



Efficient Dehydration of Glucose, Sucrose, and Fructose to 5-Hydroxymethylfurfural Using Tri-cationic Ionic Liquids

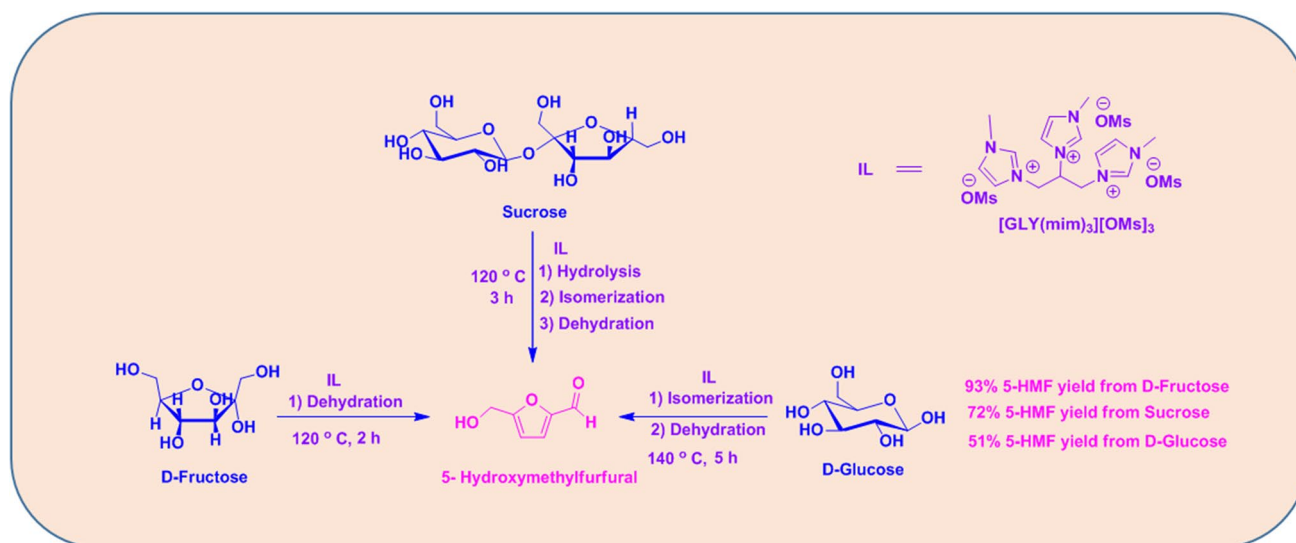
Pramod V. Rathod¹ · Rajendra B. Mujmule¹ · Wook-Jin Chung¹ · Amol R. Jadhav¹ · Hern Kim¹

Received: 4 December 2018 / Accepted: 12 January 2019
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Abstract

Imidazolium predicated room temperature tri-cationic ionic liquid (RTILs) shows highly efficient and selective dehydration of fructose, sucrose, and glucose into 5-hydroxymethylfurfural (5-HMF). The formation of 5-HMF has been investigated using different reaction parameters, such as catalyst weight, reaction time and temperature. Among different reaction parameters, 93% yield of 5-HMF was obtained from fructose in [GLY(mim)₃][OMs]₃ at 120 °C within 2 h, while 72% and 51% yield of 5-HMF were achieved from dehydration of sucrose, and glucose respectively at 120–140 °C in 3 h to 5 h. In addition, the effect of reaction time, molar ratio, and temperature with CC-SO₃H co-catalyst have been discussed. In which, 97%, 77%, and 58% yield of 5-HMF were obtained from fructose, sucrose, and glucose, respectively, in the presence of [GLY(mim)₃][Cl]₃ and CC-SO₃H catalyst at 130–140 °C within 3–5 h. Both catalytic systems showed excellent recyclability for carbohydrates to 5-HMF conversion without any loss in its catalytic activity.

Graphical Abstract



Keywords Biomass · Ionic liquid · 5-Hydroxymethylfurfural

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s10562-019-02667-0>) contains supplementary material, which is available to authorized users.

✉ Hern Kim
hernkim@mju.ac.kr

Extended author information available on the last page of the article

1 Introduction

The synthesis of value-added chemicals from renewable sources has gained much attention over the last decade [1–3]. Renewable energy is one of the most effective option

to achieve sustainable development. The nineteenth century chemistry discoveries led to use of biomass as a raw material for the production of various value-added chemicals. Furan based compounds are the very substantial precursors for various value-added chemicals, and such furan-based compound can be precisely obtained from dehydration of biomass-based carbohydrates. 5-hydroxymethylfurfural (5-HMF) is one of the furan derivatives obtained from C6 carbohydrates, which is an important bio-refinery building block [4, 5]. This compound is useful for the development of various chemical intermediates as well as liquid fuels such as 2,5-diformylfuran [6], 2,5-furan dicarboxylic acid (FDCA) [7], 2,5-dimethylfuran (DMF) [8], and levulinic acid (LA) [9], such FDCA chemical further can be polymerized into polyethylene furanoate (PEF), which is useful for bottle, films, and fibers production. 5-HMF has been listed as the top 10 value-integrated bio-predicated chemicals by the US Department of Energy.

So far, various acid catalysts has been reported for the conversion of carbohydrates into 5-HMF. In which metal chlorides, mineral acids, and HPAs give extraordinary 5-HMF yields but they lead to concerns with recycling and eco-friendliness [10]. Various homogeneous catalysts are also used to hydrolyse biomass to 5-HMF during the last century, which includes benzenesulfonic acid, HCl in water [11], H₃PO₄, or H₂SO₄ [12]. Unfortunately, such homogeneous acids suffer from drawback like corrosion, difficulties during isolation of 5-HMF, catalyst recovery, environmental pollution, etc. Several heterogeneous catalysts are also established for biomass to 5-HMF conversions, such as Sn-beta [13], HY zeolite [14, 15], Amberlyst-15 [16], phosphoric-acid-treated metal oxide, sulfonic acid-containing ionic liquids and sulfonic acid-functionalized carbon materials. However, SO₃H modified carbon derived from biomass and sulfuric acid or oleum is not a green option, since sulfuric acid is highly corrosive and oleum is dangerous especially at massive quantity which causes environmental problems.

Recently, the room temperature ionic liquids (RTILs) also employed in the dehydration of carbohydrates into 5-HMF [17–19]. RTILs are essential salt composed by cations and anions which show extraordinary characteristics such as non-flammable nature, non-volatile, chemically and thermally stable, dissolve many chemicals, and recyclable [20–22]. In particular, the RTILs can be established with a specific task through the selection or functionalization of the cation or anion and therefore, have been widely utilized in many chemical reactions, and variety of research fields [23–25]. Biomass conversion industries economic rapidly increased, since the ILs dissolves lignin, wood, and other biomass [26, 27]. So far, several research groups reported the use of ILs in biomass conversion. In 2007, Zhang et al. reported the

dehydration of sugar into 5-HMF using [C4C1im] Cl(ILs) combined with various metal salts, in which they got 70% yield of 5-HMF at 120 °C within 3 h. For the dehydration of fructose into 5-HMF, metal salt systems plus ionic liquids are reported, but the production cost of 5-HMF by these catalytic systems is very high. Besides, the reported catalytic system gives a separation problem that leads to lower 5-HMF yield [28]. The objective of the present work is to develop a new protocol for dehydration of biomass to 5-HMF using Tri-cationic room temperature ionic liquid catalysts. Tri-cationic room temperature ionic liquids (RTILs) is an environmentally friendly catalyst, relatively cheap, stable in air and easy to handle.

In this work, we have introduced Imidazolium predicated room temperature tri-cationic ionic liquids (RTILs) as catalysts for highly selective dehydration of fructose, sucrose, and glucose into 5-HMF. The present catalytic system is eco-friendly and low cost, and it can be useful for large-scale industrial production of 5-HMF.

2 Experimental Section

2.1 Materials

The chemicals were purchased from Sigma Aldrich and used without any purification. 3-methylimidazole, trimethylamine, glycerol, potassium bromide, sodium sulfate, bis(trifluoromethane-sulfonyl)imide lithium salt, methane sulfonyl chloride, potassium hexafluorophosphate, fructose, sucrose, glucose, and *p*-toluenesulfonic acid.

2.2 Preparation of Trimesylate Precursors

As-reported synthesis procedure was followed for the preparation of trimesylate precursors for the preparation of glycerol-derived ionic liquids [29, 30]. Glycerol (1.0 mmol) and triethylamine (3.0 mmol) were used as raw materials and mixed with dichloromethane (DCM) in a round bottom flask under the vigorous stirring condition to make a homogeneous mixture. The solution temperature was maintained at 0 °C using an ice bath, and methane sulfonyl chloride (3.5 mmol) was added dropwise to the above solution. The solution was allowed for 12 h at 0 °C to room temperature. After completion of the reaction, the reaction mixture was extracted by DCM, and for confirmation of the product, it was further examined by TLC. To remove its impurity, the crude product was washed several times by DI water and dried using Na₂SO₄. Finally, the organic solvent was removed using rota-evaporator at high vacuum. The obtained orange-coloured solid trimesylate precursor yield was 89%.

2.2.1 Synthesis of Glycerol-tri (3-methylimidazolium) Trimesylate

A trimesylate precursor (1.0 mmol) and 3-methylimidazolium (3.0 mmol) were used to synthesize glycerol-tri (3-methylimidazolium) trimesylate, with acetonitrile as a solvent in reflux condition for 28 h. After completion of the reaction, the reaction mixture was allowed to cool at a normal temperature. Further, it was evaporated by a high vacuum pump and to remove unreacted starting materials the residue was washed several times by ethyl acetate. The crude oil was denoted by glycerol tri(3-methylimidazolium) trimesylate (RTILs) (yield 92.5%).

2.3 Procedures of Anion Exchanges [GLY(mim)₃][PF₆]₃, [GLY(mim)₃][Br]₃ and [GLY(mim)₃][Cl]₃ Ionic Liquids

Glycerol-tri (3-methylimidazolium) trimesylate (0.17 mol) and potassium hexafluorophosphate (0.52 mol) were dissolved in acetone respectively for the synthesis of glycerol-tri (3-methylimidazolium) hexafluorophosphate [GLY(mim)₃][PF₆]₃. The reaction mixture was further stirred for 28 h at room temperature followed by evaporation using a high vacuum pump, to get resultant crude [GLY(mim)₃][PF₆]₃ product (yield 90.6%). A similar synthesis procedure was used to prepare [GLY(mim)₃][Br]₃ and [GLY(mim)₃][Cl]₃ (RTILs) by replacing potassium hexafluorophosphate with potassium bromide (0.52 mol) and potassium chloride (0.52 mol). Finally, [GLY(mim)₃][Br]₃, [GLY(mim)₃][Cl]₃ (RTILs) were obtained by filtration and Acetone was evaporated using a high vacuum pump, and the obtained yield were 93.7% and 90.3% respectively.

2.4 Typical Reaction Procedure for 5-HMF Synthesis

Ionic liquid was dried under vacuum before to use. Fructose (0.2 g)/sucrose (0.2 g), or glucose (0.2 g), and [GLY(mim)₃][OMs]₃ (RTIL) were added in a 50 mL RBF and stirred for 2–5 h at 120–140 °C. Then, the reaction was monitored by TLC, after completion of the reaction the reaction mixture was allowed to cool at room temperature. 5 mL DI water was used to dilute the reaction mixture, then ethyl acetate was

added to diluted reaction mixture and 5-HMF was extracted. A high vacuum pump was used to evaporate reaction mixture to get crude 5-HMF. The crude 5-HMF product was confirmed by ¹H NMR, ¹³C NMR, GC-Mass Spectra, HPLC, and FTIR-Spectra.

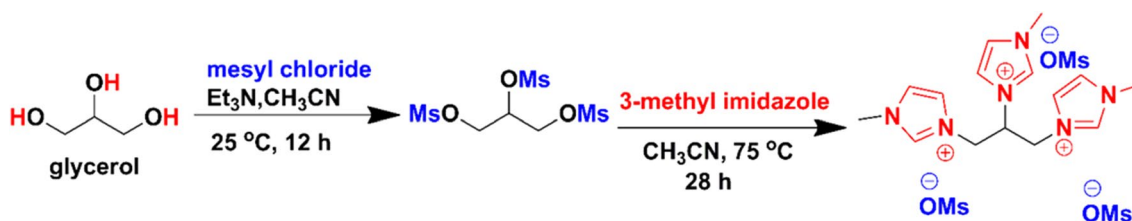
2.5 5-HMF Analysis

The crude 5-HMF product analyzed by ¹H and ¹³C NMR spectra and were confirm using previously reported NMR data. GC-mass was recorded on Agilent Technologies 5977A (EI) (Fig. S2, Supporting Information). Additionally, Crude 5-HMF was analyzed by HPLC (Agilent Technologies 1200 series), using a C18 column and a UV detector at 25 °C. Aqueous H₂SO₄ (5 mM) and methanol (9:1) were used as the mobile phase at a flow rate of 1.0 mL/min (Fig. S1, Supporting Information).

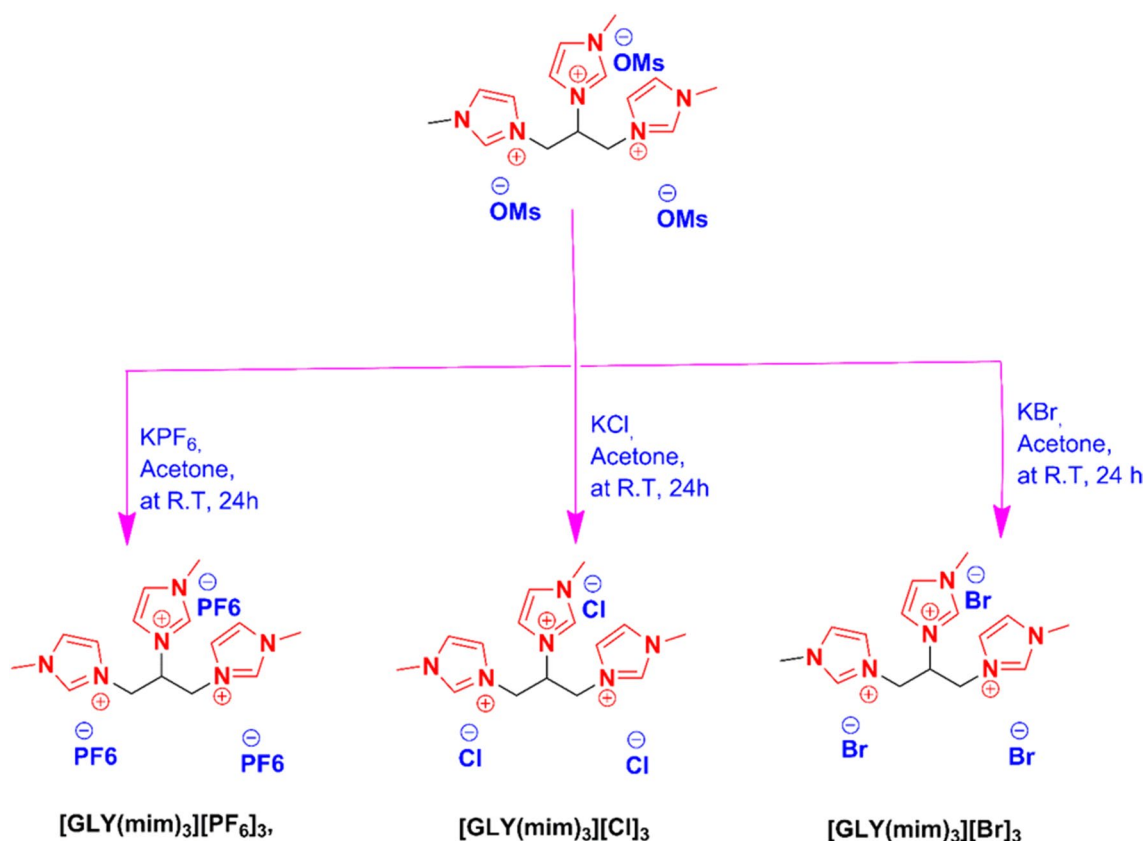
3 Results and Discussion

3.1 Catalyst Preparation and Characterization

In the first step synthesis of the trimesylate precursor, glycerol hydroxyl groups selectively protected using methanesulfonyl chloride. To the next step, using trimesylate glycerol and 3-methylimidazoles to tricationic methylimidazolium (RTILs) were prepared (Scheme 1). Ionic liquids (RTILs) with different anions were obtained by reacting *N*-methylimidazolium (RTILs) with various anionic salts such as –PF₆, –Cl and –Br. (Scheme 2). *N*-Methylimidazolium based (RTILs) were selected because of its compatibility with acids, wide availability, and low cost. The synthetic process has been described in detailed experimental sections. The tri-cationic RTILs shows a competent acidity for the production of 5-HMF from fructose, sucrose, and glucose. Prepared tri-cationic (RTILs) shows Lewis acidic nature [29]. Prepared RTILs are highly efficient and selective for conversion of fructose, sucrose, and glucose to 5-HMF mainly because of the strong hydrogen bond is produced in the sugar and mesylate (CH₃SO₃[–]) anions [17]. The hydrogen bond forming mesylate anions, nitrogen-containing tri (imidazolium) cations are beneficial to the sugar dissolution



Scheme 1 The synthesis of the tri-cationic RTIL [GLY(mim)₃][OMs]₃ from glycerol



Scheme 2 The synthesis of three different tri-cationic RTILs, metathesis of glycerol-tri (3-methylimidazolium trimesylate) RTILs

in the synthesized RTILs. Their ability to build hydrogen bonds is believed to be the main functioning of dissolving sugar [31].

For the synthesis of catalysts, D-glucose biomass component was selected as a carbon precursor, because of their wide availability. The CC-SO₃H catalyst was prepared by taking glucose and p-TSA in a clean, dry, round bottom flask, which was then stirred at 180 °C for 24 h in a nitrogen atmosphere. The temperature controlled carbonization of glucose in the presence of p-TSA has favored the structure to undergo decomposition, hydrolysis, dehydration and molecular conversion of glucose to produce a polycyclic aromatic structure integrated with active sulfonic acid, carboxylic acid, and hydroxyl groups [32]. The various characterization techniques like Fourier transform infrared (FTIR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), Energy-dispersive X-ray spectroscopy (EDX), Brunauer–Emmett–Teller (BET) surface area and X-ray photoelectron spectroscopy (XPS) were used to analyses as-prepared CC-SO₃H catalyst. Figure 1 shows the FT-IR spectrum of the CC-SO₃H. The vibration bands at 1008 cm⁻¹ and 1032 cm⁻¹ are related to –SO₃H groups which are attributed to O–S–O stretching vibrations and band peak at 1240 cm⁻¹ is related to SO₃H

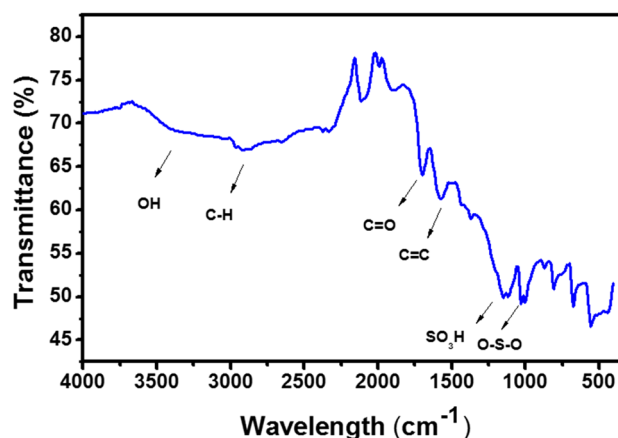


Fig. 1 FT-IR of the synthesized CC-SO₃H Catalysts

stretching. This indicates that the sulfonic acid groups were subsequently incorporated into the catalyst surface. The vibration band peaks at 1615 cm⁻¹ were allocated to the C=C aromatic carbons, the band peak at 1695 cm⁻¹ attributed is C=O stretching vibration –COOH group. Bands at 2990–2875 cm⁻¹ and 3450 cm⁻¹ are attributed for C–H and O–H stretching, respectively.

The XRD patterns of the CC-SO₃H catalyst (Fig. 2) shows the characteristic broad diffraction peak at 2θ angles of 10°–30° can be assigned to C (002) planes and a small peak at 2θ angles of 35°–46° that are assigned to typical amorphous carbon [33]. The results of Field emission-scanning electron microscopy (FE-SEM) analysis for prepared CC-SO₃H catalyst samples are shown in (Fig. 3a–c) the rough particle morphologies observed in the images (Fig. 3b). In general, the investigated CC-SO₃H catalyst

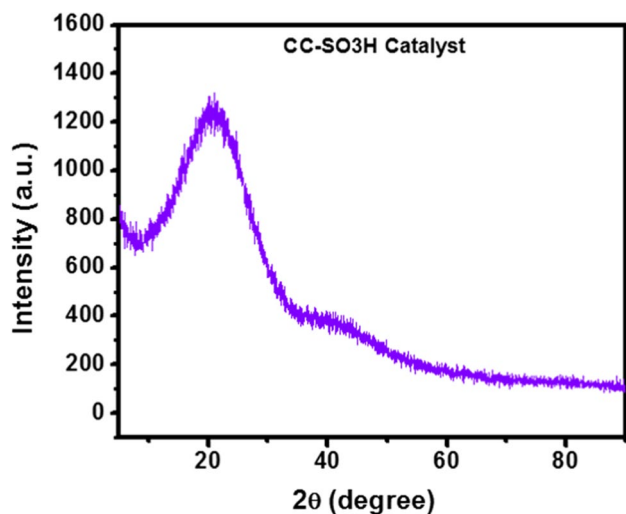


Fig. 2 X-ray diffraction (XRD) patterns of the synthesized CC-SO₃H Catalysts

have larger particle sizes. Furthermore, FE-SEM equipped with energy dispersive X-ray analysis (EDX) utilized to check the elemental composition of CC-SO₃H catalysts surface. The EDX spectra (Fig. 3d) shows the presence of carbon, oxygen, and sulfur elements (C = 69.7%, O = 23.8%, S = 6.5%). Thus showing the presence of –SO₃H, –COOH, and –OH on the catalyst surface. The acid-base titration method was used to calculate the total acid density of the catalyst [34], which was observed at 1.2 mmol/g. Brunauer–Emmett–Teller (BET) surface areas and mean pore diameter was calculated using the standard BET equation and was found to be 2.81 m²/g and 125.6 nm.

X-ray photoelectron spectroscopy (XPS) was further used to check the chemical state of elements. The full XPS survey spectra (Fig. 4a) shows the presence of C, O, S elements on the prepared composites. The peak for K and Br were observed because the sample for XPS was prepared in the form of KBr pellets. Figure 4b shows the S 2p XPS spectra of CC-SO₃H, the peak at binding energy 167 eV shows the presence of SO₃H group [35]. In high-resolution C 1s spectra (Fig. 4c), the peak at binding energy 283.5 eV, 284.5 eV, and 287.53 corresponds to C=C, C–C, and C=O functionality respectively [36]. Figure 4d shows the O 1s core level spectrum, which confirms the presence of C=O bonds.

Fig. 3 FE-SEM (a–c) and EDX (d) of the CC-SO₃H Catalysts

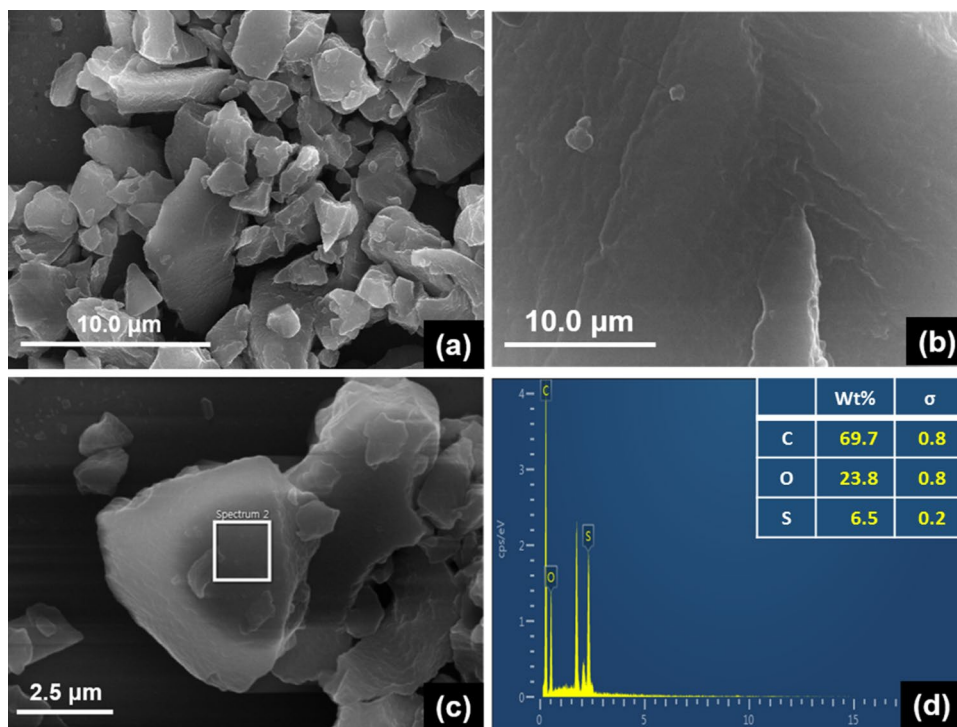
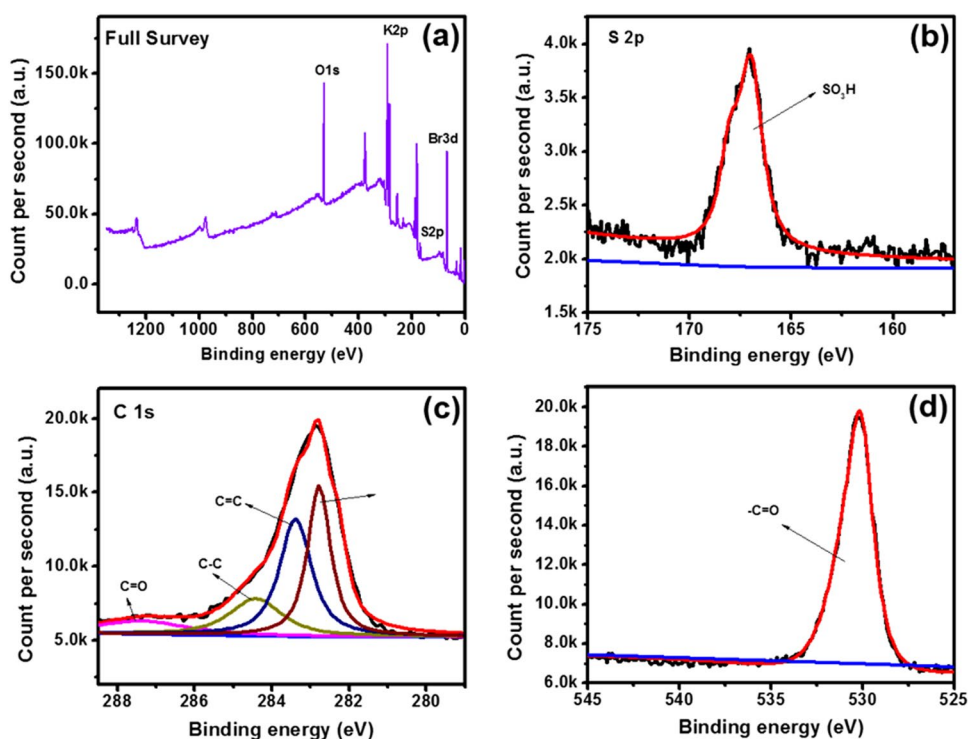


Fig. 4 Representative XPS spectra, CC-SO₃H catalysts: **a** full survey, **b** S 2p, **c** C 2s, **d** O 2s

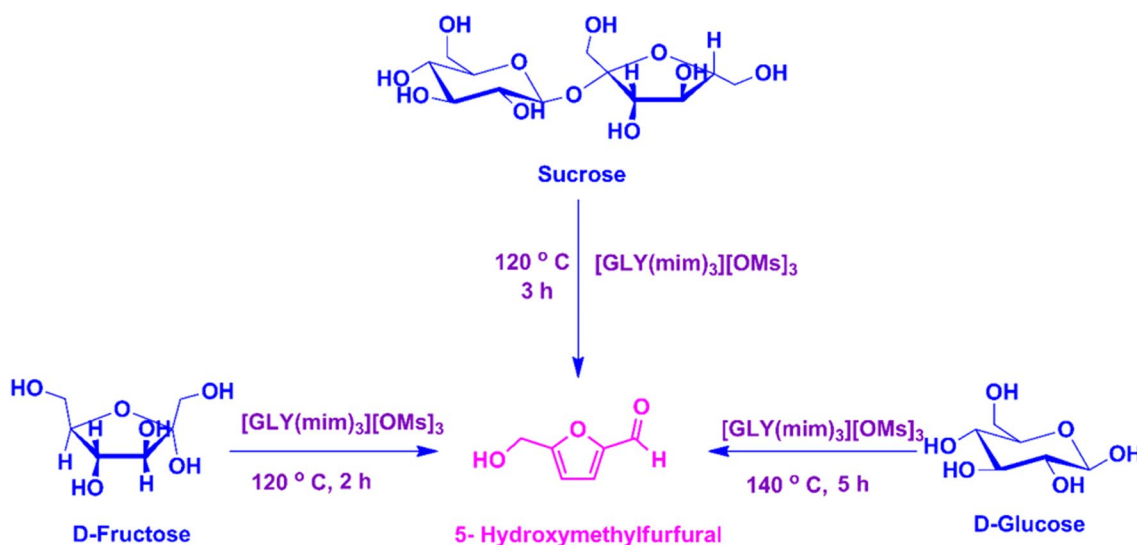


3.2 Dehydration of Fructose, Sucrose, and Glucose to 5-HMF

3.2.1 Dehydration of Fructose, Sucrose, and Glucose to 5-HMF in the Presence of Tri-cationic Ionic Liquids (Scheme 3)

Initially, the tri-cationic ionic liquids activity has been evaluated for converting fructose to 5-HMF in various

solvents system (Table 1). The reactions were conducted at 100 °C for 3 h using 1.1 mmol of fructose in the presence of [GLY(mim)₃][OMs]₃ (RTIL). It was observed that in solvents THF and IPA the yield of 5-HMF were around 7 and 14%, respectively (entry 1 and 2). However, in solvent water, the corresponding 5-HMF yield is slightly higher 21% (entry 3). Meanwhile, the biphasic solvent gave a higher yield of 5-HMF in comparison with pure organic solvent suggesting that water is crucial for dehydration of fructose, due to



Scheme 3 The synthesis of fructose, sucrose, and glucose to 5-hydroxymethylfurfural

Table 1 Study of fructose, sucrose, and glucose to 5-HMF in different solvents

Entry	Substrate	Solvent	Ionic liquids (ILs)	Yield (%) HMF ^a
1	Fructose	THF	[GLY(mim) ₃][OMs] ₃	7
2	Fructose	IPA	[GLY(mim) ₃][OMs] ₃	14
3	Fructose	H ₂ O	[GLY(mim) ₃][OMs] ₃	21
4	Fructose	H ₂ O/THF	[GLY(mim) ₃][OMs] ₃	26
5	Fructose	H ₂ O/IPA	[GLY(mim) ₃][OMs] ₃	31
6	Fructose	Neat	[GLY(mim) ₃][OMs] ₃	72
7	Fructose	Neat	Without ionic liquid	–
8	Fructose	Neat	[GLY(mim) ₃][PF ₆] ₃	19
9	Fructose	Neat	[GLY(mim) ₃][Cl] ₃	37
10	Fructose	Neat	[GLY(mim) ₃][Br] ₃	26
11	Sucrose	Neat	[GLY(mim) ₃][OMs] ₃	57
12	Glucose	Neat	[GLY(mim) ₃][OMs] ₃	16

Reaction conditions: fructose (0.2 g)/sucrose (0.2 g)/glucose (0.2), ILs (0.5 g), 100 °C, 3 h, N₂ atmosphere

^aIsolated yield

less solubility of fructose in a most organic solvent. Upon analysis of the result in Table 1, it can be seen that THF/H₂O and IPA/H₂O was the most effective response medium, According to our response scenario with 26% and 31% yield of 5-HMF respectively.

Further, we studied neat (without solvent) system in which we observed that without any solvents the corresponding 5-HMF yield is very high, as the fructose to 5-HMF yield (isolated) was 72% reached (Table 1, entry 6). But with the same reaction but in the absence of [GLY(mim)₃][OMs]₃ (RTIL) there was no 5-HMF formation observed. Further, we studied the effect of the different anion of ionic liquids on the fructose dehydration reaction. In which, we observed that the dehydration of fructose with [GLY(mim)₃][PF₆]₃, [GLY(mim)₃][Cl]₃ and [GLY(mim)₃][Br]₃ (RTILs) gives 5-HMF yield of 19, 37 and 26% respectively, using a similar reaction condition. This observation confirms the [GLY(mim)₃][OMs]₃ (RTIL) plays a significant role through a dehydration process. And also we have studied sucrose and glucose dehydration to 5-HMF, in which 57% and 16% yield of 5-HMF was observed in [GLY(mim)₃][OMs]₃ (RTIL), at 100 °C within 3 h, for sucrose dehydration, it can be initially hydrolysed to one molecule of glucose and one molecule of fructose, and then the glucose and fructose are dehydrated to produce 5-HMF [37]. Isomerization of glucose into fructose is an important step in the Lewis acid site, glucose isomerization into fructose need high Lewis acid site and high temperature [38]. During these dehydration process, 5-HMF is the only product in the presence of an acid catalyst or the [GLY(mim)₃][OMs]₃ (RTIL).

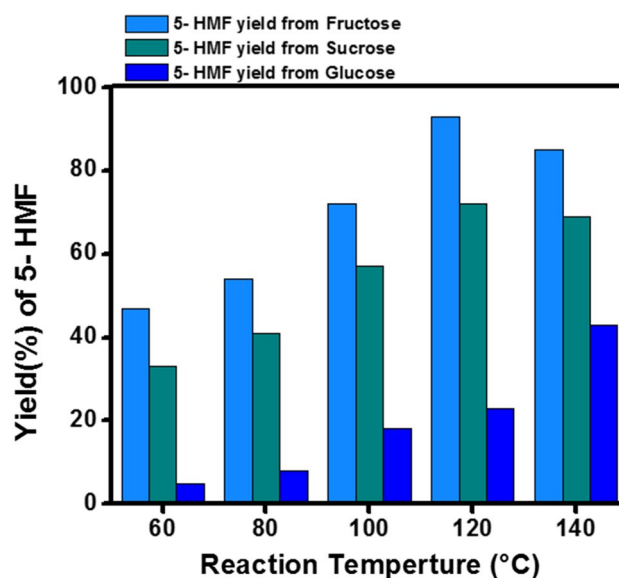


Fig. 5 Study of fructose, sucrose, and glucose to 5-HMF using [GLY(mim)₃][OMs]₃ RTIL in various temp. Reaction conditions: fructose (0.2 g)/sucrose (0.2 g)/glucose (0.2), [GLY(mim)₃][OMs]₃ IL (0.5 g), temp, N₂ atmosphere

This observation confirms the ionic liquids plays a significant role through a dehydration process. As ionic liquids have the ability to tune their chemical and physical properties to provide the best medium for a specific transformation. The presence of an acidic proton in [GLY(mim)₃][OMs]₃ (RTIL) possibly enhance the dehydration reaction rate, thereby in the presence of Ionic liquid 5-HMF yield is high. As in the absence of ionic liquid, such acidic proton is unavailable for this transformation, resulting in no 5-HMF formation, the same kind of results were also reported by Eminov and co-worker. They reported a yield of 5-HMF 96%, in the presence of [C₄C₁im]{HSO₄} ionic liquid catalyst [39]. The mildly acidic [GLY(mim)₃][OMs]₃ Ionic liquid acts as a catalyst as well as a green solvent in the reaction medium.

The effect of the reaction temperature on the yield of 5-HMF was also studied at different reaction temperature using 1.1 mmol fructose, and [GLY(mim)₃][OMs]₃ (RTIL). As shown in Fig. 5, the reaction temperature shows adverse effects on the conversion of fructose to 5-HMF, when the reaction was done at 80, 100, 120 and 140 °C. Increasing the temperature from 60 to 100 °C, resulting in the increase in yield of 5-HMF from 47 to 72% (isolated). When the reaction temperature was further increased to 120 °C, the yield of 5-HMF increased to 93% in 2 h. The results show that, due to the increased reaction temperature, the maximum 5-HMF production is not increased, but the reaction time required to reach the maximum yield of 5-HMF was reduced. But the reaction time required to reach the maximum yield of 5-HMF was reduced. But when we increase

the reaction temperature to 140 °C, It did not show any appreciable increase in the 5-HMF yield.

Same results were observed in sucrose and glucose dehydration reaction. When the reaction was done at 60 and 120 °C increasing the temperature observed Increase in yield of 5-HMF from 33 to 72% and 5 to 23% (isolated). Further, we have done in 140 °C for Sucrose dehydration, which gives a lower yield of 5-HMF, but glucose case we noted at 140 °C increasing the temperature increase in yield of 5-HMF from 43%(isolated). But, when we increased reaction temperature up to 160 °C, the yield of 5-HMF slightly decreases. Furthermore, in various reaction temperature, 5-HMF production first always grows in growth reaction temperature. When the yield of 5-HMF has reached its peak value, any further increase reaction temperature resulted in a lower yield of 5-HMF, which can lead to a higher density in the 5-HMF sub-products [40]. So finally, the sucrose and glucose reaction temperature of 120 °C and 140 °C is considered to be the most suitable for sugar conversion, with the higher productivity of 5-HMF.

Figure 6 shows the of catalyst loading effects for the yield of 5-HMF from fructose, sucrose, and glucose. In the case of fructose, sucrose, and glucose dehydration in the absence of [GLY(mim)₃][OMs]₃ (RTIL), there was no reaction proceeds even up to 24 h. But upon addition of 0.1 g of [GLY(mim)₃][OMs]₃ for dehydration of fructose, sucrose, and glucose at a reaction temperature of 120–140 °C and reaction time of 2–3 h, product formation takes place yielding 35%, 21%, and 13% of 5-HMF. Moreover, 0.2 g of [GLY(mim)₃][OMs]₃

(RTIL) has increased the 5-HMF yield up to a 54, 38% and 21% (isolated) from fructose, sucrose, and glucose, respectively. And further increased of catalyst loading from 0.3 to 0.5 g, made the generation of 5-HMF gradually increased. The highest yield of 5-HMF from fructose, sucrose, and glucose was 93%, 72%, and 44% (isolated) respectively, using the 0.5 g [GLY(mim)₃][OMs]₃ catalysts. However, in the case of fructose and sucrose dehydration, when the amount of ionic liquids loading was more than 0.5 g, the yield of 5-HMF was reduced to 92 and 70% (isolated) Meanwhile, we observed in glucose case, even with 0.6 g and 0.8 g of ionic liquid, we have achieved an increased in 5-HMF yield from 45 to 51% (isolated). glucose isomerization into fructose need high Lewis acid site and high temperature, and then the fructose will be dehydrated to produce 5-HMF [38].

It's important to know that fructose, sucrose, and glucose dehydration reaction with catalyst loading above 0.5 g and 0.9 g will not give a higher yield of 5-HMF; the decrease in the activity is possibly due to the decrease of the area and the surface acidity on the catalyst because of the increase of [GLY(mim)₃][OMs]₃ (RTIL) [41]. Additionally, the reaction time effect on sugar dehydration to 5-HMF was studied at different reaction times. As shown in Fig. 7, with increasing reaction time from 1 to 2 h, 5-HMF performance increased from 64 to 93% at 120 °C in [GLY(mim)₃][OMs]₃ (RTIL) catalyzed fructose dehydration reaction. However, further increasing the reaction time up to 5 h did not help improve the 5-HMF yield. Dehydration of fructose to 5-HMF at 120 °C in 2 h, the maximum 93% yield (isolated) of 5-HMF

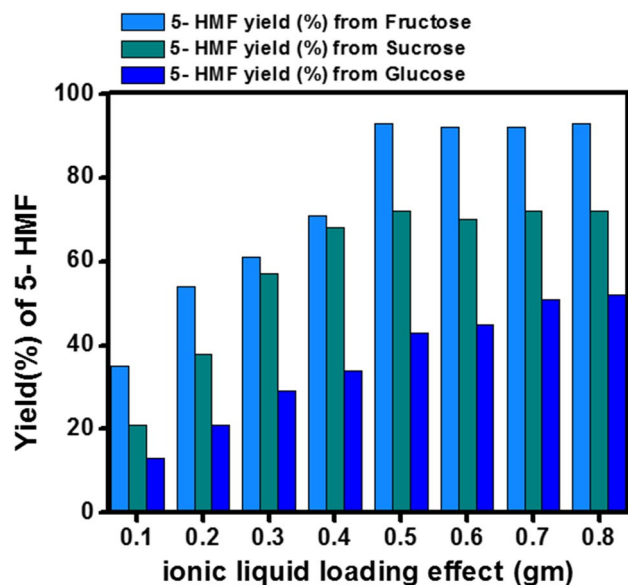


Fig. 6 Study of ionic liquid loading effect on the conversion of fructose, sucrose, and glucose to 5-HMF. Reaction conditions: fructose (0.2 g)/sucrose (0.2 g)/glucose (0.2), [GLY(mim)₃][OMs]₃(IL), 120 °C, N₂ atmosphere

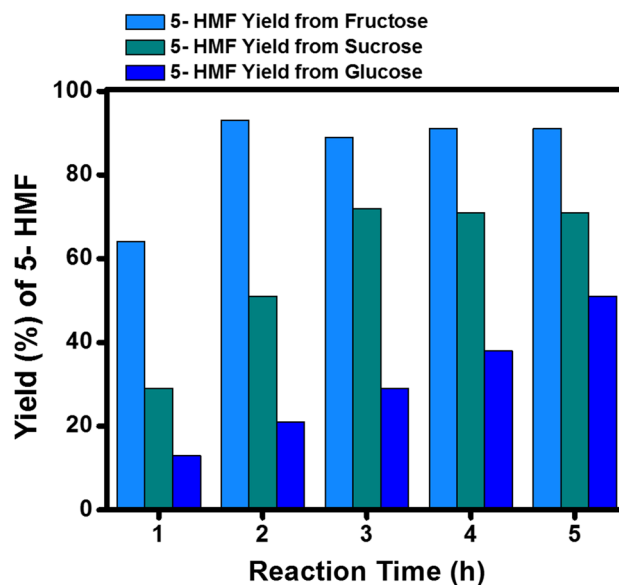
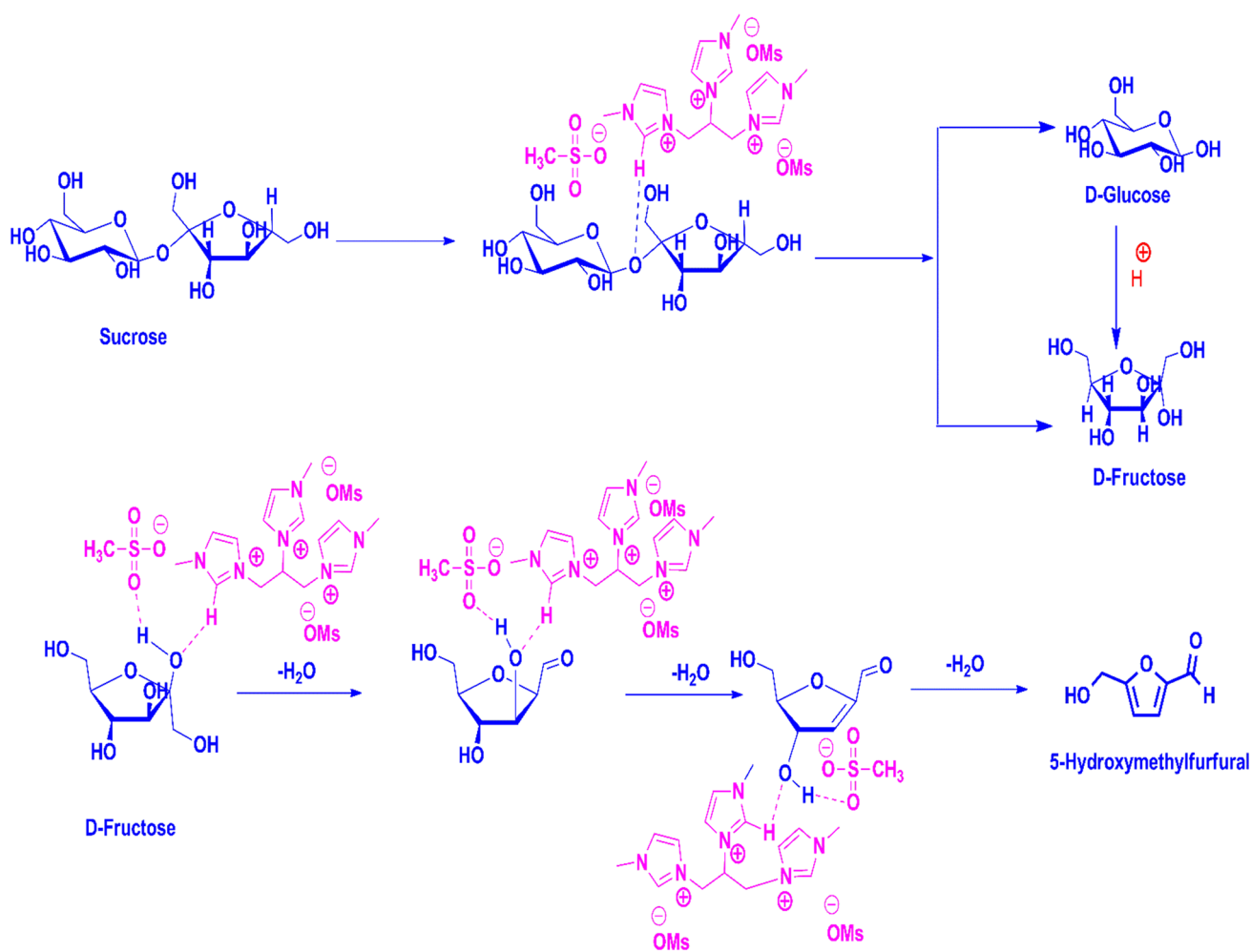


Fig. 7 Study of reaction time for dehydration of fructose, sucrose, and glucose to 5-HMF using [GLY(mim)₃][OMs]₃ (RTIL). Reaction conditions: fructose (0.2 g)/sucrose (0.2 g)/glucose (0.2), IL (0.5 g), 120–140 °C, N₂ atmosphere

was obtained with 100% fructose conversion. The same performance of 5-HMF yield was also seen for the dehydration of sucrose and glucose in the same reaction condition, with increased reaction time (Fig. 7). The increasing reaction time from 1 to 2 h, the 5-HMF yield improved 29 to 51% and 13 to 21% from sucrose and glucose. Subsequently, a similar trend were observed in the sucrose and glucose decomposition with an increase in 5-HMF yield up to 72% and 51% over 3 h and 5 h. In our results, the colour of the reaction mixture rapidly changed from light yellow to dark brown after dehydrations of fructose and sucrose for 2–3 h, and glucose dehydration for 5 h are the optimal reaction time for 5-HMF production.

The dehydration of fructose, sucrose, and glucose to 5-HMF catalyses by the acidic (RTILs) is a very complex process (as shown in Scheme 4). As mentioned above, the sucrose dehydration can be firstly hydrolysed to one

molecule of glucose and one molecule of fructose, and isomerization of glucose into fructose is an important step in the Lewis acid site, where glucose isomerization into fructose will need high Lewis acid site and high temperature, then the fructose will be dehydrated to produce 5-HMF. In general, the efficiency in the sugar dehydration is closely related to the acidity of the catalyst as well as the strong hydrogen bond is produced in the sugar and mesylate (CH_3SO_3^-) anions [42]. The mesylate anions forming hydrogen bond and nitrogen-containing tri (imidazolium) cations are beneficial to the fructose, sucrose, and glucose dissolution in the synthesized RTILs. Their ability to construct hydrogen bonds is believed to be a major function (mechanism) for solubilizing biomass and 5-HMF. The tri-cationic RTILs synthesized in this study has a Lewis acidic character. Lewis acid ILs are reported to be more effective than Brønsted acid ILs in terms of sugar conversion and 5-HMF yield [43].



Scheme 4 Possible reaction transformation for the formation of 5-HMF from sucrose with ionic liquid

3.2.2 Catalytic Study of CC-SO₃H for Fructose, Sucrose, and Glucose to 5-HMF Conversion in the Presence of Tri-cationic Ionic Liquids

Above results show a conversion of fructose, sucrose, and glucose to 5-HMF with 93%, 72%, and 51% yield, respectively obtained in [GLY(mim)₃][OMs]₃ RTIL at 120–140 °C, showing used catalytic system is highly efficient for sugar to 5-HMF conversion. The effect of the different anion (ionic liquids) with metal-free co-catalyst used for dehydration reaction of fructose, sucrose, and glucose. For comparison purposes, we studied a neat system for the same reaction. In which we observed that without solvent the corresponding 5-HMF yield is very high; such that the fructose to 5-HMF selectivity increase resulted in 100% conversion and the corresponding isolated reached 93% 5-HMF yield. However, under the same reaction but in the absence of [GLY(mim)₃][OMs]₃ ionic liquid, no 5-HMF product formation took place. Moreover, we observed that in presence of [GLY(mim)₃][Cl]₃, [GLY(mim)₃][PF₆]₃ and [GLY(mim)₃][Br]₃ the dehydration of sugar to 5-HMF reaction rate is low as the isolated 5-HMF yield was very low as compared to [GLY(mim)₃][OMs]₃ (RTIL).

But when we combined the above mentioned ionic liquids (RTILs) and CC-SO₃H co-catalyst, we observed the corresponding 5-HMF yield is high. We observed the dehydration of fructose with [GLY(mim)₃][PF₆]₃, [GLY(mim)₃][Cl]₃ and [GLY(mim)₃][Br]₃ (RTILs) with co-catalyst CC-SO₃H at 100 °C gives 5-HMF yield of 56%, 71% and 61% (isolated) respectively, using a similar reaction condition. In the presence of [GLY(mim)₃][Cl]₃ ionic liquid, we got a high yield of 5-HMF as compared with other ionic liquids. Further, we investigated different reaction parameter effect on dehydration of fructose, sucrose, and glucose to 5-HMF in the presence of [GLY(mim)₃][Cl]₃ (RTIL). Initially, we chose fructose as the substrate. As expected, as the temperature increases, the conversion of fructose increases with increasing temperature. More importantly, the yield of 5-HMF not only increases, but also the reaction time decreases with increasing temperature. As we observed after the 24 h at the low temperature of 80 °C, the obtained 5-HMF yield was 32%. However, by increasing the reaction temperature to 100 °C, just within 8 h the 5-HMF yield increased significantly to 71%, indicating that higher temperatures improve reaction rate resulting in an increase in 5-HMF yield in a shorter time. When further reaction temperature increased up to 130 °C, the yield of 5-HMF increased to 97% within 3 h. But, when we increased reaction temperature up to 150 °C, the yield of 5-HMF slightly decreases. So finally, the reaction temperature of 130 °C is considered to be the most suitable for the higher productivity of 5-HMF.

Similar results were observed for sucrose to 5-HMF conversion reaction. When the reaction was done at 80, 100

and 130 °C, with increasing the reaction temperature the 5-HMF yield increase from 24%, 61%, and 77% respectively. But when we have done above reaction at 150 °C, we got a decrease in 5-HMF yield. The decrease in 5-HMF yield is possible because the 5-HMF is unstable at high temperature as it could be transformed into levulinic acid by alcoholysis thus leading to a low yield of 5-HMF as illustrated [40]. Table 2 shows the influence of reaction temperature on the yield of 5-HMF yield from glucose. It is clear from the Table 2 that the increase of temperature from 120 to 140 °C had a significant effect on 5-HMF yield from glucose. The yield of 5-HMF increased from 36 to 58%. Increasing reaction temperature upto 160 °C slightly decreases 5-HMF yield may be due to the instability of 5-HMF at high temperatures. Therefore, 140 °C was considered to be the optimum reaction temperature for this system.

Table 3 shows the effect of CC-SO₃H catalyst loading on the fructose to 5-HMF conversion. In which we observed that when the catalysts amount was increased from 0.025, 0.050 and 0.100 g the yield of 5-HMF improved from 78, 85 and 97% (isolated). But further increasing catalysts loading above 0.100 g doesn't give a higher yield of 5-HMF. The decrease in activity possibly because of the area and the surface acidity on the catalyst decreases due to the increase of CC-SO₃H concentration [44]. We have also studied the

Table 2 Study of fructose, sucrose, and glucose to 5-HMF using CC-SO₃H Catalyst in various temperature

Entry	Substrate	Ionic liquid (IL)	Temp °C	Time (h)	Yield (%)HMF ^a
1	Fructose	[GLY(mim) ₃][Cl] ₃	80	24	32.6
2	Fructose	[GLY(mim) ₃][Cl] ₃	100	12	71.4
3	Fructose	[GLY(mim) ₃][Cl] ₃	130	3	97.0
4	Fructose	[GLY(mim) ₃][Cl] ₃	150	3	92.1
5	Sucrose	[GLY(mim) ₃][Cl] ₃	80	24	24
6	Sucrose	[GLY(mim) ₃][Cl] ₃	100	15	61
7	Sucrose	[GLY(mim) ₃][Cl] ₃	130	3	77
8	Glucose	[GLY(mim) ₃][Cl] ₃	120	5	36
9	Glucose	[GLY(mim) ₃][Cl] ₃	140	5	58
10	Glucose	[GLY(mim) ₃][Cl] ₃	160	5	54

Reaction conditions: fructose (0.2 g) / Sucrose (0.2 g) / glucose (0.2), [GLY(mim)₃][Cl]₃ IL (0.5 g), CC-SO₃H catalyst (0.1 g), without solvent, N₂ atmosphere

^aIsolated yield

Table 3 Study of fructose, sucrose, and glucose to 5-HMF using loading effect CC-SO₃H catalyst

Entry	Substrate	Catalyst loading mg	Ionic liquid (IL)	Temp °C	Time (h)	Yield (%) HMF ^a
1	Fructose	–	[GLY(mim) ₃][Cl] ₃	130	24	–
2	Fructose	0.025	[GLY(mim) ₃][Cl] ₃	130	5	78
3	Fructose	0.050	[GLY(mim) ₃][Cl] ₃	130	4	85
4	Fructose	0.100	[GLY(mim) ₃][Cl] ₃	130	4	96
5	Fructose	0.150	[GLY(mim) ₃][Cl] ₃	130	3	94
7	Sucrose	0.025	[GLY(mim) ₃][Cl] ₃	130	8	15
8	Sucrose	0.050	[GLY(mim) ₃][Cl] ₃	130	5	51
9	Sucrose	0.100	[GLY(mim) ₃][Cl] ₃	130	3	77
10	Glucose	0.050	[GLY(mim) ₃][Cl] ₃	140	5	22
11	Glucose	0.100	[GLY(mim) ₃][Cl] ₃	140	5	58
12	Glucose	0.150	[GLY(mim) ₃][Cl] ₃	140	5	55

Reaction conditions: fructose (0.2 g)/sucrose (0.2 g)/glucose (0.2), CC-SO₃H catalyst, [GLY(mim)₃][Cl]₃ IL(0.5 g), N₂ atmosphere

^aIsolated yield

CC-SO₃H catalysts loading effect on sucrose dehydration to 5-HMF using a different ratio of the catalyst. The 5-HMF yield was 15, 51, and 77%, when the amount of CC-SO₃H was 0.025, 0.050, and 0.100 g respectively. And we have also observed CC-SO₃H catalyst uses different proportions of catalyst to load glucose to dehydrate into 5-HMF. When CC-SO₃H catalysts loading were 0.050, 0.100, 0.150 g respectively, the yield found of 22%, 58%, and 55% (isolated) respectively. From the results as mentioned earlier, the ionic liquid plus CC-SO₃H catalyst system is highly efficient for fructose, sucrose, and glucose conversion to 5-HMF with 97%, 77%, and 58% yield respectively.

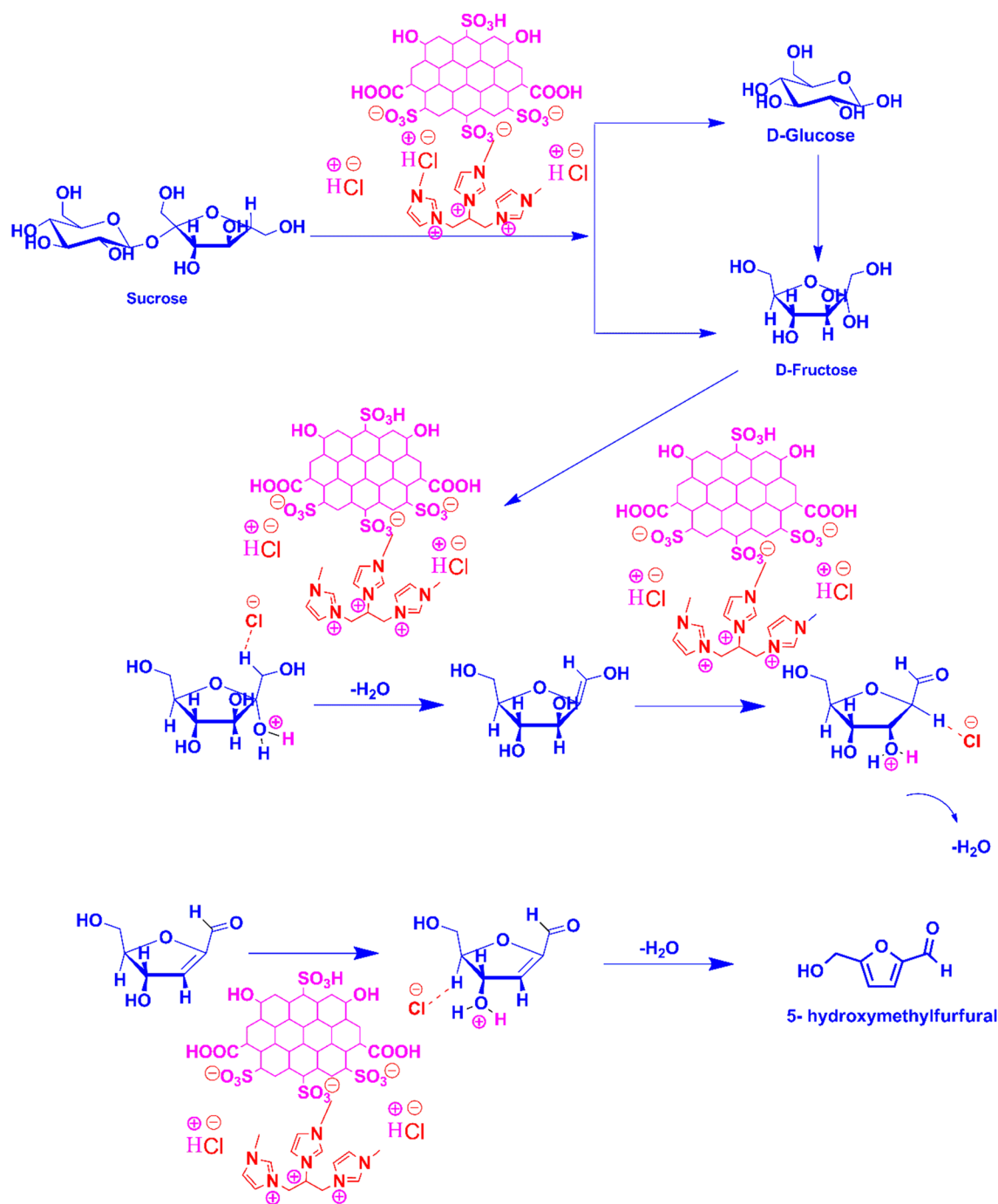
In fructose, sucrose, and glucose dehydration reaction both [GLY(mim)₃][Cl]₃ (RTIL) and CC-SO₃H catalyst play an important role. As, in acid catalyzed reaction the strength of an acid is an important factor of the action of the catalyst, for sugar hydrolysis. Practical aspects of the reaction, concerning the homogeneous nature of the catalysis in spite of using a CC-SO₃H catalyst. Scheme 5 shows the reaction mechanism for this reaction. As shown in the mechanism, the adding CC-SO₃H catalyst into [GLY(mim)₃][Cl]₃ ionic liquid starts an ion-exchange process, resulting in H⁺ ions release [45]. So, the number of the concentration of the H⁺ ions in the reaction mixture depends on the loading of the catalyst. And as expected the effect of the CC-SO₃H catalyst loading shows the effect on the reaction performance. As shown in the mechanism, the homogeneous nature of the catalysis in spite of using a solid acid indicates that the slow release of H⁺ species governs the initial rate of the dehydration of sugar using CC-SO₃H. The overall dehydration reaction rate depends on the total number of H⁺ as well as the reaction temperature [46].

Eminov et al. used CrCl₃·6H₂O as catalyst in the presence of Brønsted IL [BMIM⁺][HSO₄⁻] and Lewis IL [BMIM⁺

[Cl⁻]. They used this combination for sugar conversion. Their previous work with fructose showed that [BMIM⁺][HSO₄⁻] could be a suitable co-catalyst to produce 5-HMF, due to the anion being mildly acidic and abundant in the medium [39]. This low acidity prevents the over-dehydration usually observed with stronger acids. However, the low yields obtained from glucose with [BMIM⁺][HSO₄⁻] suggested that [HSO₄⁻] prevents the isomerization of glucose to fructose, which tends to be base catalyzed. A probable explanation is that, in the presence of CrCl₃, [Cl⁻] leads to the formation of [CrCl₄⁻], which catalyzes glucose-fructose isomerization. On the other hand [HSO₄⁻], appears to form a non-active complex with CrCl₃, which is preferred over [CrCl₄⁻] (Table 4).

3.2.3 Catalyst Recyclability

A catalyst is considered effective only if it can be recycled and reused. For the practical large-scale production of 5-HMF from sugar, the reusability of catalysts and ionic liquids are a very important consideration. The reusable catalytic system significantly reduces production costs. In this work, for both systems, the recyclability of catalysts and the ionic liquids was tested to study their stability and activity. After completion of one cycle of the fructose dehydration reaction. The product was extracted by using ethyl acetate four times and in the remaining reaction mixture, 15 mL of acetonitrile was added and the resulting solution was stirred vigorously at room temperature for 20 min. Separation of acetonitrile layer containing RTILs done by decantation, and were dried using Na₂SO₄. Finally, the RTILs were obtained by removing organic solvent using rota-evaporator at high vacuum. This ionic liquid was reused for a minimum of four runs and showed no significant decrease yields of 5-HMF



Scheme 5 An ion-exchange process involving [GLY(mim)₃]⁺ and H⁺ species possible reaction transformation for the formation of 5-HMF from sucrose

(as shown in Fig. 8). The ionic liquids were found to be sufficiently stable and reactive even after four runs. The further ionic liquid was analysed using ¹H NMR which clearly indicated that ionic liquid was stable after reuse (Fig. S5 Supporting Information).

Also, we have done recyclability test for CC-SO₃H co-catalyst system. After completion of the reaction, the catalyst

was separated from the reaction mixture using a simple filtration method followed by washing with 5 mL of DI water and ethanol for a couple of times and dried at 100 °C. In the filtrate, ethyl acetate was added in DI water and 5-HMF was extracted. A high vacuum pump was used to evaporate ethyl acetate to get crude 5-HMF. The spent catalysts were analyzed using XRD (Fig. S3, support information), which

Table 4 Reported catalysts comparison with [GLY(mim)₃][OMs]₃ for fructose, sucrose, and glucose to 5-HMF conversion

Sr. No	Substrates	Catalysts	Solvent	Time (h)	Temp of °C	5-HMF yield (%)	References
1	Glucose	CrCl ₃	[C4C1im]Cl	0.1	140	43	[47]
2	Glucose	CrCl ₃	BmimHSO ₄	0.1	70	12	[48]
3	Glucose	CrCl ₃	BmimCl	2	125	65.5	[49]
4	Fructose	CrCl ₃ ·6H ₂ O	[C4C1im]{HSO ₄ }	3	100	96	[39]
5	Fructose	WO ₃ /SnO ₂	DMSO	2	100	93	[41]
6	Fructose	ZrP	H ₂ O–diglyme	1	150	80	[50]
7	Sucrose	ZrP	H ₂ O–diglyme	2	180	53	[50]
8	Glucose	Nb ₂ O ₅ /TiO ₂	–	3	100	60	[51]
9	Fructose	HCP-x, eSO ₃ H	DMSO	0.5	140	96.7	[52]
10	Glucose	LaOCl/Nb ₂ O ₅	DMSO	3	180	49	[53]
11	Glucose	H-ZSM-5	NaCl aq. phase/MIBK	0.5	195	42	[54]
12	Glucose	SnPO	EMIMBr	3	120	58.3	[55]
13	Fructose	[GLY(mim) ₃][OMs] ₃	Neat	2	120	93	This work
14	Sucrose	[GLY(mim) ₃][OMs] ₃	Neat	3	120	72	This work
15	Glucose	[GLY(mim) ₃][OMs] ₃	Neat	5	140	51	This work
16	Fructose	CC-SO ₃ H/	[GLY(mim) ₃][Cl] ₃	3	130	96	This work
17	Sucrose	CC-SO ₃ H/	[GLY(mim) ₃][Cl] ₃	3	130	77	This work
18	Glucose	CC-SO ₃ H/	[GLY(mim) ₃][Cl] ₃	5	140	58	This work

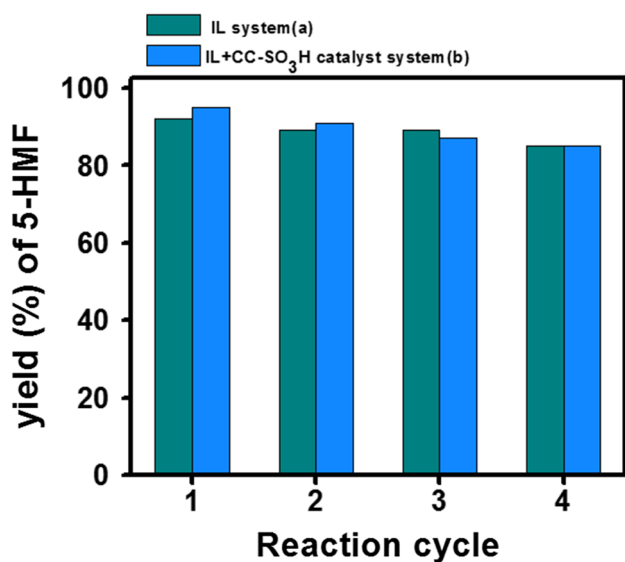


Fig. 8 Catalyst recycling study. (a) IL system. Reaction conditions: fructose (0.2 g), [GLY(mim)₃][OMs]₃ IL (0.5 g), 120 °C for 2 h, N₂ atmosphere. (b) IL + CC-SO₃H catalyst system. Reaction conditions: fructose (0.2 g) CC-SO₃H catalyst (0.1 g), [GLY(mim)₃][Cl]₃ IL (0.5 g), 120 °C for 3 h, N₂ atmosphere

confirms the catalyst was stable after reuse. And the same procedure was followed for extraction of [GLY(mim)₃][Cl]₃ (RTIL). The extracted ionic liquid from the reaction mixture was also characterized using ¹H NMR, and results show ionic liquid was stable after reuse, as no changes appeared

in its ¹H NMR spectra (Fig. S4, Supporting Information). The dried catalyst and ionic liquid were used directly for the next reaction by adding an equal amount of fructose under the same condition. The catalyst and ionic liquid retained its activity up to 4 successive cycles with 94.2% yield of 5-HMF (as shown in Fig. 8). It is important that the catalyst exhibited reusability without any pre-treatment. This represents the high stability as well as the activity of the CC-SO₃H catalyst with ionic liquids for the fructose dehydration reaction.

4 Conclusion

In this study, a new catalytic system has developed for the efficient conversion of fructose, sucrose, and glucose to 5-HMF first-time using tri-cationic ionic liquids. The strong hydrogen bond is produced in the sugar and mesylate (CH₃SO₃⁻) anions are beneficial for dehydration reaction. The [GLY(mim)₃][OMs]₃ (RTIL) showed fructose, sucrose, and glucose decompositions with 93%, 72% and 51% yield (isolated) of 5-HMF at 120–140 °C for only 2–5 h respectively. And co-catalyst system, the excellent 5-HMF yield of 97%, 77% and 58% (isolated) was obtained from fructose, sucrose, and glucose in the presence of [GLY(mim)₃][Cl]₃, and CC-SO₃H catalyst at 130–140 °C for only 2–5 h. For fructose, sucrose, and glucose to 5-HMF conversion, both Ionic liquid and solid acid catalysts play a significant role through H⁺ source. The present catalytic system is shown

recyclability up to 4 successive cycles. The developed catalytic system is highly economical and environmentally friendly gives high 5-HMF yield. Importantly, the present catalytic system is scalable and could be useful for industrial level 5-HMF production.

Acknowledgements This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2018R1D1A1B07048146) and by the Korea Institute of Energy Technology Evaluation and Planning (KETEP)—Grants funded by the Ministry of Trade, Industry & Energy (MOTIE) (No. 20174010201160).

Compliance with Ethical Standards

Conflict of interest The authors declare no conflicts of interest.

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Affiliations

Pramod V. Rathod¹ · Rajendra B. Mujmule¹ · Wook-Jin Chung¹ · Amol R. Jadhav¹ · Hern Kim¹ 

¹ Department of Energy Science and Technology, Smart Living Innovation Technology Center, Myongji University, Yongin, Gyeonggi-do 17058, Republic of Korea