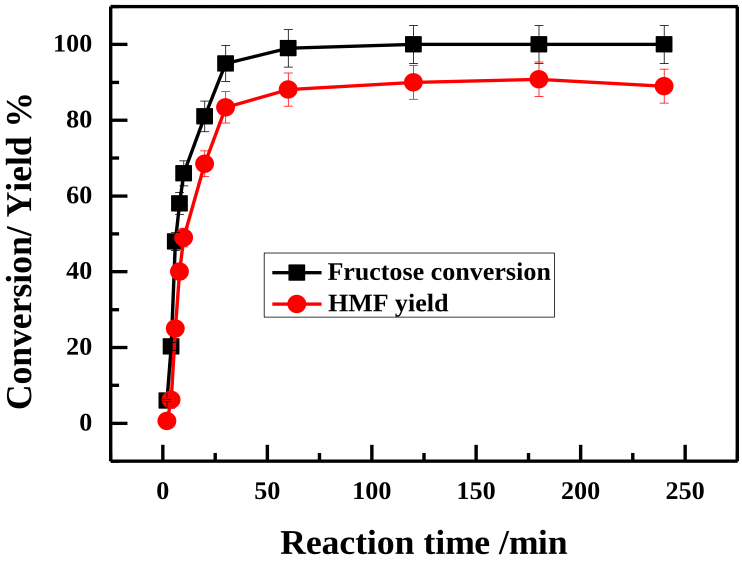


Fig.3 Effect of reaction time on fructose dehydration reaction. Experimental conditions: 0.1 g [HO_2CMMIm]Cl, 0.1 g fructose, 3.0 g isopropanol, reaction temperature of 110°C.

3.4 Effect of catalyst loading

In order to determine the optimal amount of [HO_2CMMIm]Cl catalyst, the effect of catalyst loading on fructose conversion and HMF yield was examined. Varying amount of catalyst was added to the solution containing 0.1 g fructose and the reaction was carried out under 110 ℃ with a reaction time of 30 minutes, giving the results summarized in Fig. 4. As shown in the figure, fructose conversion correlated positively with catalyst loading, meaning a higher catalyst loading can result in higher fructose conversion rate. However, as catalyst loading increased from 60 mg to 100mg, HMF yield also increased, reaching 83.4% with 0.1 g [HO_2CMMIm]Cl catalyst. An extra increase of catalyst loading, however, slightly decreased HMF yield, namely 79.2% at 120 mg, indicating that excess catalyst loading might cause the side reactions to produce humins or other compounds[45, 46]. Therefore, 0.1g [HO_2CMMIm]Cl loading (0.1 g fructose) was found to be optimal for the reaction under studied reaction configurations.

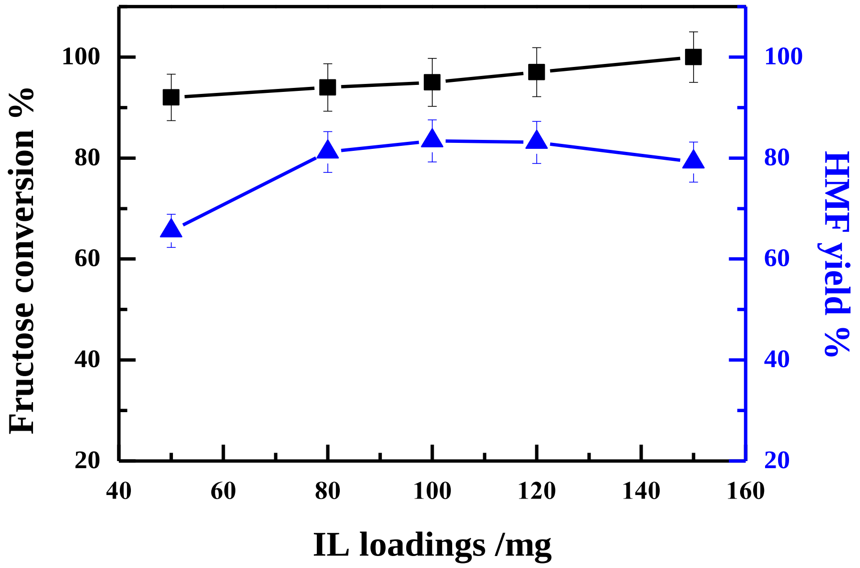


Fig.4 Effect of catalyst loading on fructose dehydration. Experimental conditions:3 g isopropanol, 0.1 g fructose, reaction temperature of 110 ℃, reaction time of 30 minutes.

3.5 Effect of substrate loading

The effect of the amount of fructose on the HMF yield was also studied with other reaction conditions being as below: the amount of [HO_2CMMIm]Cl of 0.1 g, reaction temperature of 110 ^oC and reaction time of 30 minutes. As shown in Fig. 5, HMF yield decreased from 91.2% to 74.3% with the amount of fructose increasing from 50 mg to 150 mg. This may arise from increased concentration of fructose in isopropanol, which likely favored side reactions such as polymerization and rehydration producing humins as the main by-product[45, 46].

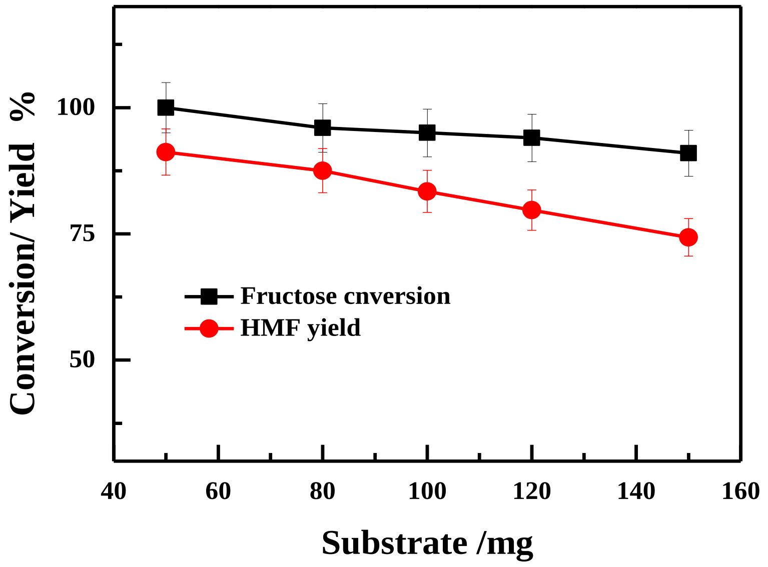


Fig.5 Effect of substrate loading on fructose dehydration. Experimental conditions:3 g isopropanol, 0.1 g [HO_2CMMIm]Cl, reaction temperature of 110 ℃, reaction time of 30 minutes.

3.6 Catalyst separation and reusability

In contrast to previously reported studies[47, 48] where the mother liquor after each reaction can be used multiple times for sugar dehydration, the current thermo-regulated catalyst recovery strategy provided the advantage of a more straightforward and easy catalyst recycling method. As depicted in Fig. 1, catalyst in this study can be separated from the reaction medium by simply cooling down the solution. Indeed, as shown in Fig.6, before the reaction, both fructose and [HO_2CMMIm]Cl catalyst were insoluble in solvent (Fig.6a), whereas fructose and [HO_2CMMIm]Cl were completely dissolved in the solution (Fig. 6b) when the solution was heated above 80 ℃. When the reaction was complete, the solution was cooled down to room temperature, thereby precipitating [HO_2CMMIm]Cl out from the solvent for subsequent reaction runs(Fig. 6c). The successful thermo-regulated catalyst separation allowed for easy catalyst recovery and reuse of [HO_2CMMIm]Cl.

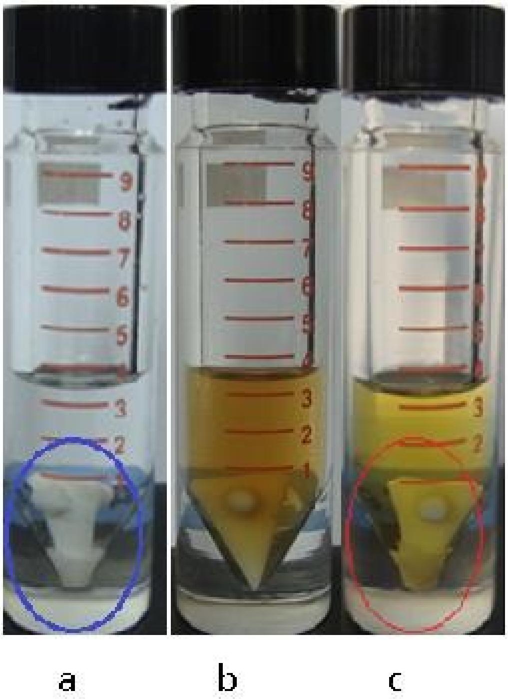


Fig. 6. Physical state of catalyst at different course of reaction: a) before the reaction; b) during the reaction; c) after the reaction

The recyclability of [HO_2CMMIm]Cl catalyst was further examined. The reactions were performed at 110 °C for 30 minutes in the presence of [HO_2CMMIm]Cl. After the reaction, the solution was cooled down and the supernatant was transferred out, leaving [HO_2CMMIm]Cl catalyst inside the reactor. The solid ionic liquid was washed briefly with isopropanol and the same amount of isopropanol and fructose were added for the next run. As shown in Fig. 7, the catalyst could be reused at least five times without considerable performance in the HMF production, revealing the efficacy of such thermo-regulated catalyst system using the combination of [HO_2CMMIm]Cl and isopropanol.

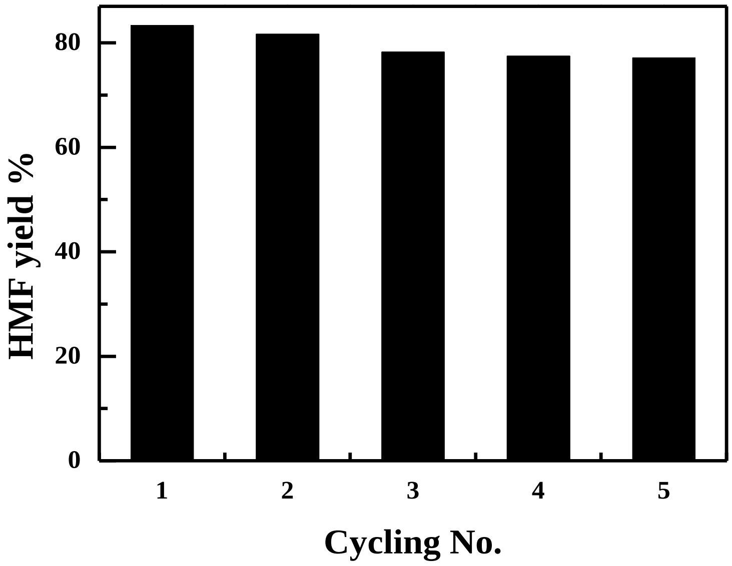


Fig. 7 Reusability of [HO_2CMMIm]Cl for fructose dehydration. Experimental conditions: 3 g isopropanol, 0.1 g [HO_2CMMIm]Cl, 0.1 g fructose, reaction temperature of 110 ℃, reaction time of 30 minutes.

3.7 Kinetics studies with fructose as feedstock

Kuster[49] and Vogel[34] reported a reaction order of 1 on substrate for the dehydration of fructose. In accordance with this result, a kinetic analysis of the dehydration of fructose in isopropanol over [HO_2CMMIm]Cl catalyst was performed according to previously described methods[13, 34, 35, 50]. Plots of lnk versus reaction time (t) were used to obtain first-order kinetic constants. As summarized in Table.1, the value of k increases with increasing temperature, indicating that higher temperature accelerated fructose dehydration reaction rate. An Arrhenius plot was obtained, as shown in Fig. 8. Based on these data, the kinetic parameters for [HO_2CMMIm]Cl catalyzed dehydration of fructose to HMF can be calculated and summarized in Table 2. An apparent activation energy of 62.1 KJ/mol was obtained for fructose dehydration.

Table.1Reaction rate constants (k) of fructose dehydration at different reaction temperatures[a]

Entry	Temperature ^oC	K (min^{-1})	Correlation coefficient
1	90	0.0202	0.9878
2	100	0.0871	0.9986
3	110	0.1480	0.9945

[a] Experimental conditions: reaction time of 3 h, 0.1 g [HO_2CMMIm]Cl , 0.1 g fructose and

3ml isopropanol.

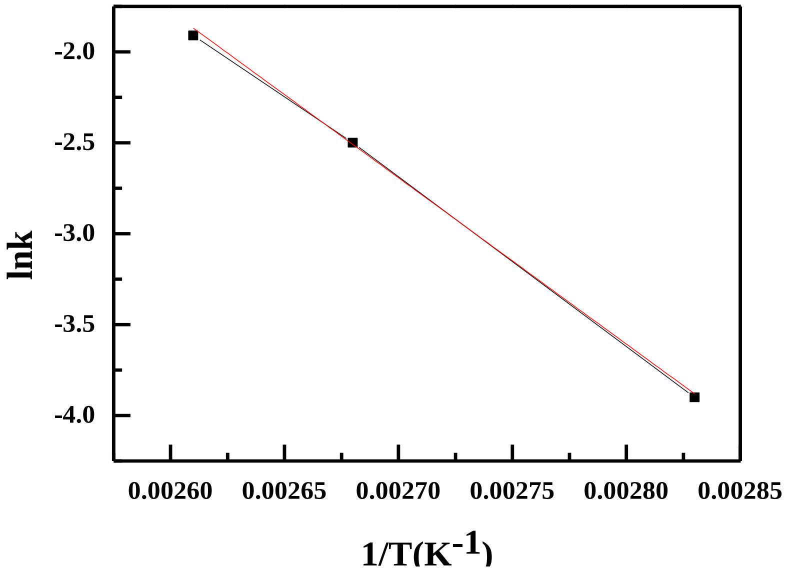


Fig. 8 Arrhenius plot for the dehydration of fructose in isopropanol over $[HO_2CMMIm]Cl$

Table 2 Kinetic parameters for the dehydration of fructose[b]

Reaction order, n	1.0
Activation energy, Ea (kJ mol − 1)*	62.1
Pre-exponential factor, A (min − 1)*	$5.7x10^7$
Correlation coefficient	0.9948

[b] Experimental conditions: reaction temperature of 110 ^oC, 0.1 g $[HO_2CMMIm]Cl$, 0.1 g fructose and 3ml isopropanol.

4. Conclusion

In summary, a thermo-regulated recyclable catalytic system using a combination of $[HO_2CMMIm]Cl$ and isopropanol for the production of HMF from fructose was developed. It has been demonstrated that fructose and $[HO_2CMMIm]Cl$ ionic liquid were insoluble in isopropanol before the reaction at room temperature, while they could be completely dissolved solvent isopropanol under reaction conditions. Interestingly, when the system was cooled down to room temperature after the reaction, $[HO_2CMMIm]Cl$ could readily precipitated thus making an appealing thermo-regulated catalyst recovery strategy possible. Several factors were found to play a role in determining the rate and selectivity of fructose dehydration, such as reaction temperature, reaction time, and catalyst/substrate loadings. A high HMF yield of 91.2% could be obtained with 0.05g fructose, 0.1g $[HO_2CMMIm]Cl$ in 3ml isopropanol, reaction temperature of 110 ^oC and reaction time of 30 min. Moreover, this thermo-regulated system has been shown to be highly recyclable, maintaining the catalytic performance for 5 consecutive runs without appreciable loss of activity. In addition, a kinetic analysis was carried out and values of the activation energy and pre-exponential factor for the IL-catalyzed fructose dehydration to HMF were obtained. The efficient, simple, and recyclable catalytic system has great potential for a wide range of acid-catalyzed reactions in addition to the studied fructose dehydration as a model reaction in the present work.

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