A two-step approach for the catalytic conversion of glucose to 2,5-dimethylfuran in ionic liquids

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Lignocellulosic biomass is an attractive resource for producing transportation fuels, and consequently novel approaches are being sought for transforming the lignin and cellulosic constituents of biomass to fuels or fuel additives. Glucose, the monomer of cellulose, is a good starting material for exploring such chemistries. We report here the results of an investigation aimed at identifying catalysts for the dehydration of glucose to 5-hydroxymethylfurfural (HMF) dissolved in ionic liquids and the subsequent conversion of HMF to 2,5-dimethylfuran (DMF), a high-energy content product that could be used as a fuel or fuel additive. Heteropoly acids were found to be exceptionally active and selective catalysts for the dehydration of glucose. Nearly 100% yield of HMF could be achieved using 12-molybdophosphoric acid (12-MPA) in a solution of 1-ethyl-3-methylimidazolium chloride (EMIMCl) and acetonitrile. The addition of acetonitrile to EMIMCl suppressed the formation of humins from glucose. The high HMF selectivity achievable with heteropoly acid catalysts is ascribed to stabilization of 1,2-enediol and other intermediates involved in the dehydration of glucose and the avoidance of forming the 2,3-enediol intermediate leading to furylhydroxymethyl ketone (FHMK). Carbon-supported metals, and in particular Pd/C, were effective in promoting the hydrogenation of HMF dissolved in EMIMCl and acetonitrile to DMF. The following intermediates were observed in the hydrogenation of HMF to DMF: 5-methylfurfural (MF), 5-methylfurfyl alcohol (MFA), and 2,5-dihydroxymethylfuran (DHMF). The relative rate of formation and consumption of these compounds was explored by using each of them as a reactant in order to identify the reaction pathway from HMF to DMF. It was also observed that HMF produced *via* glucose dehydration could be converted to DMF without isolation, if the dehydration catalyst, 12 MPA, was replaced by the hydrogenation catalyst, Pd/C. This two-step catalytic approach provides the basis for completely converting glucose to HMF and further converting HMF to DMF.

1 Introduction

It has been estimated that up to one third of the US need for transportation fuels could be obtained from lignocellulosic biomass.[1] One of the approaches for producing fuels from this renewable resource involves its pretreatment in order to access its cellulosic component, followed by hydrolysis of the cellulosic and hemicellulosic components to produce sugars that are subsequently converted to fuel components by either fermentation or chemical reaction. Since the first of these three steps is demanding, various approaches have been examined for the pretreatment of biomass, *e.g.*, treatment with weak acid,[2] *etc.* Recent studies have shown that a possible alternative is the dissolution of lignocellulosic biomass in an ionic liquid (IL).[3] What make this approach attractive is that all of the components of biomass—cellulose, hemicelluloses, and lignin—are soluble in ILs, enabling one to consider the conversion of dissolved lignocellulosic biomass to fuels without the need to isolate the dissolved cellulosic and lignin components. The initial efforts made in this direction are encouraging and provide motivation for further research.[4] For example, it has been shown that cellulose and/or sugars dissolved in ILs can be hydrolyzed and dehydrated by acid catalysis to produce a mixture of glucose and 5-hyroxymethylfurfural (HMF).[5] $CrCl_2$ and $CrCl_3$ have been shown to be particularly effective catalysts for promoting the dehydration of glucose to HMF with near 85% selectivity.[6] Aqueous phase dehydration of sugars to HMF has also been studied extensively.[7] While HMF is not an attractive fuel component, it can be used as a starting point to produce a variety of potential furan derivatives and chemical intermediates.[8] The most attractive of these is 2,5-dimethylfuran (DMF), which has an energy content of 31.5 MJ L^{-1}, similar to that of gasoline (35 MJ L^{-1}) and 40% greater than that of ethanol (23 MJ L^{-1}).[9] To date, though, the conversion of HMF to DMF has only been investigated using an organic solvent, such as butanol.[10] Since HMF can be produced from glucose dissolved in an IL, it is of interest to establish whether this same reaction could be carried out in an IL. The aim of this present work was to identify catalysts for the conversion of IL-dissolved glucose into HMF in high yield using acid catalysts and to explore the extent to

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which HMF dissolved in an IL could be converted to DMF by metal catalyzed hydrogenation.

2 Results and discussions

2.1 Glucose dehydration

Seven liquid acid catalysts were screened for the dehydration of glucose in 1-butyl-3-methylimidazolium chloride (BMIMCl). In all cases the molar ratio of catalyst to glucose was 0.01. It should be noted that some of the acids were introduced as an aqueous solution, but the amount of water brought in to the BMIMCl solution constituted less than 266 ppm. As shown in Table 1, in the absence of added acid 8% of the dissolved glucose was converted to HMF, FHMK (furylhydroxymethyl ketone), LG (levoglucosenone), and humins. The addition of acid increased the overall conversion of glucose and altered the distribution of products formed. It is noted that for CH_3SO_3H, HCl, and CF_3SO_3H, 5-chloromethylfurfural (CMF) was formed in modest amounts, in addition to HMF, FHMK, LG, and humins. The formation of CMF was very likely due to acid-catalyzed substitution of Cl^- anions at the hydroxyl (OH^-) group of HMF. It is notable that in no case was there any evidence for the decomposition of HMF to levulinic and formic acids. Unreacted glucose was also observed in the products as well as a small amount of black powder, presumed to be humins derived from glucose. The amount of unreacted glucose was always less than that calculated as the difference between the amount of glucose submitted to reaction and the sum of all glucose-derived products observed. The selectivity to humins was estimated by assuming that any of the initial glucose submitted to reaction that did not appear in soluble products or unconverted glucose was converted to humins. The conversion of glucose to products depended on the composition of the liquid acid, decreasing in the order H_2SO_4 > CF_3SO_3H > CH_3SO_3H > CF_3COOH > HNO_3 > HCl > H_3PO_4. The selectivity to HMF plus CMF was also affected by acid composition, and decreased in the order H_3PO_4 > HCl > HNO_3 > CF_3COOH > CH_3SO_3H > H_2SO_4 > CF_3SO_3H. Further effects of acid composition were observed in the selectivity to FHMK, in which case the selectivity decreased in the order $H_2SO_4 \approx CF_3SO_3H$ > HCl > HNO_3 > CH_3SO_3H $\approx CF_3COOH$ > H_3PO_4. While a clear relationship between product selectivity and acid composition cannot be discerned, it is evident that acids resulting in high glucose conversion, such as H_2SO_4 and CF_3SO_3H, exhibit low selectivities to HMF and CMF, as well as moderate selectivities to FHMK and LG. Likewise, H_3PO_4, which exhibits low activity, is selective for the formation of HMF. The selectivity to humins decreased in the order CF_3SO_3H > $CF_3COOH \approx H_2SO_4$ > HNO_3 > HCl > CH_3SO_3H > H_3PO_4.

The second group of acid catalysts investigated were the heteropoly acids, 12-tungstophosphoric acid (12-TPA ($H_3PW_{12}O_{40}$)), 12-molybdophosphoric acid (12-MPA ($H_3PMo_{12}O_{40}$)), 12-tungstosilicic acid (12-TSA ($H_3SiW_{12}O_{40}$)), and 12-molybdosilicic acid (12-MSA ($H_3SiMo_{12}O_{40}$)), all of which are moderately strong acids.[11] While these catalysts are solids initially, they dissolved completely in BMIMCl, as well as other ILs. The glucose conversions observed (Table 1) using heteropoly acid catalysts were comparable to those observed with liquid acids, and decreased in the order of the decreasing acidity of the heteropoly acid.[11] The selectivity to HMF was generally higher than that observed with liquid acids, and none of the heteropoly acid catalysts produced CMF. FHMK formation was only observed with 12-TPA, whereas the selectivity to LG was comparable to that observed for liquid acids. Here too, a small amount of black solid was observed after reaction, presumed to be humins. The selectivity of glucose conversion to humins ranged from 7 to 14%.

12-MPA was selected for further investigation, since this catalyst produced a moderate conversion of glucose, 71%, and a high selectivity to HMF, 89% (see Table 1). Experiments were conducted to identify the effects of IL composition and the influence of adding a cosolvent. Fig. 1a shows glucose conversion of ~70% and a HMF selectivity of 90% were obtained using either EMIMCl (1-ethyl-3-methylimidazolium chloride) or BMIMCl (1-butyl-3-methylimidazolium chloride). However, utilization of BDMIMCl (1-butyl-2,3-dimethylimidazolium chloride) as the solvent reduced the glucose conversion to 57% and the

Table 1 Effect of catalyst composition on the dehydration of glucose in 1-butyl-3-methylimidazolium chloride (BMIMCl)

Entry	Catalysts	Conversion (%)	Selectivity (%)				
			HMF	FHMK	LG	CMF	Humins
1	None	8	65	27	5	0	3
Liquid acids							
2	H_2SO_4	93	66	17	1	0	16
3	CF_3SO_3H	87	46	16	5	12	21
4	HNO_3	56	77	9	2	0	12
5	CF_3COOH	58	75	7	2	0	16
6	HCl	53	62	11	6	21	14
7	CH_3SO_3H	73	58	14	5	12	11
8	H_3PO_4	13	95	1	0	0	4
Solid acids							
9	12-TPA	82	81	5	7	0	7
10	12-MPA	71	89	0	1	0	10
11	12-TSA	69	82	0	4	0	14
12	12-MSA	34	91	0	0	0	9

Reaction conditions: BMIMCl (15 mmol, 2.0 g); glucose (1 mmol, 180 mg); catalysts (0.01 mmol, total acid concentration); temperature (393 K); reaction time (180 min).
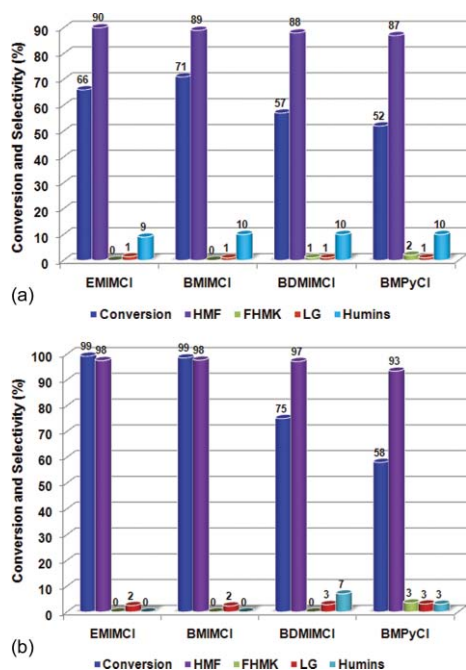
Fig. 1 (a) 12-MPA catalyzed glucose dehydration in different ionic liquids. Reaction conditions: ionic liquid (15 mmol, 2.0 g); glucose (1 mmol, 180 mg); 12-MPA (0.01 mmol, 18 mg); temperature (393 K); reaction time (3 h). (b) 12-MPA catalyzed glucose dehydration using acetonitrile as cosolvent in different ionic liquids. Reaction conditions: ionic liquid (15 mmol, 2.0 g); acetonitrile (18 mmol, 0.79 g); glucose (1 mmol, 180 mg); 12-MPA (0.01 mmol, 18 mg); temperature (393 K); reaction time (3 h).

HMF selectivity decreased slightly to 88%. When BMPyCl (1-butyl-3-methylpyridinium chloride) was used as the solvent, the glucose conversion decreased to 52% and the HMF selectivity decreased further to 87%, and the selectivity to LG 1%. The cause for the lower conversions observed in BDMIMCl and BMPyCl is not fully understood; however, it is possible that the observed changes are attributable to changes in the acid and base properties of the IL. The lower activity of 12-MPA in BDMIMCl relative to BMIMCl or EMIMCl might be related to the loss of the acidic proton on the imidazolium cation. By contrast, the lower activity of 12-MPA in BMPyCl relative to BMIMCl or EMIMCl might be due to presence of the basic nitrogen atom on the pyridinium ring. Further support for the hypothesis that acid–base properties of the solvent may influence the activity of 12-MPA is discussed below. Irrespective of the IL used as the solvent, the selectivity to humins was approximately 10%.

A significant increase in the glucose conversion could be obtained by dissolving 12-MPA in a mixture of 18 mmol of acetonitrile and 15 mmol of IL. Fig. 1b shows an increase in glucose conversion in every case relative to that observed in Fig. 1a, but virtually no loss in the high selectivity to HMF. Most remarkably, it was possible to achieve glucose conversions of 99% and HMF selectivities of 98% using 12-MPA dissolved in either EMIMCl or BMIMCl. HPLC analysis of the products showed the complete absence of glucose in these cases, consistent with the conclusion reached by analysis of the products by GC. Further consistent with this evidence was the complete absence of humins. It should be noted that as in

the case of the experiments reported in Fig. 1a, the properties of the IL affect the conversion of glucose. While conversions of glucose was increased upon addition of acetonitrile to BDMIMCl or BMPyCl solutions of 12-MPA, these levels were noticeably lower that what could be attained with EMIMCl or BMIMCl. As noted above, the effects of IL composition is due possibly to a reduction in the acidity of the solvent. This hypothesis is supported by the observation that the addition of 1% of methylimidazole, a common impurity in EMIMCl and BMIMCl, resulted in a nearly five-fold reduction in the conversion of glucose albeit without a loss in selectivity. Since methylimidazole is a relatively strong base, its effect is thought to be one of reducing the availability of acid centers needed to catalyze the dehydration of glucose. Likewise, it was found that when the dehydration of glucose was carried out using pure acetonitrile, the conversion of glucose decreased to 7%.

The results presented in Table 1 demonstrate that the composition of liquid acids and heteropoly acids dissolved in EMIMCl affect the conversion of glucose to dehydration products. It is further observed that liquid acids tend to exhibit moderate selectivities to FHMK, and in some instances to CMF, relative to heteropoly acids. These observations suggest that while protons are required to catalyze the dehydration of glucose, the associated anions of the acid affect the reaction chemistry, possibly through interactions with cationic intermediates. A further issue is the extent to which the acid catalyst is dissociated. While the pK_a's of the liquid acids used in this work are well known in water, their values are not established for IL's. Furthermore, it is clear from Table 1 that the pK_a of a liquid in aqueous solution is not a predictor of its activity for glucose dehydration in IL solution. Thus, while the acidity decreases (i.e., increasing pK_a) in the order CF_3SO_3H (−15) > HCl (−7) > H_2SO_4 (−3) > CH_3SO_3H (−2) > HNO_3 (−1.4) CF_3SO_3H (0.3) > H_3PO_4 (2.1), the catalytic activity of these acids decreases in the order H_2SO_4 > CF_3SO_3H > CH_3SO_3H > CF_3COOH > HNO_3 > HCl > H_3PO_4. Comparison of these two series suggests that while high acidity (low pK_a) contributes to high glucose dehydration activity, the anion composition is also a factor. The relationship of acidity to dehydration activity is clearer in the case of the heteropoly acids since both acidity[11] and activity decrease in the order 12-TPA > 12-MPA > 12-TSA > 12-MSA.

An illustration of how an anion might affect the reaction pathway for the dehydration of glucose is shown in Scheme 1 for the case of 12-MPA. For the sake of clarity, only one sixth of the whole heteropoly anion is shown. In this scheme it is assumed at least one of the three protons in 12-MPA ($H_3PMo_{12}O_{40}$) remains associated with the anion. The key step in this scheme is the formation of 1,2-enediol,[12] which is envisioned to be stabilized by the heteropoly anion. Protonation and deprotonation of this intermediate and subsequent water removal lead to the formation of HMF. LG is thought to form by protonation of the second to last intermediate on the path to HMF. The very low selectivity to LG suggests that this step is highly unfavorable. The principal difference in the product distributions observed for liquid acids versus heteropoly acids is the appearance of FHMK. Scheme 2 suggests that in the presence of liquid acids, 1,2-enediol may undergo protonation at the carbon atom of the intermediate, resulting in intramolecular hydrogen transfer

Table 2 Effect of catalyst composition on the hydrogenation of HMF in EMIMCl

Entry	Catalyst	Conversion (%)	Selectivity (%)						
			MF	DHMF	MFA	DMF	MTHFA	HD	UI
1	Pd/C	19 (47)[a]	51 (36)	9 (1)	7 (8)	13 (32)	5 (0)	7 (10)	8 (12)
2	Pt/C	11	75	16	0	2	0	2	5
3	Ru/C	23	78	12	4	0	0	3	3
4	Rh/C	16	83	3	2	6	0	3	3

Reaction conditions: EMIMCl (20 mmol, 3.0 g); HMF (1 mmol, 126 mg); catalyst (0.02 mmol, metal content); temperature (393 K); H_2 pressure (62 bar); stirring speed (600 rpm); reaction time (60 min). [a] Results obtained with the addition of acetonitrile (25 mmol, 1.18 g).

Table 3 Hydrogenation of HMF using three sources of HMF

Entry	Substrate	Conversion (%)	Selectivity (%)						
			MF	DHMF	MFA	OMBM	DMF	HD	UI
1	Neat HMF	47	36	1	8	1	32	10	12
2	Extracted HMF	46	36	1	19	1	30	7	6
3	HMF in EMIMCl-CH₃CN	44	38	2	16	0	28	9	7

Reaction conditions: EMIMCl (20 mmol, 3.0 g); acetonitrile (25 mmol, 1.18 g); HMF (1 mmol, 126 mg); Pd/C (0.02 mmol, 2.13 mg, metal content); temperature (393 K); H2 pressure (62 bar); stirring speed (600 rpm); reaction time (60 min).

to form 2,3-enediol. Once formed, this intermediate can react further to form FHMK.[13]

It is noted that the mechanism proposed for the dehydration of glucose does not involve the isomerization of glucose to fructose as the first step of the reaction. The reason for this is as follows. Under reaction conditions identical to those used for the experiments reported in Fig. 1a and 1b, the dehydration of fructose to HMF, catalyzed by 12-MPA in either EMIMCl or a mixture of EMIMCl and acetonitrile occurs three times faster than the dehydration of glucose to HMF. What this means is that if fructose were an intermediate in the dehydration of glucose, it then should have been seen as an intermediate in the reaction products. While the capability to observe fructose was sufficient, this product was never observed. It is for this reason that we have proposed that glucose dehydration proceeds *via* ring opening of the pyranose form of glucose.[12]

The role of acetonitrile in promoting the activity of 12-MPA is not understood. It is observed that upon addition of 33% acetonitrile to 10 wt% glucose–EMIMCl solution the viscosity decreased from >82 cp to 5 cp.[14] It is conceivable that the lower viscosity of the acetonitrile-containing solution reduces the tendency of the glucose to form humins, thereby allowing a larger fraction of the glucose to undergo dehydration. Another possibility is that acetonitrile interacts with the protons of the acid and thereby moderates their activity for the conversion of glucose to humins. Consistent with this idea, it was observed that increasing the amount of 12-MPA used to promote the dehydration of glucose from 0.01 mmol to 0.10 mmol, in a solution containing 1 mmol of glucose dissolved in a mixture of 15 mmol EMIMCl and 18 mmol of acetonitrile decreased the conversion of glucose to dehydration products from 99% to 71% without changing the distribution of products. However, the use

of the higher catalyst concentration promoted the formation of humins.

2.2 HMF hydrogenation

The hydrogenation of HMF was investigated using carbon-supported Pd, Pt, Ru, and Rh. Table 2 shows the results of these experiments carried out using pure EMIMCl as the solvent. Six principal products were observed: 5-methylfurfural (MF), 2,5-dihydroxymethylfuran (DHMF), 5-methylfurfuryl alcohol (MFA), 2,5-dimethylfuran (DMF), 5-methyltetrahydrofurfuryl alcohol (MTHFA), and 2,5-hexadione (HD). Small amounts of unknown products were also produced. The HMF conversion after 1 h of reaction ranged from 11% for Pt/C to 23% for Ru/C. The selectivity to DMF, the desired final product, was highest for Pd/C, 13%, for which an HMF conversion of 19% was achieved. In the light of these findings, it was decided to explore the hydrogenation of HMF over Pd/C using a mixture of EMIMCl and acetonitrile as the solvent. As shown by the figures given in parentheses in Table 2, the addition of acetonitrile to EMIMCl increased the conversion of HMF to 47% and raised the selectivity of DMF to 32%. However, if the reaction was carried out in pure acetonitrile, the conversion decreased to 12%, and the selectivities to MF, DHMF, MFA, DMF, HD and UI became 35, 0, 20, 17, 21, and 7%, respectively.

Hydrogenation of HMF obtained from glucose dehydration and *in situ* hydrogenation of HMF following glucose dehydration were done and the results were compared to those obtained using neat HMF. The data shown in Table 3 indicate that the source of HMF had very little effect on the conversion of HMF or the distribution of products. These data demonstrate that
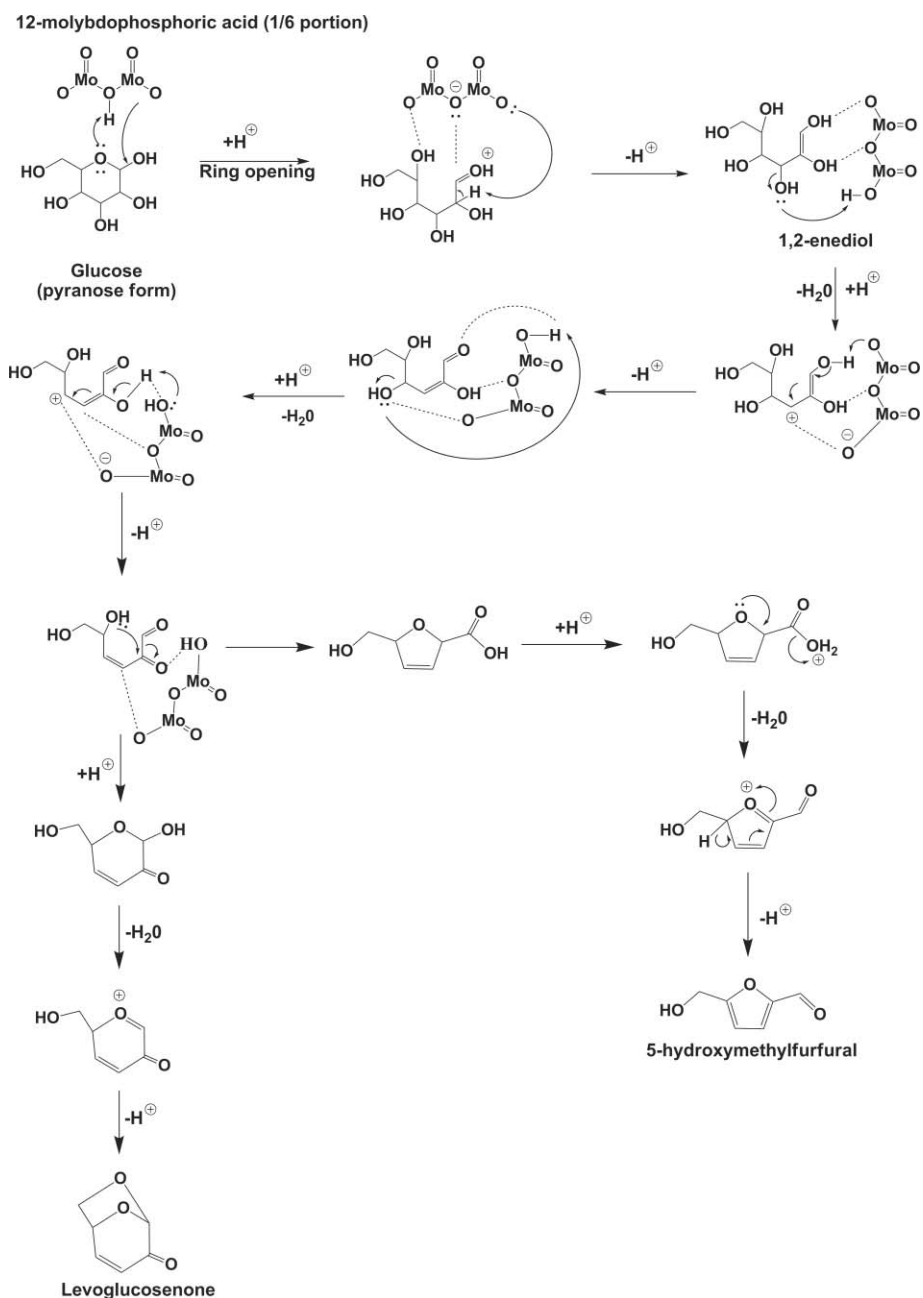
Scheme 1 Proposed reaction mechanism for the dehydration of glucose catalyzed by 12-MPA.

HMF produced by dehydration of glucose catalyzed by 12-MPA will readily undergo hydrogenation to form DMF.

The results of HMF hydrogenation in ILs presented in Fig. 2 and Table 3 can be compared with those obtained for HMF hydrogenation in butanol reported by Dumesic and coworkers[10a] and by Binder and Raines.[10b] Working at 493 K and 6.8 bar of H_2, Dumesic and coworkers obtained a DMF yield of 71% using a Cu–Ru/C catalyst after 10 h of reaction. Using the same catalyst and reaction conditions, Binder and Raines reported a DMF yield of 49%.[10b] They attributed the higher yield of DMF in butanol *versus* water to the higher solubility of H_2 in the former solvent. By contrast, we obtained a DMF yield of 16% with 47% conversion of HMF in 1 h working at 393 K and 60 bar

using a Pd/C catalyst. We attribute the lower DMF yield in our work to the lower temperature and time of reaction, as well as the low solubility of H_2 in ILs.

To understand the temporal evolution of products formed during the hydrogenation of HMF, the reaction was studied as a function of time. Fig. 2 shows the evolution of products at 393 K, using Pd/C as the catalyst. As time increased from 15 min to 60 min, the total conversion of HMF increased from 7% to 47% and the distribution of products changed in a complex manner. The principal product observed after 15 min were MF and 5,5′-(oxybis(methylene))bis(2-methylfuran) (OMBM), which we believe was formed by the self condensation of MF. With continuing reaction time, the yield of OMBM decreased rapidly
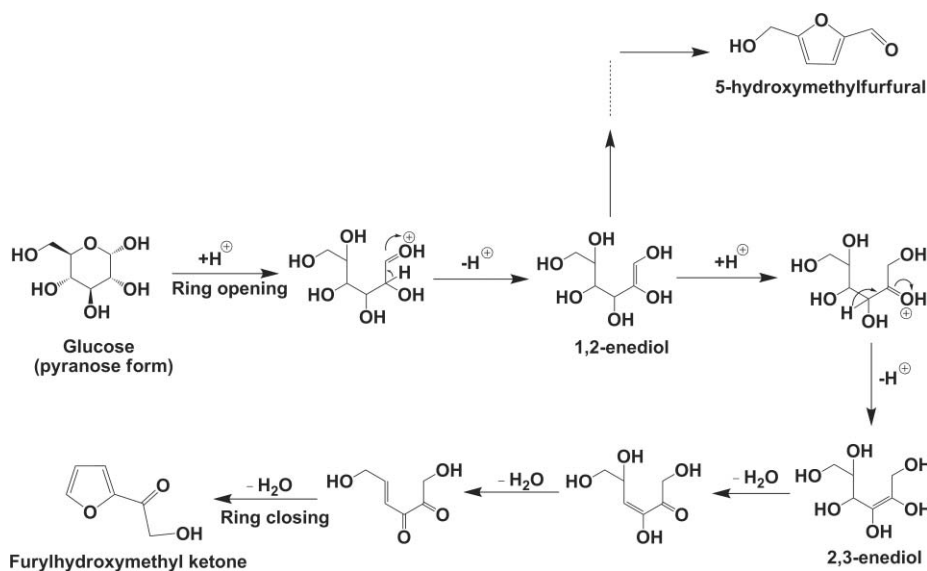
Scheme 2 Proposed reaction pathway for the dehydration of glucose to furylhydroxymethylketone (FHMK) in liquid acids.
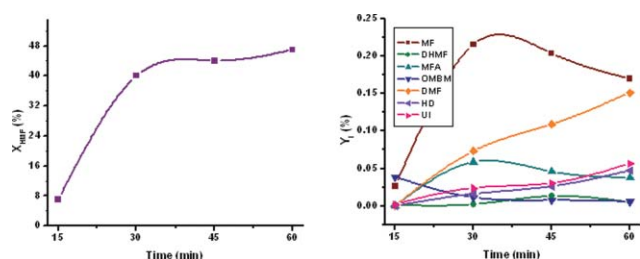
Fig. 2 Temporal evolution of conversion and product yields observed during the hydrogenation of HMF. Left: conversion of HMF. Right: product yields. Reaction conditions: EMIMCl (20 mmol, 3.0 g); acetonitrile (25 mmol, 1.18 g); HMF (1 mmol, 126 mg); Pd/C (0.02 mmol, 2.13 mg, metal content); temperature (393 K); H_2 pressure (62 bar); stirring speed (600 rpm).

to zero due either to its conversion to DMF and MFA or conversion back to MF *via* reaction with water produced by the removal of OH groups. By contrast, the yield of MF rose, achieved a maximum after 30 min, and then decreased. The yield of MFA also increased and passed through a maximum at 30 min, as did the yield of DHMF, which reached its maximum after 45 min of reaction. The yield of DMF increased monotonically, as did the yield of HD and the unidentified products, but to a lesser degree. Increasing the reaction time from 1 to 12 h increased the conversion of HMF hydrogenation 47% to 63% and raised the selectivities to MF, DHMF, MFA, DMF, HD, and UI to 28, 4, 7, 28, 18, and 15%, respectively. Additional experiments were done with 0.01 and 0.04 mmol of Pd; however, the conversion of HMF and the distribution of products formed were very similar to those observed using 0.02 mmol of Pd.
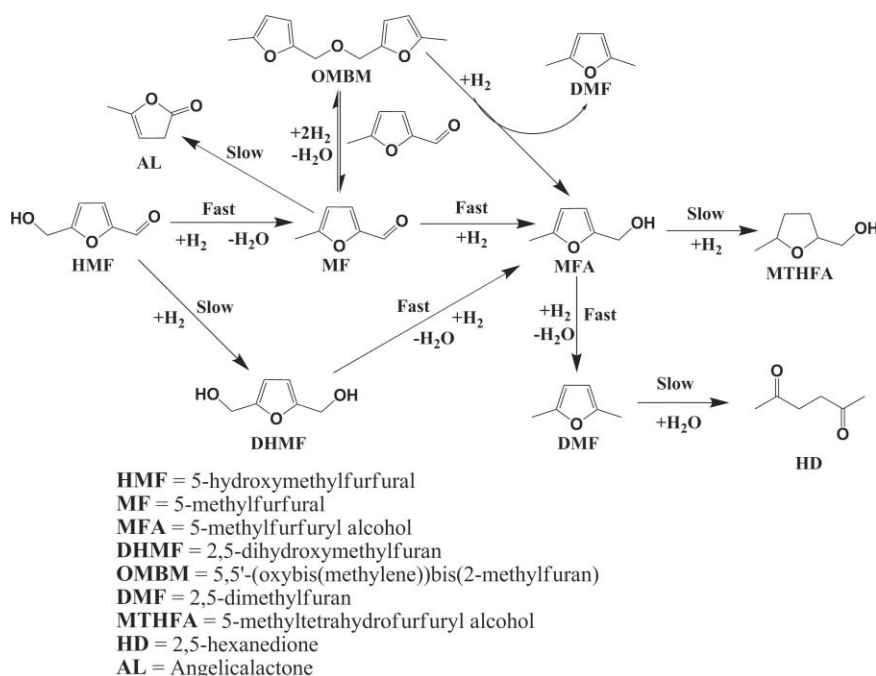
The relationship of the products observed during the hydrogenation of HMF (see Fig. 2) is illustrated in Scheme 3. To test the validity of the proposed reaction sequences, experiments were conducted with MF, MFA, and DHMF as the starting reagent, and the results are shown in Fig. 3–5. Fig. 3 demonstrates that MF is quite reactive. Within the first 15 min of

reaction, this intermediate is converted principally to MFA and DMF, and as the reaction time increases, the yield of MFA decreases and that of DMF increases. The results of this experiment suggest that the rate of MF hydrogenation to MFA is fast, as is the subsequent hydrogenolysis of MFA to DMF. Small yields of HD, MTHFA, and unidentified species were observed to build up on the same time scale as the yield of DMF. Based on the literature the formation of HD is envisioned to occur *via* the hydration of DMF.[15] The conversion of MFA is very rapid, and as can be seen in Fig. 4, 90% conversion of this intermediate, primarily to DMF, is achieved in 60 min. The hydrogenation of DHMF was also investigated. The results shown in Fig. 5 demonstrate that while this intermediate is moderately reactive, it forms MFA primarily, but relatively little DMF. The high reactivity of MFA to DMF seen in Fig. 4, suggests that the presence of DHMF inhibits the hydrogenolysis of MFA, very likely due to competitive adsorption on the surface of Pd. To test this hypothesis, increasing amounts of DHMF were added to a solution containing a fixed amount of MFA. The results presented in Table 4 clearly demonstrate that the presence of DHMF inhibits the conversion of MFA to DMF and that relatively small amounts of DHMF have a strong effect. Thus, the low yield of DMF observed during the hydrogenation of

Table 4 Effect of DHMF on the hydrogenation of MFA

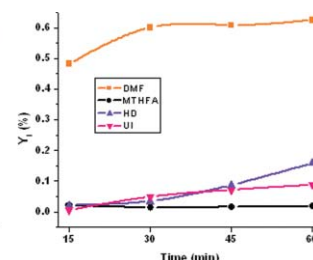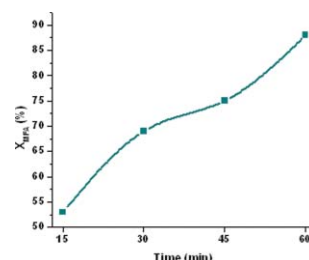| Entry	DHMF (initial, mmol)	MFA (final, mmol)	DMF (mmol)	DMF/MFA (mmol)
1	0	0.12	0.62	5.20
2	0.1	0.43	0.26	0.58
3	0.5	0.47	0.19	0.40
4	1.0	0.50	0.11	0.22

Reaction conditions: EMIMCl (20 mmol, 3.0 g); acetonitrile (25 mmol, 1.18 g); MFA (1 mmol, 112 mg); Pd/C (0.02 mmol, 2.13 mg, metal content); reaction time (60 min); temperature (393 K); H_2 pressure (62 bar); stirring speed (600 rpm).

HMF = 5-hydroxymethylfurfural
MF = 5-methylfurfural
MFA = 5-methylfurfuryl alcohol
DHMF = 2,5-dihydroxymethylfuran
OMBM = 5,5'-(oxybis(methylene))bis(2-methylfuran)
DMF = 2,5-dimethylfuran
MTHFA = 5-methyltetrahydrofurfuryl alcohol
HD = 2,5-hexanedione
AL = Angelicalactone

Scheme 3 Reaction pathway for the hydrogenation of HMF in EMIMCl and acetonitrile solvent using Pd/C as catalyst.
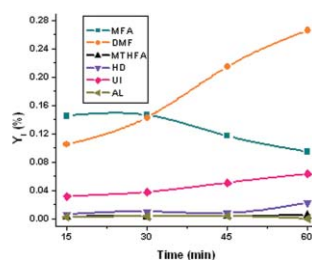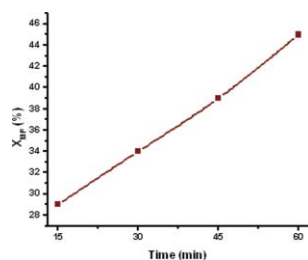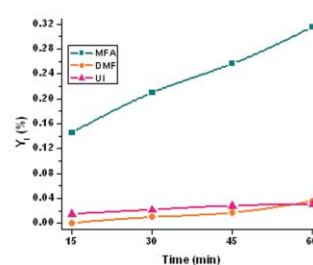

Fig. 3 Temporal evolution of conversion and product yields during the hydrogenation of MF. Left: conversion of MF. Right: product yields. Reaction conditions: EMIMCl (20 mmol, 3.0 g); acetonitrile (25 mmol, 1.18 g); MF (1 mmol, 110 mg); Pd/C (0.02 mmol, 2.13 mg, metal content); temperature (393 K); H$_2$ pressure (62 bar); stirring speed (600 rpm). MTHFA (5-methyltetrahydrofurfuryl alcohol).

HMF (see Fig. 2) can be attributed to the inhibiting effect of DHMF formed from HMF.

3 Experimental

3.1 Materials

All chemicals were reagent grade and used without further purification. 1-Ethyl-3-methylimidazolium chloride (EMIMCl, 98%), 1-butyl-3-methylimidazolium chloride (BMIMCl, 98%), 5-hydroxymethylfurfural (HMF, 99%), 5-methylfurfural (MF, 99%), 2,5-dimethylfuran (DMF, 99%), levulinic acid (LA, 98%), angelicalactone (AL, 98%), 2,5-hexanedione (HD, 98%), trifluoroacetic acid (CF$_3$COOH, 98%), phosphoric acid (H$_3$PO$_4$, 85%), trifluoroacetic acid (CF$_3$SO$_3$H, 98%), Methanesulfonic acid (CH$_3$SO$_3$H, 98%), and carbon-supported Rhodium (Rh/C, 5 wt% rhodium, surface area 920 m^2 g^{-1}, and 90% of particles <80 μm in diameter) were purchased from Sigma-Aldrich, USA. 1-Butyl-2,3-dimethylimidazolium chloride (BDMIMCl,
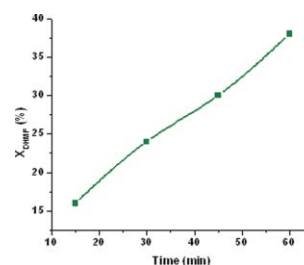

Fig. 4 Temporal evolution of conversion and product yields during the hydrogenation of MFA. Left: conversion of MFA. Right: product yields. Reaction conditions: EMIMCl (20 mmol, 3.0 g); acetonitrile (25 mmol, 1.18 g); MFA (1 mmol, 112 mg); Pd/C (0.02 mmol, 2.13 mg, metal content); temperature (393 K); H$_2$ pressure (62 bar); stirring speed (600 rpm).

Fig. 5 Temporal evolution of conversion and product yields during the hydrogenation of DHMF. Left: conversion of DHMF. Right: product yields. Reaction conditions: EMIMCl (20 mmol, 3.0 g); acetonitrile (25 mmol, 1.18 g); DHMF (1 mmol, 128 mg); Pd/C (0.02 mmol, 2.13 mg, metal content); temperature (393 K); H$_2$ pressure (62 bar); stirring speed (600 rpm).

98%) and 1-butyl-3-methylpyridinium chloride (BMPyCl, 98%) were obtained from Iolitec, Germany. USP grade glucose was purchased from Hyclone USA. 12-Molybdophosphoric acid (12-MPA), 12-molybdosilicic acid (12-MSA), 12-tungstosilic

acid (12-TSA), and 12-tungstophosphoric acid (12-TPA) were procured from Strem Chemicals, USA. Levoglucosenone (LG, 98%) was purchased from Carbosynth, UK. Carbon-supported palladium (Pd/C, 10 wt% palladium, surface area 800 m^2 g^{-1} and 90% of particles <90 μm in diameter), carbon-supported platinum (Pt/C, 5 wt% platinum, surface area 900 m^2 g^{-1} and 85% of particles <85 μm in diameter), and carbon-supported ruthenium (Ru/C, 5 wt% ruthenium, surface area 900 m^2 g^{-1} and 90% of particles <85 μm in diameter) were from Acros Chemicals, USA. 5-Methylfurfuryl alcohol (MFA, 98%) and 2,5-dihydroxymethylfuran (DHMF, 98%) were obtained from Chemos, Germany. Sulfuric acid (H$_2$SO$_4$, 98%), hydrochloric acid (HCl, 36%), and nitric acid (HNO$_3$, >62%), were from Acros, Fisher, and Acros, respectively. HPLC-grade ethyl acetate and acetonitrile were from Fisher Scientific, USA.

Prior to each experiment, ionic liquids were dried overnight under vacuum (−30 Hg) at 383 K. Glucose and all metal catalysts were dried for 2 h at 378 K in an air atmosphere.

3.2 Dehydration of glucose

The dehydration of glucose was carried out using a Symyx High Throughput Core Module. In a typical experiment, ionic liquid (15 mmol, 2.0 g, density was considered as 1 g cm^{-3} since Sigma-Aldrich EMIMCl does not carry the density) was added to 5 ml vials equipped with magnetic spin bars and loaded on the Core Module at 393 K. Glucose (1 mmol, 180 mg) was then introduced and the solution was stirred until the glucose dissolved completely. Glucose dehydration was initiated by addition of 0.01 mmol of catalyst to the stirred liquid. After the reaction had proceeded for a specified time, the sample was cooled to 303 K, and 2 ml of water was added. The contents of each vial were transferred to a centrifuge tube, neutralized with 0.0233 mmol of sodium carbonate (Na$_2$CO$_3$), and centrifuged at 4000 rpm and 293 K for 20 min. 10 μL of supernatant was removed for glucose analysis. The remaining supernatant was extracted with 5 × 10 ml of ethyl acetate and treated with excess sodium sulfate (Na$_2$SO$_4$) to remove the water, and centrifuged. The ethyl acetate solution was then transferred to a 50 ml volumetric flask.

For the results presented in Fig. 1b, acetonitrile (18 mmol, 0.79 g) was mixed with ionic liquid at 333 K. Glucose was then added to this solution and stirred until completely dissolved. Finally, 12-MPA (0.01 mmol, 18 mg) was introduced. The vials were sealed with air tight caps and transferred to 393 K. Reaction was continued for 3 h, after which the contents of the vial were subjected to the same work up procedure described above.

3.3 Hydrogenation of 5-hydroxymethylfurfural

The hydrogenation of HMF was carried out using either neat HMF or HMF obtained by dehydration of glucose. In the latter case, the ethyl acetate mixture obtained from glucose dehydration using EMIMCl–acetonitrile as solvent and 12-MPA as catalyst (for *e.g.* sample of Fig. 1b, EMIMCl) was subjected to rotary evaporation at 363 K until ethyl acetate and acetonitrile were collected completely. The sample was then dried further under vacuum overnight at 373 K and used without further purification. All reactions were carried out in a Parr autoclave (75 ml). The autoclave was heated by an oil bath and the contents

were stirred by a magnetic spin bar. In a typical experiment, 1 mmol (126 mg) of HMF was added to 20 mmol (3.0 g) of EMIMCl and acetonitrile (25 mmol, 1.18 g) contained in the reactor at 323 K. The reactor contents were mixed thoroughly and then 0.02 mmol (metal content) of carbon-supported catalyst was introduced. The reactor was sealed, purged three to four times with hydrogen, and pressurized to 62 bar with H$_2$ because of the low solubility of H$_2$ in ILs.[16] Reaction was initiated by placing the reactor into an oil bath preheated to 393 K, stirring of the reactor contents was maintained at 600 rpm for the required reaction time. After the reaction was completed, the reactor was cooled to room temperature and the unreacted H$_2$ was released. Then, 1 ml of water was introduced; the contents of the reactor were transferred to a centrifuge tube and centrifuged at 4000 rpm in order to separate the suspended catalyst. The supernatant liquid was then extracted with 5 × 10 ml of ethyl acetate. This solution was then contacted with excess Na$_2$SO$_4$ in order to remove the water, centrifuged, and 50 ml of the resulting ethyl acetate solution was retained for analysis. The same procedure was followed for hydrogenation of MF, MFA, and DHMF.

3.4 Hydrogenation of 5-hydroxymethylfurfural produced *in situ* by glucose dehydration

Hydrogenation of HMF produced *in situ* by glucose dehydration using 12-MPA in a solution of EMIMCl and acetonitrile was carried out in the following manner. After completion of glucose dehydration reaction, the mixture was cooled down to 323 K, and Na$_2$CO$_3$ was added to neutralize the acid. The contents of the vial were transferred to a centrifuge tube and centrifuged at 4000 rpm and 293 K for 20 min to remove any suspended particles (precipitated Na$_3$PMo$_{12}$O$_{40}$ and a small amount of humins). The supernatant in the centrifuge tube was loaded into a Parr autoclave and 1 g of EMIMCl and 0.39 g of acetonitrile was added to bring the amounts of these solvents to the levels used in the hydrogenation of pure HMF. Pd/C was then added to the autoclave, and the hydrogenation of HMF carried out following the procedure described in the preceding section.

3.5 Analytical methods

Ethyl acetate solutions were analyzed by gas chromatography–mass spectrometry (GC/MS) for product identification, and gas chromatography (GC) was then used to quantify product formation. These analyses were carried out using a Varian CP-3800 gas chromatograph equipped with a flame ionization detector coupled to a Varian 320-MS mass spectrometer. Products were separated using a FactoFour capillary column (VF-5 ms, 30 m length, 0.25 mm diameter) coated with a 0.25 μm thick stationary phase (5% phenyl and 95% dimethylpolysiloxane). Product identities suggested by GC/MS were confirmed by analysis of pure components, which were also used to develop calibration curves for quantitative GC analysis. To identify OMBM, GC-MS/MS and silylation analyses were done.

The 10 μL supernatant solution obtained after glucose dehydration was analyzed in the following manner. First, 990 μL of water was added to this solution, after which 10 μL of the diluted solution was further diluted with 990 μL of water, filtered through micro-filters using Sartorius 0.22 μm membrane

size filter, and then analyzed by a Dionex ICS-3000 High Pressure-Anion Exchange Chromatograph (HP AEC) equipped with a Carbopack PA20 column and a Pulsed Ampherometric Detector (PAD) to identify unreacted glucose. 18 mM sodium hydroxide was used as mobile phase and the temperature of the column was kept at 303 K.

The conversion of glucose was based on the concentration of products obtained multiplied by 100 and divided by the concentration of substrate used. Further, selectivity was calculated as concentration of a particular product obtained multiplied by 100 and divided by the concentration of total products. Furylhydroxymethyl ketone (FHMK) and 5-chloromethylfurfural (CMF) were quantified using HMF calibration data since they have an almost similar type of structure to HMF and could not be obtained commercially.

4 Conclusions

We have shown that heteropoly acids are very good catalysts for promoting the dehydration of glucose to 5-hydroxymethylfurfural (HMF) in ionic liquids, particularly in the presence of acetonitrile as a cosolvent. Using 12-MPA as the catalyst, it was possible to achieve a glucose conversion of 98% with a HMF selectivity of 99% after 3 h of reaction at 393 K in a mixture of either EMIMCl or BMIMCl and acetonitrile. The observed selectivity to HMF was much higher than that observed using liquid acids. With the exception of phosphoric acid, liquid acids exhibited moderate selectivity to FHMK and, in some cases, CMF. It is proposed that the HMF high selectivity of heteropoly acids is attributable to stabilization of the reaction intermediates involved in formation of HMF (see Scheme 1). A key intermediate in the reaction pathway to HMF is believed to be 1,2-enediol. We propose that acid-catalyzed isomerization of this species to 2,3-enediol leads to the formation of FHMK. In the absence of acetonitrile as a cosolvent, moderate amounts of humins were formed. Hydrogenation of HMF in a mixture of EMIMCl and acetonitrile promoted by carbon-supported transition metals produced a series of products, and in particular DMF, a product of particular interest because of its high-energy content. The highest yield of DMF was obtained using Pd/C. The reaction pathway by which HMF is converted to DMF was explored by using the intermediates as starting materials. It was also observed that HMF produced by the dehydration of glucose in the presence of 12-MPA could be converted to DMF (after removal of 12-MPA and replacement by Pd/C) with the same yield as that obtainable by starting with pure HMF. In summary, this study shows that it is possible to dehydrate glucose to HMF in IL–acetonitrile solution with near 100% yield and to convert HMF to DMF with reasonable yield by subsequent hydrogenation under relatively mild reaction conditions.

Acknowledgements

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