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This article can be cited before page numbers have been issued, to do this please use: K. Kumar, F. Parveen, T. Patra and S. Upadhyayula, *New J. Chem.*, 2017, DOI: 10.1039/C7NJ03146G.

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DOI: 10.1039/C7NJ03146G

Hydrothermal Conversion of Glucose to Levulinic acid using Multifunctional Ionic Liquids: Effect of metal ion co-catalysts on Product Yield

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ABSTRACT

Efficient conversion of glucose to levulinic acid (LA) was achieved with –SO_3H functionalized ionic liquids in combination with catalytic amount of metal salts under environmentally benign mild reaction conditions. Ionic liquids having different Bronsted acidic functional groups were prepared in the laboratory. The acidity of these ionic liquids was determined on the basis of Hammett acidity function using UV-Visible spectroscopy. These catalysts were then screened in the glucose conversion to LA using batch autoclave under autogenous pressure at 140 to 175 °C temperature range. Structure-activity relationship of these multifunctional ionic liquids was correlated based on Hammett function (H_o) and catalytic activity results obtained in terms of glucose conversion and LA yield. The catalytic activity of functionalized ionic liquids decreased in the order: IL-SO_3H>IL-COOH>IL-OH, which is in good agreement with their Bronsted acidity trends. Furthermore, a metal salt based Lewis acidic co-catalyst, with metal ions (Fe, Co, Ni, Cu and Zn), was used in combination with the laboratory prepared Bronsted acidic functionalized ionic liquids in the efficient conversion of glucose to LA. Among all the investigated catalyst and co-catalyst systems, the -SO_3H functionalized ionic liquid with Nickel

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sulfate ($NiSO_4.6H_2O$) showed highest LA yield (56.33%) and selectivity (56.37%). The synergistic effect of the metal ions helps in improving the LA yield by 10% as observed in our investigations. The co-catalytic effect of the transition metal chlorides and metal nitrates was not obvious as compared to transition metal sulfates. The catalyst could be recovered easily and reused three times without significant loss of activity.

Keywords: Metal ions; Glucose; Ionic liquids; Catalytic conversion; Levulinic acid.

1. Introduction

Production of industrially important fine and bulk chemicals from readily available lignocellulosic biomass has become the new trend in catalysis.[1] Lignocellulosic biomass is composed of lignin, cellulose and hemicellulose, found to be the natural renewable carbon resource.[2] Cellulose is readily and is sustainable biomass-derived raw material, made up of D-glucose units linked together by β-1, 4 glycosidic bonds.[3] Cellulose can be hydrolyzed to glucose and further isomerization of glucose leads to the production of industrial important chemicals such as LA, 5-hydroxymethyl furfural (HMF) and lactic acid as shown in **Scheme 1**.[4] LA is the rehydrated product that can be produced from the rehydration of HMF, an intermediate that can be obtained by the catalytic conversion of lignocellulosic biomass.[5] LA with two active, carbonyl and carboxyl functional groups can be converted to γ-valerolactone and other liquid transportation fuel through hydrogenation reactions.[6]

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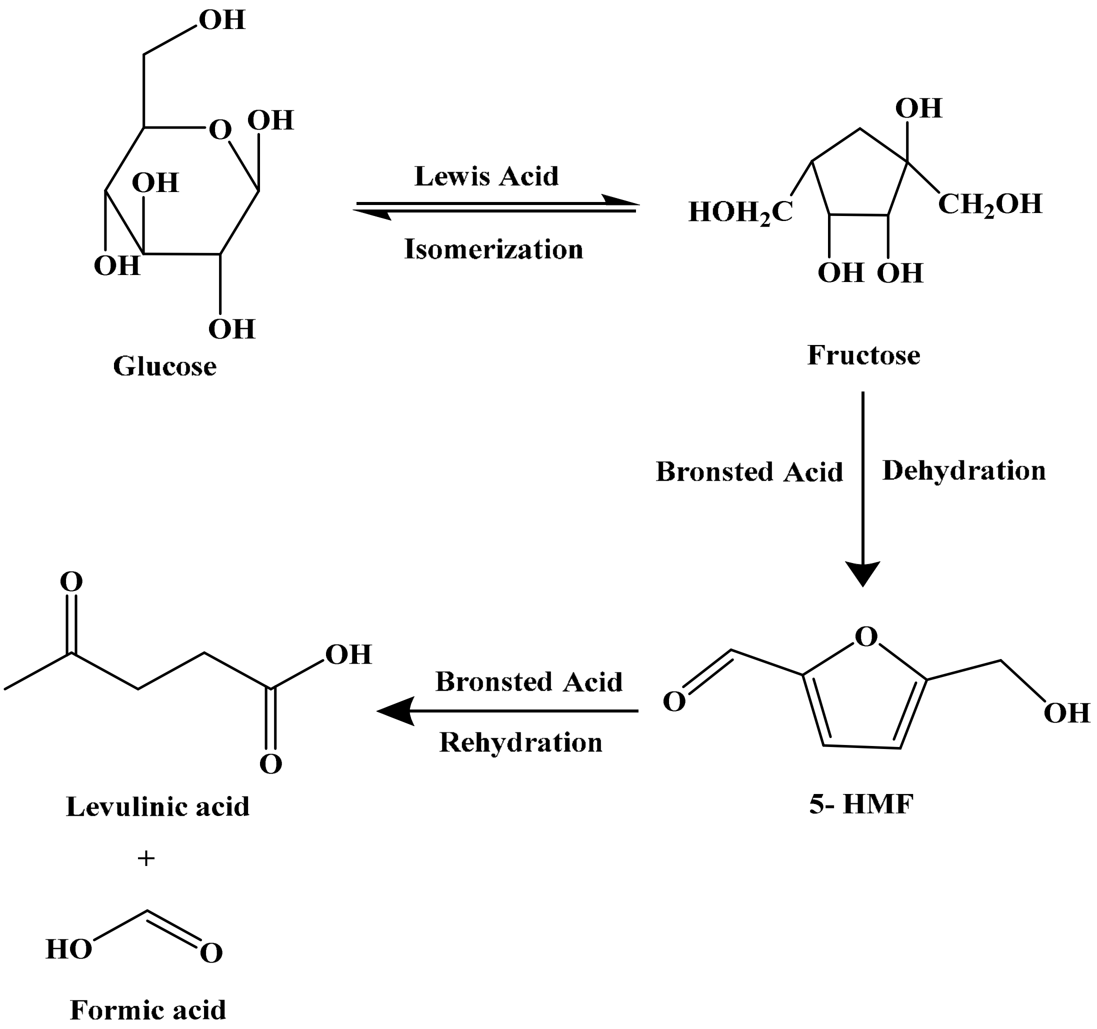

Scheme 1. Mechanistic representation of formation of LA and formic acid from Glucose.

Till date, several studies have been reported on conversion of lignocellulosic biomass to LA using mineral acids,[7] metal sulfates[8] and heteropoly acid as catalyst. Despite the good yield, the above processes possess the disadvantage of product separation, recycling of catalyst, reactor corrosion, selectivity to the desired products and economically expensive heteropoly acids. Recently, ionic liquids have been reported as solvents as well as catalysts for catalytic transformation of cellulose to LA.[9] Ionic liquids are also known as the designer solvents due to their unique properties of low vapor and task specificity that can be achieved by the modification of cation and anion.[10–13] Tao et al. recently reported functionalized carboxylic acid based ionic

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liquids for alcoholysis reaction.[14] Yu et al. reported high glucose conversion using Bornsted acidic ionic liquid as a catalyst and metal chlorides as a co-catalyst to HMF.[15] Amin et al. reported the conversion of glucose to LA using dual Bronsted and Lewis acidic ionic liquid with tetrachloroferrate as an anion.[16] However, available literature on glucose conversion to LA still lacks a detailed study of the effect of transition metal ions (chlorides, sulfates, and nitrates) as co-catalyst along with the ionic liquid as catalyst.

In this study, ionic liquids with varied functional groups (IL-SO_3H, IL-COOH, IL-OH) were employed in catalytic conversion of glucose to LA. Moreover, the effect of metal salts (MSO_4, MCl, MNO_3) in combination with the ionic liquids has been investigated. The effect of various reaction conditions like time and temperature was also investigated on the glucose conversion to LA. The recyclability of the ionic liquids was also investigated for the cost-optimization of the process.

2. Materials and Methods

Glucose, fructose (99%), LA (99%), 5-hydroxymethylfurfural (98%) (HMF), Formic acid (99%) (FA) were purchased from Fischer Scientific, India. 1, 6-Anhydro-ß-D-glucose (99%), 5-chlorovaleric acid (96%) was purchased from TCI chemicals, USA. 4-chloro 1-butanol (85%), 1-methylimidazole (99%), 1,4-butane sultone (99%) were purchased from Alfa Aesar, China. Diethyl ether, $FeCl_3$ (97%), $CoCl_2$ (97%), $NiCl_2$ (98%), $CuCl_2$ (98%) and $ZnCl_2$ (97%) were purchased from Merck, India. $FeSO_4.7H_2O$ (98%), $CoSO_4.7H_2O$ (97%), $NiSO_4.6H_2O$ (97%), $CuSO_4.5H_2O$ (99%) and $ZnSO_4.7H_2O$ (95%) were purchased from, Sigma Aldrich and BDH chemicals. Metal nitrates $Fe(NO_3)_2.7H_2O$ (99%), $Co(NO_3)_2.7H_2O$ (97%), $Ni(NO_3)_2.6H_2O$ (98%), $Cu(NO_3)_2.5H_2O$ (99%) and $Zn(NO_3)_2.7H_2O$ (96%) were purchased from CDH chemicals. 1-

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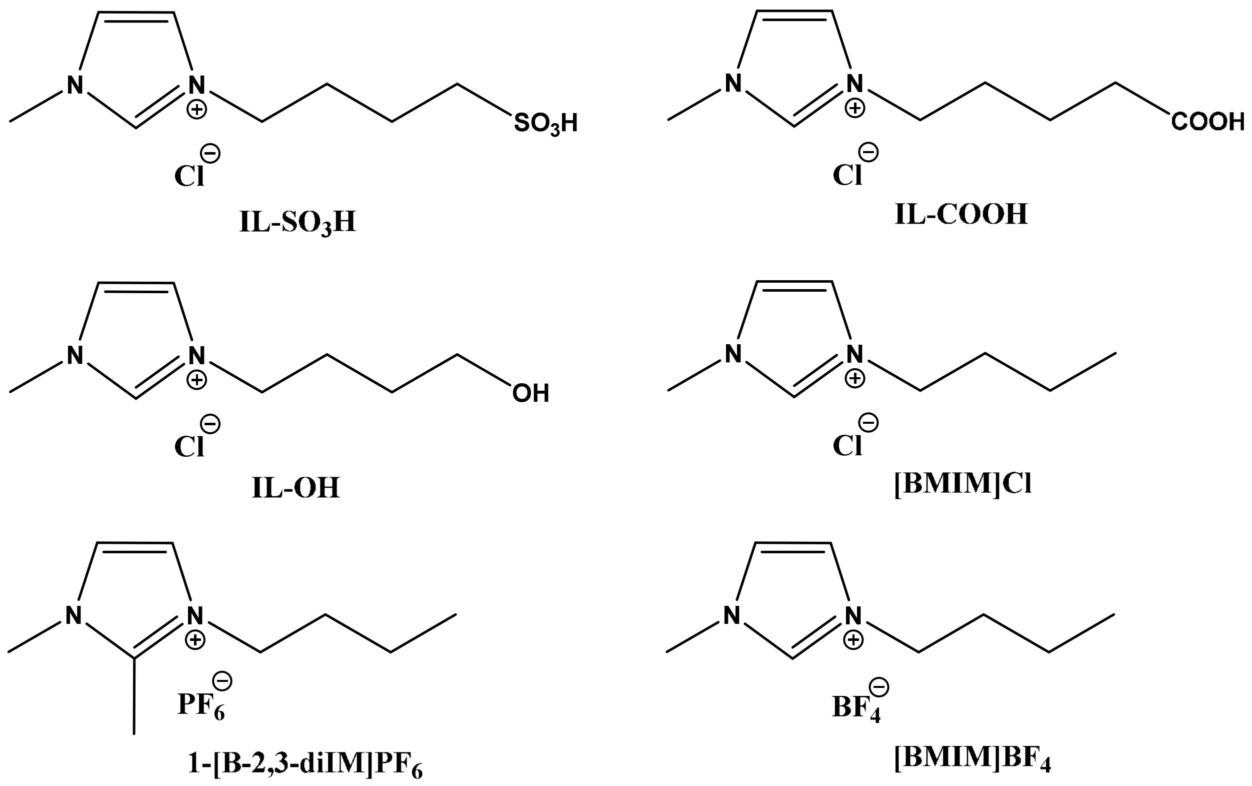
Butyl-2, 3-dimethyl-imidazolium hexafluorophosphate (98%), 1-Butyl-3-methyl-imidazolium tetrafluoroborate (98%) were purchased from Merck, Germany.

2.1 Synthesis of functionalized ionic liquids

A series of Bronsted acid functionalized ionic liquids were synthesized as shown in **Scheme 2** for the catalytic conversion of glucose to LA and their catalytic activity was compared with literature reported ionic liquids.



Scheme 2. Chemical structures of the functionalized ionic liquids used in this study.

2.1.1 1-(4-sulfonic acid) butyl-3-methylimidazolium chloride

Sulfonic acid functionalized ionic liquid was synthesized according to the reported literature.[17–22] 1-Methyl imidazole and 1, 4 butane sultone in 1: 1.2 equimolar amounts were mixed in a flask with toluene as a solvent and stirred at 80 °C for 6 h to obtain the solid zwitterion. Zwitterionic solid was washed three times (8 mL×3) with diethyl ether and dried under vacuum at room

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temperature for 8 h. The resultant zwitterion was neutralized by adding equimolar amount of hydrochloric acid with stirring at room temperature for 8-9 h. The yield of the synthesized ionic liquid, IL-SO_3H, was obtained to be 89%. **^{1}H NMR**: (400 MHz, D_2O): δ (ppm) 1.67-1.74 (m, 2H), 1.95-2.02 (m, 2H), 2.88-2.92 (t, 2H), 3.86 (s, 3H), 4.19-4.23 (t, 2H), 7.41-7.47 (d, 2H), 8.71 (s, 1H). **^{13}C NMR**: (100 MHz; D_2O): δ (ppm) 20.84, 28.02, 35.58, 48.80, 49.98, 122.06, 123.55, 135.88.

2.1.2 1-(5-Carboxypentyl)-3-methylimidazolium Chloride

Carboxylic acid functionalized ionic liquid was synthesized by stirring the mixture of equimolar amount of 1-methylimidazole and 5-chlorovaleric acid at 70 °C for 12 h. The resultant pale yellow mixture was washed with ether (50 mL × 3). The yellow sticky product was dried under vacuum at 40°C overnight. The yield of the synthesized ionic liquid, IL-COOH, was found to be 92%. **^{1}H NMR**: (400 MHz; D_2O): δ (ppm) 1.52-1.58 (m, 2H), 1.85-1.89 (m, 2H), 2.35-2.39 (t, 2H), 3.87 (s, 3H), 4.18-4.22 (t, 2H), 7.43-7.49 (d, 2H), 8.68(s, 1H). **^{13}C NMR**: (100 MHz, D_2O): δ (ppm) 20.98, 28.65, 35.60, 35.81, 49.09, 122.17, 123.60, 135.88, and 178.01.

2.1.3 Synthesis of 1-(4-Hydroxybutyl)-3-methylimidazolium Chloride

Ionic liquid containing OH as functional group was synthesized according to the reported procedure by.[23] 1-Methylimidazole and 4-chloro-1-butanol were mixed in 1:1.2 molar ratios and stirred at 80 °C for 5 h. The desired ionic liquid was obtained in a viscous liquid form and the unreacted materials were washed off by diethyl ether (8 mL × 3). The reminiscent diethyl ether was removed under reduced pressure at room temperature. The yield of the obtained colorless viscous ionic liquid, IL-OH, was found to be 89%. **^{1}H NMR** (400 MHz, D_2O) δ (ppm) 1.59-1.62 (2H, m, CH_2), 1.95-1.98 (m, 2H, CH_2), 3.94 (s, 3H, N–CH_3), 3.63-3.66 (t, 2H, N–CH_2), 4.28 (dt,

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2H, CH_2-OH), 7.50, 7.56 [two singlets, 2H, C(4,5)–H], 8.74 [s, 1H, C(2)–H]. **^{13}C NMR**: (100 MHz, D_2O): δ (ppm) 26.24, 28.00, 35.59, 49.29, 60.88, 122.21, 123.04 and 135.93.

2.1.4 Synthesis of [BMIM]Cl

Ionic liquid [BMIM]Cl was synthesized following the reported literature.[24] 1-methyl imidazole and 1-chlorobutane was stirred at 60 °C for overnight. The unreacted material was washed by diethyl ether and acetonitrile. The diethyl ether was removed by reduced pressure followed by heating at room temperature. The resultant ionic liquid was characterized using ^{1}H NMR and ^{13}C NMR prior to use. **^{1}H NMR** (400 MHz, D_2O) δ (ppm) 0.797 (3H, t, CH_3), 1.18 (m, 2H, CH_2), 1.707 (m, 2H, CH_2), 3.75 (s, 3H, N–CH_3), 4.03-4.08 (t, 2H, N–CH_2), 4.60 (s, 2H, CH_2-OH), 7.29-7.34 [two singlets, 2H, C(4,5)–H], 8.584 [s, 1H, C(2)–H]. **^{13}C NMR**: (100 MHz, D_2O): δ (ppm) 12.81, 18.84, 31.32, 35.75, 49.28, 122.22, 123.49 and 135.57.

2.2 Catalytic activity tests in Glucose conversion to LA

Catalytic conversion of glucose to LA was carried out in a 25 mL autoclave by heating aqueous reaction mixture in the temperature of 140-175 °C. In a typical reaction, 0.56 mmol glucose, 1.8 wt% metal salts and 1 g of aqueous solution of the ionic liquid were charged into the autoclave. After the reaction, heating was terminated and reaction was quenched by cooling the autoclave in an ice bath. During the separation of the product, viscosity of the reaction mixture was reduced by adding some amount of the distilled water. Recycling of the ionic liquids was done as described in the reported literature.[4,25,26]

2.3 Product analysis from HPLC

Quantitative analysis of the liquid sample was performed using high pressure liquid chromatography (HPLC). The liquid samples were collected from the reactions aliquot and the samples were filtered by using cellulose acetate membrane filters (0.2 µm) and analyzed by

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Agilent HPLC using HPX-87H column equipped with RID using 5mM sulfuric acid as the mobile phase.

Conversion of the glucose was estimated according to the Eq. (1):

Conversion of glucose (%) = {(Initial no of moles of glucose − remaining moles of the glucose after reaction) / Initial moles of the glucose added} $*$ 100% (1)

Yield of LA was estimated according to Eq. (2):

Yield of LA (%) = (Moles of LA obtained/ Initial moles of Glucose) * 100% (2)

2.4 Determination of acidity of ionic liquids using UV–vis spectroscopy

The Bronsted acid strength of the synthesized ionic liquids was determined using Hammett function. Solution of 4-nitroaniline was used as indictor to trap the dissociated acidic proton of ionic liquids in water using literature reported procedure.[24,27–32] The acidity function (H_o) value was estimated according to Eq. (3):

$$Ho = pK\,(I)_{aq} + \log\left(\frac{[I]}{[IH]^{+}}\right) \quad (3)$$

Where $pK(I)_{aq}$ is the pKa value of the indicator, and [I] and [IH^+] are the molar concentrations of unprotonated and protonated forms of the indicator in the solvent, respectively. The absorbance of the probe (4-nitroaniline solution) and probe in presence of different concentrations of ionic liquids was recorded at 380 nm using HALO DB-20 UV-visible double beam spectrophotometer.

3. Results and discussion

3.1 Screening of ionic liquids for glucose conversion to LA

The effect of different functional group on the conversion of glucose and selectivity of LA was studied at 155 °C for 5 h as shown in the **Figure 2**. From the **Figure** 2, it is evident that Bronsted acid functionalized ionic liquid (IL-SO_3H, IL-COOH, IL-OH) showed higher catalytic conversion of glucose to LA as compared to the non-functionalized ionic liquids. Among

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Bronsted acidic ionic liquids, IL-SO_3H showed maximum conversion which can be attributed to its highest acidity as shown in **Table 1** and **Figure 1**, and possess maximum Bronsted acidity with minimum value of Hammett function (H_0).

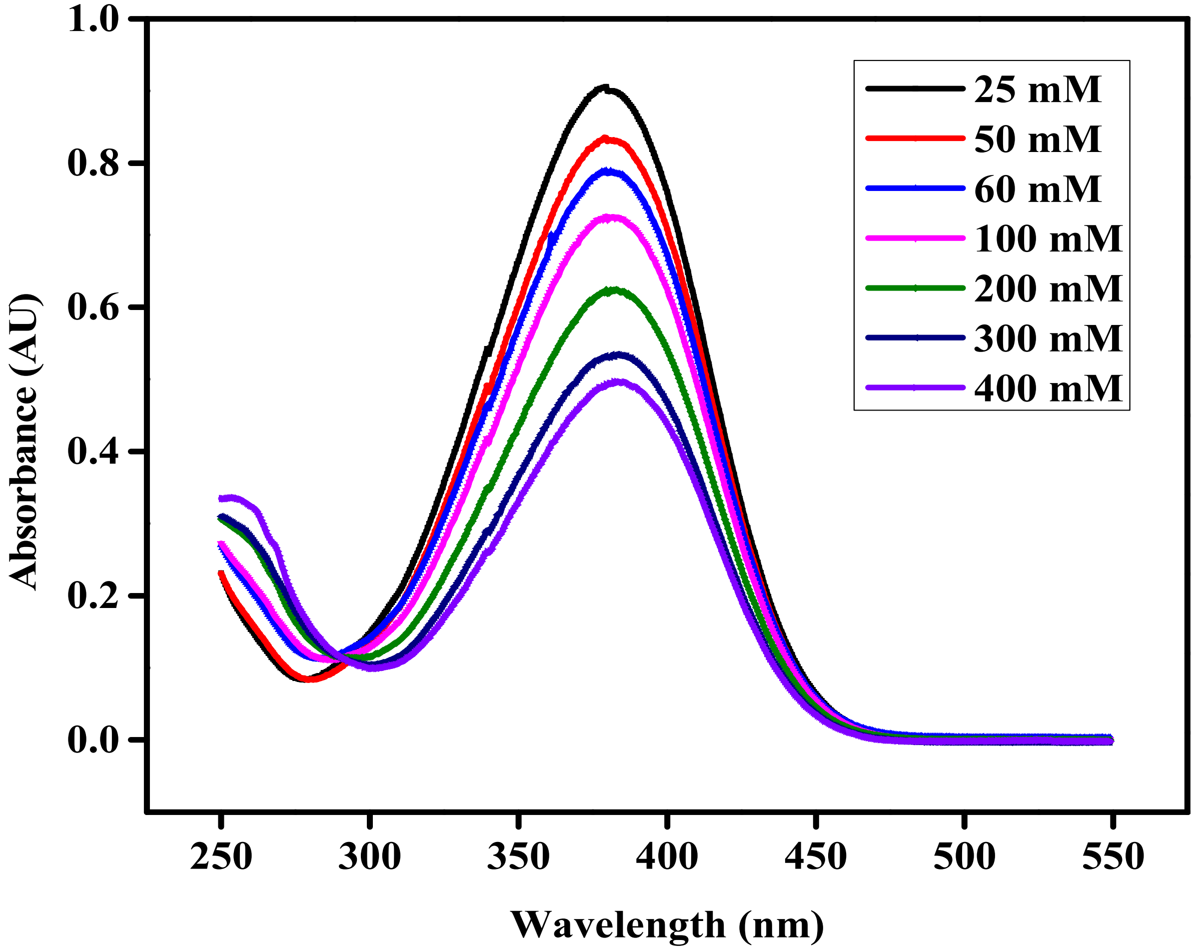

Figure 1. Absorption spectra of 4-nitroaniline in presence of various concentration of IL-SO_3H in H_2O.

Further, the highly acidic proton of IL-SO_3H and chloro anion create polar environment through hydrogen bonding that is required for glucose conversion to LA.[33] Among non-functionalized ionic liquids [BMIM]Cl gave higher conversion of glucose but low selectivity of the LA due to the absence of the Bronsted acidity. The presence of non-interacting hydrophobic cation in [BMIM]Cl results in free chloro groups to be more reactive than the BF_4^- and PF_6^- anion.

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Table 1. The Hammett acidity function (H_o) values of all Bronsted acidic ionic liquids in water.

ILs	**Amax**	**[I](%)**	**$[IH^+]$%**	**$[H_o]$**
None	1	100	0	-
IL-SO_3H	0.83	93.29	6.71	1.97
IL-COOH	0.84	94.93	5.07	2.12
IL-OH	0.86	97.13	2.87	2.39

From the **Figure 2**, the order of activity is observed to be IL-SO_3H>IL-COOH>IL-OH>[BMIM]Cl>1-[B-2,3-diIM]PF_6>[BMIM]BF_4>Blank. This trend can be explained by the Hammett function of the acidic ionic liquid and reactivity of the anion of non-functionalized ionic liquid. Thus, it can be concluded that IL-SO_3H having higher Bronsted acidity results in almost 100% conversion of glucose with the yield of LA as high as 46.60%.

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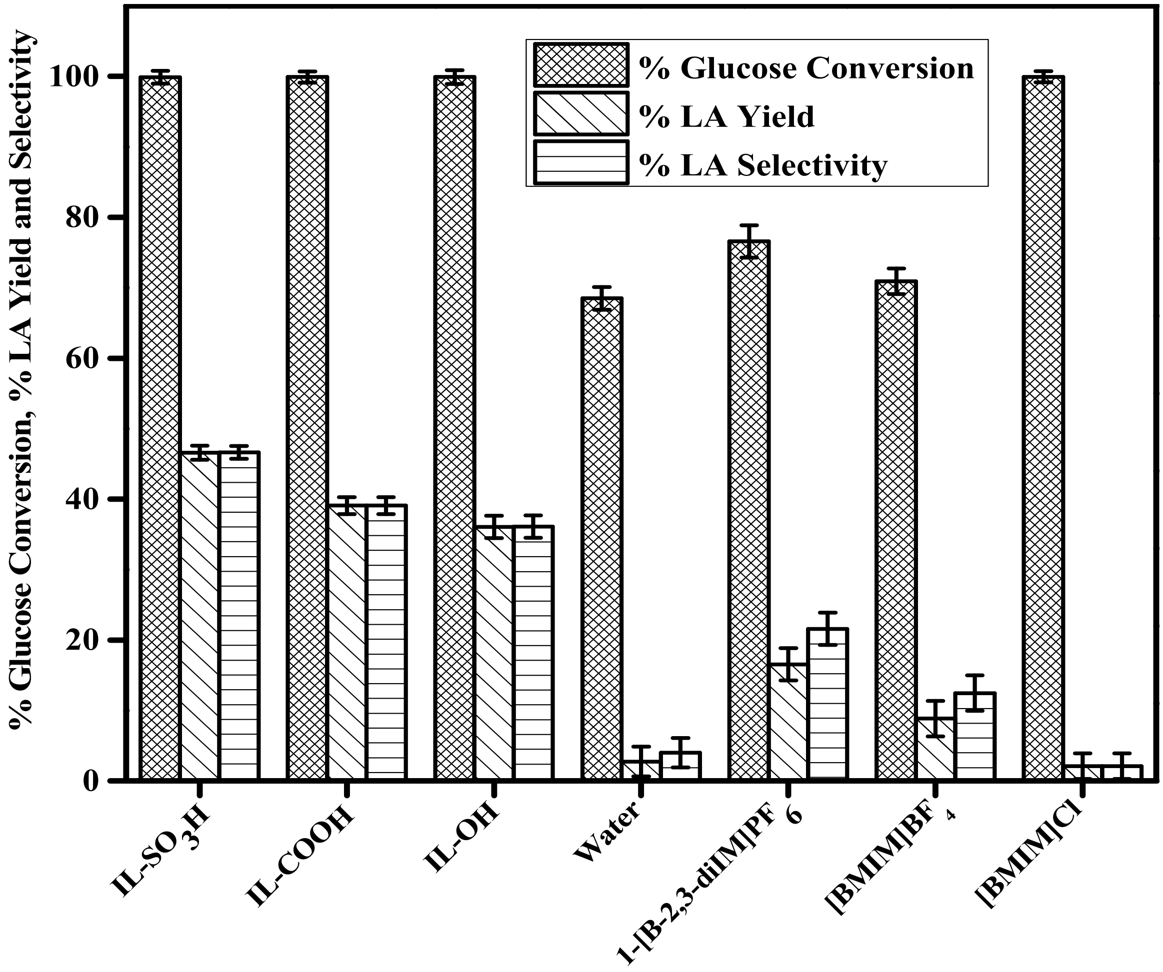

Figure 2. Effect of different ionic liquids on catalytic conversion of glucose. Reaction conditions: 100 mg glucose, 400 mg ionic liquid, 0.6 mL water, T=155 °C, t= 5 h.

3.2 Effect of temperature on LA yield

The effects of reaction parameters were studied using IL-SO$_3$H as the catalyst to determine the optimum reaction conditions for the glucose conversion to LA. The reactions were carried out in a temperature range of 140-175 °C. From **Figure 3**, it is evident that 155 °C reaction temperature and reaction time of 5 h are optimum reaction conditions for glucose conversion to LA. The maximum glucose conversion and LA yield achieved are 99.90% and 46.60% respectively at 155 °C and 5 h. **Figure 3** illustrates the significant effect of temperature and time on the yield of LA.

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At lower reaction temperature of 140 °C, the maximum glucose conversion and yield of LA were obtained to be 99% and 43%, respectively. This can be attributed to the formation of HMF at lower temperature rather than rehydrated product LA that requires higher reaction temperature. Whereas, at higher temperatures of 165 °C and 175 °C the yield of LA further decreased due the formation of humins and other side products.[34,30] Hence, it can be concluded that 155 °C is the optimum temperature for glucose conversion to LA since at lower temperatures HMF resist to rehydrate to LA and at higher temperature side reactions occur.

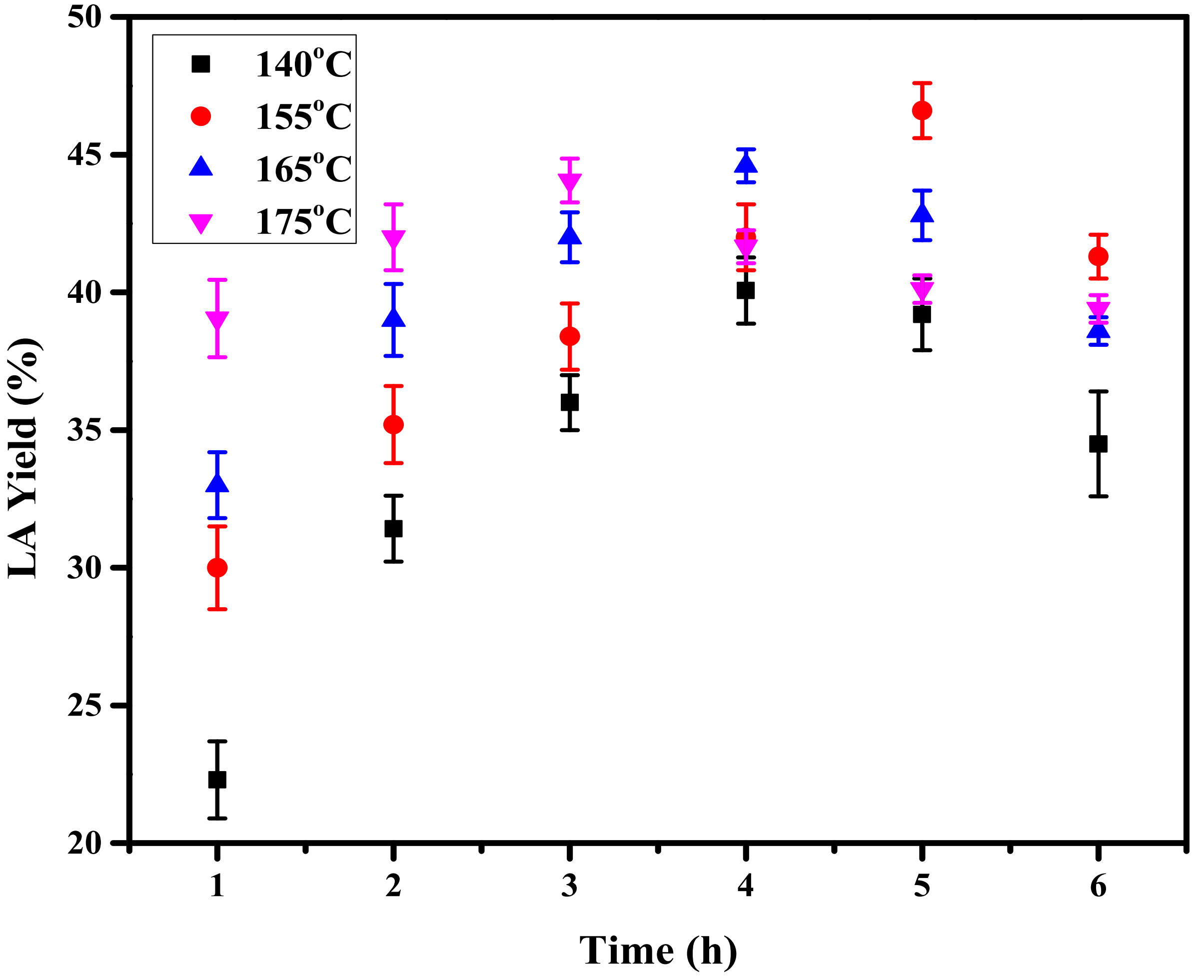

Figure 3. Effect of reaction temperature and reaction time on conversion of glucose to LA using IL-SO_3H as the catalyst. Reaction conditions: 100 mg glucose, 400 mg ionic liquid, 0.6 mL water.

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3.3 Effect of transition metal chlorides as co-catalysts on LA yield

A series of reactions were performed in order to gain a better perspective of the effect of the metal chlorides as a co-catalyst with the ionic liquid, IL-SO_3H. Around 1.8 wt% metal chloride salts were added in the reaction mixture as co-catalyst and the reaction was conducted for 5 h at 155 °C reaction temperature. **Table 2** summarizes the performance of the IL-SO_3H with different transition metal chlorides as co-catalyst in the conversion of glucose into LA. From **Table 2**, it is clear that in absence of the metal chlorides, 100% glucose conversion and 46.60% yield of the LA was obtained at 155 °C reaction temperature within 5 h reaction time. Moreover, in presence of only water, around 68.52% glucose conversion was obtained with only 2.76% yield of levulinic acid (LA). However, in presence of catalytic amounts of metal chlorides like $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$, higher catalytic activity was obtained as compared to IL-SO_3H. In case of $NiCl_2$, the maximum LA yield of 49.65% was obtained with LA selectivity as high as 49.68%. However, not all metal chlorides were effective co-catalyst. The conversion of glucose and yield of LA using these metal chlorides was found in the order: Water<$FeCl_3$<IL-SO_3H<$CuCl_2$<$CoCl_2$<$ZnCl_2$<$NiCl_2$ under the same reaction conditions. While the selectivity to LA followed the order: Water<$FeCl_2$<IL-SO_3H<$CuCl_2$<$CoCl_2$<$ZnCl_2$<$NiCl_2$. Based on the results shown in **Table 2,** it is evident that IL-SO_3H zwitterionic form is highly stable and it shows acidity via *in situ* HCl. This is evident from the experimentally obtained incremented yield of LA (46.60%) at 155 °C within 5 h reaction time. However, addition of similar types of the metal chloride salts cannot affect significant changes to the LA yield except in the case of $NiCl_2$. These results further imply that nickel acts as an active metal as a co-catalyst and hence, plays important role in glucose conversion and LA yield as compared to other transition metals used in this study. Moreover, in addition to the *in situ* formation of HCl, metal chlorides in

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aqueous solution similarly produce metal hydrate complexes. Hence, regeneration possibility of the similar acidity during aqueous phase reaction mixture causes the less affectivity of the metal chlorides in the reaction system. A plausible reaction mechanism is proposed based on the catalytic activity results as shown in **Figure 4** to summarize all the possible observations and experimental outcomes in order to explain the effect of these metal chlorides (Co, Ni, Cu and Zn) as co-catalysts in combination with Bronsted acidic ionic liquids.[31] The metal salts in the complex form $[MCl_x(H_2O)_n]^{(x-2)-}$ bind with the –OH groups of the glucose molecule through the hydrogen bonding. Similar mechanism is followed in case of $FeCl_3$ as the co-catalyst in the complex form $[MCl_x(H_2O)_n)]^{(x-1)-}$. The hydrated metal salt complex promotes the rapid conversion of the α-anomers of glucose to the β-anomers through hydrogen bonding between Cl-atom of the complex and –OH group of glucose. However, the extent of hydrogen bonding capability of Cl-atom is not high enough to alter the process to a greater extent. Hence, metal halides were also found to be less active in aqueous phase, overall outcomes of the reaction were also mentioned in earlier literature reports.[35]

Table 2. Effect of metal chlorides in conversion of Glucose and yield of LA.

Catalysts	**LA Yield (%)**	**LA Selectivity (%)**	**Glucose Conversion (%)**
Water	2.76	4.02	68.52
IL-SO_3H	46.60	46.64	99.90
IL-SO_3H + $FeCl_3$	37.24	37.29	99.86
IL-SO_3H + $CoCl_2$	47.32	47.35	99.92
IL-SO_3H + $NiCl_2$	49.65	49.68	99.93
IL-SO_3H + $CuCl_2$	47.08	47.10	99.94
IL-SO_3H + $ZnCl_2$	48.28	48.28	99.99

Reaction conditions: 100 mg glucose, 400 mg ionic liquid, 0.6 mL water, T=155 °C; t= 5 h; amount of MCl_x used= 1.8 wt%.

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3.4 Effect of the transition metal sulfates as co-catalysts on LA yield

Furthermore, to investigate the effect of metal sulfates as co-catalyst, along with IL-SO_3H on the conversion of glucose and yield of LA, a series of the transition metal sulfate salts were added into the reaction system to carry out the catalytic reactions at a reaction temperature of 155 °C for 5 h. Several combinations of cations and anions in the reaction system showed significant effects on LA production as shown in **Table 3**. The conversion of glucose followed the order: Water<$CoSO_4.7H_2O$<$FeSO_4.7H_2O$<$CuSO_4.5H_2O$<IL-SO_3H<$ZnSO_4.7H_2O$<$NiSO_4.6H_2O$. While the selectivity to LA followed the order: Water<$CoSO_4.7H_2O$<$FeSO_4.7H_2O$<$CuSO_4.5H_2O$<IL-SO_3H<$ZnSO_4.7H_2O$<$NiSO_4.6H_2O$. The catalytic activity trends of the metal sulfates were in the following order $CoSO_4.7H_2O$<$FeSO_4.7H_2O$<$CuSO_4.5H_2O$<$ZnSO_4.7H_2O$<$NiSO_4.6H_2O$. The yield of LA varied from 40.37% to 56.33% in the presence of these metal sulfates as co-catalysts as compared to only IL-SO_3H catalyzed reactions (46.60%). The first three metal salts show negative synergy effect on the yield of LA. Among the metal sulfates, the IL-SO_3H-$NiSO_4.6H_2O$ system showed highest synergistic effect in terms of LA yield.

Table 3. Effect of metal sulfates in conversion of Glucose and yield of LA.

Catalysts	**LA yield (mol %)**	**LA Selectivity (%)**	**Glucose conversion (mol%)**
Water	2.76	4.02	68.52
IL-SO_3H	46.60	46.64	99.90
IL-SO_3H + $FeSO_4.7H_2O$	41.09	41.25	99.61
IL-SO_3H + $CoSO_4.7H_2O$	40.37	40.38	99.97
IL-SO_3H + $NiSO_4.6H_2O$	56.33	56.37	99.92
IL-SO_3H + $CuSO_4.5H_2O$	41.45	41.54	99.77
IL-SO_3H + $ZnSO_4.7H_2O$	52.30	52.35	99.90

Reaction conditions: 100 mg glucose, 400 mg ionic liquid, 0.6 mL water, T=155 °C; t= 5 h, amount of $MSO_4.nH_2O$ used= 1.8 wt%.

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Furthermore, as is evident from **Table 3**, the effect of metal sulfates as co-catalyst more predominant in this reaction as compared to the metal chlorides (as shown in **Table 2**). The higher activity of the sulfates can be attributed to the reduced side product formation in this reaction. Moreover, these observations indicate that the Bronsted acidity alone is not the sole factor affecting the glucose conversion to LA. The anions play significant roles in the glucose dehydration and rehydration process to yield LA as per the plausible mechanism shown in **Figure 4**. The sulfate salts in the complex form $[M(SO_4)_x(H_2O)_n]^{(2x-2)-}$ co-ordinate with the –OH groups of the α-anomers of glucose by forming stronger hydrogen bonds than the chloride salts. Consequently, metal sulfates play significant role in the rapid conversion of the α-anomers to β-anomers to facilitate the dehydration process.

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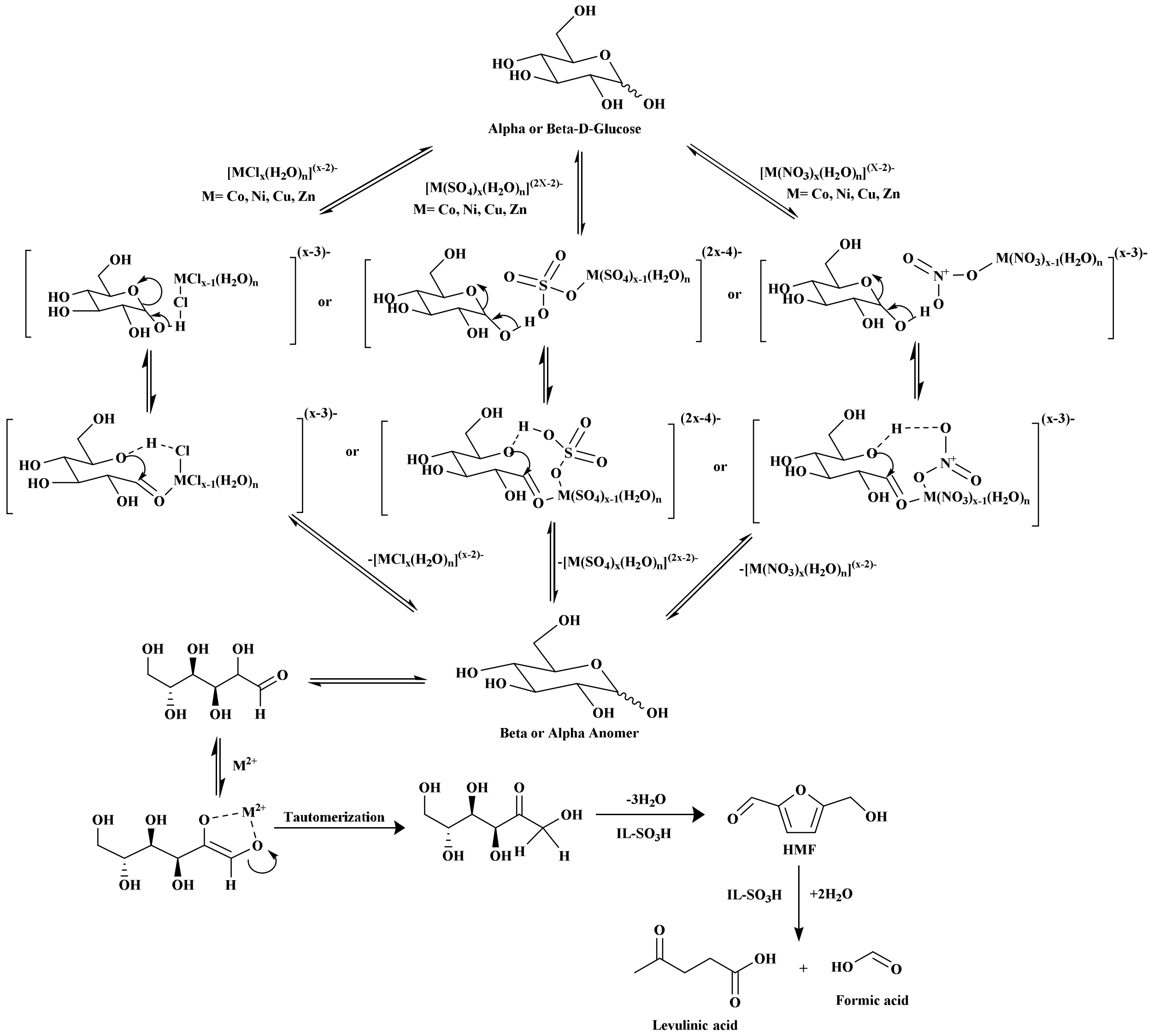

Figure 4. Plausible reaction mechanism of glucose conversion to LA and formic acid in presence of metal salts.

3.5 Effect of transition metal nitrates as co-catalysts on LA yield

To investigate the role of metal nitrate salts as co-catalyst with IL-SO$_3$H, a series of reactions were performed at a reaction temperature of 155 °C for 5 h. The addition of the transition metal nitrates of Fe, Co, Ni, Cu and Zn with IL-SO$_3$H, resulted in negative synergistic effect on the yield of LA as shown in **Table 4**. The negative synergistic effect for the metal nitrates can be attributed to the formation of more side products via multiple side reactions. The co-catalytic

DOI: 10.1039/C7NJ03146G

effect of the Cu, Fe, Co and Zn metal nitrates effectively decreased the yield of the LA due to the formation of the other side products during the reaction which is unfavorable for the formation of the LA. The decreased yield during the LA synthesis from the glucose can be attributed to the formation of soluble polymers and insoluble humins, dark-colored tarry solids. The maximum yield of the LA drop from 47.16% in case of Ni to 37.29% in case of Fe. The conversion of glucose followed the order: Water <$CuNO_3.5H_2O$ <$FeNO_3.7H_2O$ <$CoNO_3.7H_2O$ <$ZnNO_3.7H_2O$ <IL-SO_3H <$NiNO_3.6H_2O$. While the selectivity of LA followed the order: Water <$CuNO_3.5H_2O$ <$FeNO_3.7H_2O$ <$CoNO_3.7H_2O$ <$ZnNO_3.7H_2O$ <IL-SO_3H <$NiNO_3.6H_2O$. The transition metal nitrate salts in the form $[M(NO_3)_x(H_2O)_n]^{(x-2)-}$ bind less weakly with the –OH groups of the α-anomers of glucose. Hence, the rate of their conversion to the β-anomers decreases and consequently, the conversion of glucose to LA also decreases. Moreover, nitrates are inherently weaker ligands to form stable coordination bond with the α-anomer. In general, nitrates possess strong oxidizing property and can oxidize glucose to other insoluble products, which is effectively unfavorable for the conversion of glucose into LA.[26] The obtained glucose conversion in case of nitrates were found to be comparable with the metal chlorides and sulfates with a distinct change in yield of LA. This indicates that the converted glucose formed more side products other than LA. This is also evident from the decreasing glucose conversion and LA yield as shown in **Table 4**.

Table 4. Effect of metal nitrates in conversion of Glucose and yield of LA.

Catalysts	**LA Yield (Mol%)**	**LA Selectivity (%)**	**Glucose Conversion (Mol%)**
Water	2.76	4.02	68.52
IL-SO_3H	46.60	46.64	99.90
IL-SO_3H + $FeNO_3.7H_2O$	37.29	40.15	92.87

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IL-SO_3H + $CoNO_3.7H_2O$	41.10	41.17	99.82
IL-SO_3H + $NiNO_3.6H_2O$	47.16	47.21	99.89
IL-SO_3H + $CuNO_3.5H_2O$	37.98	38.56	98.49
IL-SO_3H + $ZnNO_3.7H_2O$	43.51	44.31	98.18

Reaction conditions: amount of MCl_x used= 1.8 wt%; T=155 °C; t= 5 h; amount of $MNO_3.nH_2O$ used= 1.8 wt%.

3.6 Reusability of catalyst

Reusability of the ionic liquid catalyst was investigated in the glucose conversion to LA with IL-SO_3H as well as with IL-SO_3H with Ni metal salt. Ionic liquids were regenerated following the earlier reported literature.[4,10,26] After completion of the reaction, the reaction mixture was diluted with 2 mL deionized water to reduce the viscosity. The products were extracted using ethyl acetate and the rest of the solution contained ionic liquid-water or ionic liquid-Ni metal salt mixture. Water was removed from the ionic liquid or ionic liquid-Ni metal salt mixture by drying overnight under reduced pressure (0.01 Torr) at 120 °C. The recovered ionic liquids or ionic liquid-Ni metal salt mixtures were subjected to further catalytic runs and the results are summarized in **Table 5**. Glucose conversion and yield of LA were almost retained till the first three recycle reactions. The decrease in recyclability in the further recycle experiments can be attributed to the increasing water content as well as side products accumulating in each step of the reaction, which required harsh recycling conditions.

Table 5. Recyclability of IL-SO_3H and IL-SO_3H with Ni metal salt.

No. of Runs	LA Yield [a] (Mol%)	LA Selectivity [a] (%)	Glucose Conversion [a] (Mol%)	LA Yield [b] (Mol%)	LA Selectivity [b] (%)	Glucose Conversion [b] (Mol%)
Fresh run	46.60	46.64	99.90	56.33	56.37	99.92
Recycle 1	42.40	44.25	95.80	51.46	55.17	93.27

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Recycle 2	39.60	46.37	85.40	47.86	57.70	82.94
Recycle 3	37.30	46.33	80.50	43.92	55.82	78.67

Reaction conditions: Reaction temperature=155 °C; reaction time= 5 h.

[a] LA yield and selectivity and conversion of glucose in presence of only IL-SO_3H; [b] LA yield and selectivity and conversion of glucose in presence of only IL-SO_3H with Ni metal salt.

4. Conclusions

In this study, glucose conversion to LA was investigated using multifunctional ionic liquids containing -OH, -COOH and -SO_3H groups. The ionic liquids were synthesized in the laboratory and characterized using spectroscopic techniques like ^1H NMR and ^{13}C NMR. From the detailed catalytic activity study, -SO_3H functionalized ionic liquid was found to be the most efficient catalyst in terms of LA selectivity and high conversion of glucose. The parameters like reaction temperature and reaction time were optimized and maximum LA yield of 46.60% was obtained using IL-SO_3H at 155 °C temperature within 5 h. From the recyclability experiments, IL-SO_3H and combination of IL-SO_3H with Ni metal salt were found to retain their catalytic activity upto 3 recycles. Furthermore, to investigate the effect of transition metal salts as co-catalysts along with the IL-SO_3H, a series of transition metal chlorides, sulfates and nitrates were added and the reactions were carried out at optimum reaction conditions. Metal sulfates showed predominant synergistic effect on the catalytic activity in terms of the LA yield as compared to the chloride and nitrate salts. Among these catalyst and co-catalyst combinations, IL-SO_3H-$NiSO_4$ showed highest catalytic efficiency with highest LA yield of 56.33% at 155 °C within 5 h reaction time with 56.37% LA selectivity. This study is highly beneficial for the development of an efficient catalytic system for glucose conversion into high value platform chemical.

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DOI: 10.1039/C7NJ03146G

Acknowledgements

Komal Kumar and Firdaus Parveen thanks University Grants Commission (UGC), India, for a research fellowship. Tanmoy Patra thanks the Council of Scientific and Industrial Research (CSIR) for research fellowship. Dr. Sreedevi Upadhyayula thanks Indian Institute of Technology Delhi for the research grants. The authors are also thankful to NRF (Nanoscale Research Facility) for providing High pressure liquid chromatography (HPLC) for the detection of LA yield and conversion of glucose.

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View Article Online
DOI: 10.1039/C7NJ03146G

Table of Contents

Efficient catalytic system comprised of Bronsted acidic ionic and Lewis acidic metal salts for hydrothermal glucose conversion to platform chemicals