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Single pot conversion of furfuryl alcohol to levulinic esters and γ -valerolactone in the presence of sulfonic acid functionalized ILs and metal catalysts†

Amol M. Hengne, Sumit B. Kamble and Chandrashekhar V. Rode*

Ionic liquids functionalized with acidic anions, HSO_4 , $CISO_3H$, PTSA, TFA (MIm), HSO_4 and TFA (NMP) were found to efficiently (99% conversion) catalyze the alcoholysis of furfuryl alcohol (FAL) in the presence of methanol, ethanol, n-butanol and isopropyl alcohol (IPA) to the corresponding levulinic acid esters under mild temperature (90–130 °C) conditions. The extended alkyl chain length of [MIm] using 1,4-butane sultone enhanced the Brønsted acidity of [BMIm-SH][HSO_4] catalyst resulting into the highest selectivity of >95% to Me-LA. An increase in both temperature and catalyst concentration increased the furfuryl alcohol conversion and selectivity to levulinate esters. In contrast, an increase in the substrate concentration from 5 to 15% caused a decrease in Me-LA selectivity due to accumulation of intermediate ethers of furfuryl alcohol. Using a combination of [BMIm-SH][HSO_4] and 5% Ru/C catalyst, direct conversion of FAL to γ -valerolactone (GVL) is shown for the first time. A complete conversion of FAL with the highest selectivity of 68% to GVL could be achieved under optimum conditions while higher Ru loading enhanced the GVL selectivity to 94% in the hydrogenation step of this tandem approach. Our catalyst system could be efficiently recycled five times retaining the original activity and selectivity levels.

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Introduction

The exploitation of bio-based fuels and fuel additives is imperative due to its role in effective remediation of greenhouse gas levels in the atmosphere and to mitigate the economic consequences of the depleting fossil resources. 1,2 Firstgeneration biofuels (i.e. ethanol and biodiesel) are presently produced from sugars, starch and vegetable oils, creating important compatibility and energy density issues. One promising alternative to overcome these limitations of oxygenated fuels is to use more abundant, cheaper and potentially more sustainable non-edible lignocellulosic biomass.^{3,4} The present paper reports the most promising route to achieve this transformation by developing a selective and versatile catalyst system involving acid and metal functions together for alcoholysis and hydrogenation reactions, respectively, in a single step. These two are the primary unit processes for the conversion of the monomeric carbohydrate building blocks, i.e., mainly C5 sugars, such as xylose and arabinose, and C6 sugars in the form of glucose and their respective secondary products,

furfural and levulinic acid into the potential fuel additives.^{5,6} Furfural produced by the hydrolysis and dehydration of xylan contained in lignocellulose can be easily hydrogenated to furfuryl alcohol.

Hence, direct conversion of furfuryl alcohol to levulinic esters followed by its in situ hydrogenation to γ-valerolactone (GVL) becomes a new alternative route for the production of biofuel.7 Levulinic esters (LA) are mainly obtained by a series of reactions involving, first, acid catalyzed esterification of levulinic acid produced from hexose sugars. LA is then hydrogenated to give 4-hydroxy LA followed by its ring cyclization to GVL. 8-10 GVL, along with levulinic esters which also can be used as diesel additives, form sustainable liquid transportation fuels replacing ethanol in a gasoline ethanol blend. 11,12 In addition, another product of single step catalytic hydrogenation of levulinic acid is methyl tetrahydrofuran (MTHF) which has been also approved by the US-DOE as a component of P Series type fuels. 13,14 The formation of levulinic acid and its esters from cellulose and hemicelluloses is possible by two different routes: (i) hexose triple dehydration to 5-hydroxymethylfurfural (5-HMF) and its rehydration with two water molecules to produce levulinic and formic acids, and (ii) hydrolysis of pentose sugars to produce a mixture of C5 monomers, mainly furfural which is then reduced to furfuryl alcohol followed by its rehydration to produce levulinic acid/ester. 15-18 A commercial Biofine process for the production of levulinic

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acid requires 3.5 tons of 3.5 wt% sulfuric acid, thus creating serious environmental pollution and involving tedious work up for the recovery of pure LA. 19,20 Attempts are being made to overcome such drawbacks by developing heterogeneous catalysts. For example, Lange et al. have reported ion-exchange resins and zeolites as solid acid catalysts for the conversion of furfuryl alcohol to ethyl levulinate, but with a very low selectivity to ethyl levulinate due to the formation of compounds with high boiling points as byproducts.21 Organo-inorganic hybrid solid acids were proposed by Zhang et al. for the production of butyl levulinate with 93% yield but without showing the catalyst reusability.²² Some of the other novel approaches include the use of biphasic systems with new solvents such as 2-sec-butylphenol (SBP) and 4-propyl guaiacol (PG) for the recycling of mineral acid in the production of furfural and levulinic acid from the hemicellulose portion of lignocellulose giving a yield of 60-70%.²³ The direct conversion of the cellulose unit of glucose to methyl levulinate was reported by Tominaga et al. using homogeneous mixed Lewis and Brønsted acid systems resulting in a poor selectivity of 20-50% to methyl levulinate.²⁴ The imidazolium and pyridinum based ILs functionalized with (SO₃H, PTSA and ClSO₃H) acidic groups studied by Saravanamurugan et al. in the presence of naphthalene as an added solvent showed 70% selectivity to methyl levulinate with hydroxy methyl furfural ether as a byproduct.²⁵ A tandem approach combining acid hydrolysis and hydrogenation reactions together over heterogeneous (Ru/C) and acid catalysts (mineral acid) has also been proposed for the catalytic conversion of cellulose into platform chemicals.²⁶

In the present paper, we report a single pot catalytic conversion of furfuryl alcohol to levulinic acid ester and GVL via the alcoholysis/hydrogenation sequence using sulfonic acid-functionalized ionic liquids (SO₃H-ILs) and carbon supported Ru, Re, Ir and Ag catalysts. Our novel approach for direct conversion of furfuryl alcohol to GVL has several advantages: (i) the yield of methyl levulinate is higher than that for hydrolysis of C6 sugars due to humin elimination in alcohol medium, (ii) no separation step is required for downstream conversion of levulinic acid/esters, (iii) complete atom efficiency in the conversion of FAL to GVL and (iv) elimination of metal leaching and deactivation of the catalysts used for LA hydrogenation to GVL. To the best of our knowledge, this approach for direct conversion of C5 furfuryl alcohol to C5 GVL has not been reported so far. We found that 5% Ru/C + [BMIm-SH][HSO₄] showed complete alcoholysis of furfuryl alcohol with 95% selectivity to methyl levulinate followed by its hydrogenation with the highest selectivity of 94% to GVL in a batch reactor.

Results and discussion

Two major objectives of the present work were (i) to design a novel, environmentally benign acid catalyst for the efficient alcoholysis of furfuryl alcohol to levulinic esters and (ii) to develop a tandem approach for synthesizing GVL directly from furfuryl alcohol. For the first stage of this work, we prepared

Table 1 Catalyst screening for alcoholysis of furfuryl alcohol to methyl levulinate^a

			% Selectivity			
Entry	Catalyst	% Conversion	Methyl LA	Methoxy FAL	Other	
1	No catalyst	2	<0.01	81	19	
2	$[H_2SO_4]$	68	74	16	10	
3	Amberlyst-15	99	40	51	9	
4	SO ₄ -ZrO ₂	99	74	19	7	
5	20% DTP-SiO ₂	69	25	61	14	
6	20% DTP-MMT	73	24	63	13	
7	$[MIm][HSO_4]$	96	65	21	14	
8	[MIm][TFA]	10	1	95	4	
9	[NMP][HSO ₄]	99	98	1	1	
10	[NMP][TFA]	11	2	94	4	
11	[BMIm-SH][ClSO ₃ H]	98	90	4	6	
12	[BMIm-SH][PTSA]	95	76	11	13	
13	[BMIm-SH][HSO ₄]	99	95	2	3	

^a Reaction conditions: furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; N_2 atm., catalyst, 0.3 g; reaction time, 2 h.

several acid functionalized ILs and their performance evaluation results are shown in Table 1. The initial control experiment without any catalyst (entry 1, Table 1) showed that furfuryl alcohol conversion was <2% confirming that the alcoholysis of furfuryl alcohol was a catalytic reaction. Among the various solid acid catalysts, almost complete conversion was obtained with Amberlyst-15 and SO₄-ZrO₂ but the selectivity to MeLA was only 74% with the remaining FAL ethers (entries 3 and 4, Table 1). With the other two solid acid catalysts, the conversion achieved was less than 75% with a very poor selectivity of 25% to Me-LA. Thus, a simultaneous high activity and selectivity for furfuryl alcoholysis to Me-LA was not possible using any of the solid acid catalysts screened in this work (entries 5 and 6, Table 1). This fact is also evident from the reported literature. 10,22,26 Therefore, we explored the use of ILs having Brønsted acidity which was systematically varied with anions such as ClSO₃H, SO₃H, PTSA, and TFA with the same cation MIm. It was observed that a furfuryl alcohol conversion of >95% was achieved with cations such as HSO₄ and Cl-SO₃H (entries 7 and 11, Table 1) while only 10% conversion was obtained with the TFA anion (entry 8, Table 1). However, with only the HSO₄ anion, the selectivity to methyl levulinate was the highest, 98% (entry 9, Table 1). As can be seen from Table 1, the choice of the anion was critical, because with TFA both the cations MIm and NMP exhibited very poor activities in terms of furfuryl alcohol conversion in the range of only 10-11%. HSO₄ with both the cations, MIm and NMP, showed very high conversion (>95%) while the selectivity to methyl levulinate was only 65% in the case of [MIm][HSO₄]. Hence this catalyst was further modified by extending its alkyl chain with 1,4-butane sultone so that the resulting IL (BMIm-SH) would be more stable and also acquire the enhanced Brønsted acidity. To our expectation, this was actually observed, as the [BMIm-SH][HSO₄] catalyst gave a dramatic increase in selectivity of methyl levulinate up to 95% [entry 13, Table 1]. The

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Scheme 1 Alcoholysis of furfuryl alcohol to methyl-levulinate.

appropriate combination of the anion and the cation is emphasized by the fact that incomplete alcoholysis gave appreciable formation of intermediate FAL ethers (Scheme 1) in the case of [MIm][HSO₄] and [BMIm-SH][PTSA] catalysts [entries 7 and 12, Table 1]. Using HSO₄ as the anion, NMP showed almost complete conversion of furfuryl alcohol and selectivity to methyl levulinate [entry 9, Table 1]. However, when this catalyst was recovered and was attempted to be recycled, its activity dropped by 50% [ESI, Fig. 1[†]] as against the successful complete recyclability of [BMIm-SH][HSO₄] catalyst several times (discussed later). Hence, a further study on the effect of parameters was carried out using [BMIm-SH]-[HSO₄] catalyst. Along with the catalyst, equally important was the choice of reaction medium as the selectivity to levulinic acid dropped to 31% in an aqueous medium over the same active catalyst [BMIm-SH][HSO4], obviously due to humin formation.²⁷ Humin formation also makes separation of the catalyst and the product very much tedious. Hence, direct alcoholysis of furfuryl alcohol in the presence of methanol without the formation of levulinic acid is the most advantageous strategy from a process point of view.8,28

The efficiency of our [BMIm-SH][HSO $_4$] catalyst was further established for the synthesis of a variety of alkyl levulinates by carrying out the alcoholysis of furfuryl alcohol in the presence of different alcohols. Fig. 1 shows that a consistent activity (99% conversion) was achieved for all the alcohols studied in this work.

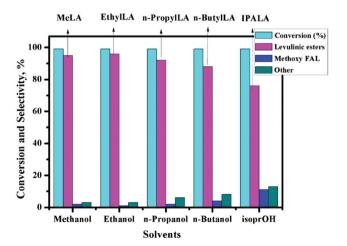


Fig. 1 Screening of solvents for the alcoholysis of furfuryl alcohol. Reaction conditions: furfuryl alcohol, 5% (w/w); solvent, MeOH, EtOH, *n*-PrOH, *n*-BuOH and IsoPrOH (95 mL); temperature, 130 °C; N₂ atm., catalyst, 0.3 g (acidic IL); reaction time, 2 h.

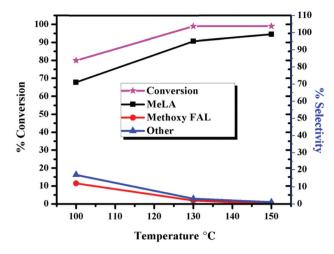


Fig. 2 Effect of temperature on the alcoholysis of furfuryl alcohol. Reaction conditions: furfuryl alcohol, 5% (w/w); solvent, MeOH, (95 mL); temperature, 90-130 °C; N_2 atm., catalyst, 0.3 g (acidic IL); reaction time, 2 h.

However, alkyl levulinate selectivity was found to decrease from 99 to 85% with an increase in alcohol chain length from ethanol to *n*-butanol. The decrease in Me-LA selectivity was associated with the formation of respective ethers of FAL depending on the alcohols used (shown as blue and green bars in Fig. 1). In the case of a branched alcohol such as isopropanol, the corresponding ester (IPA-LA) selectivity decreased to the extent of 68%. This indicates that the steric factor played an important role in the alcoholysis of furfuryl alcohol.

The influence of temperature on the alcoholysis of furfuryl alcohol was studied in a range from 90 to 130 °C keeping other parameters constant and the results are shown in Fig. 2. Almost complete conversion could be achieved as the temperature increased from 90 to 110 °C, and remained constant beyond 110 °C up to 130 °C. Similarly, the selectivity to Me-LA also increased linearly from 65 to 95% with an increase in temperature from 90 to 130 °C. At higher temperature, the conversion of ethers of FAL to Me-LA was facilitated, proving that the reaction pathway (Scheme 1) involves first the etherification of FAL followed by rehydration of the intermediate ethers to Me-LA.

The study on the effect of catalyst loading on the alcoholysis of furfuryl alcohol showed that the conversion of furfuryl alcohol increased from 84 to 99% with an increase in catalyst loading from 0.1 to 0.3 g (Fig. 3). Moreover, the selectivity to methyl levulinate increased by 1.5 times (>80%) due to increased rehydration of the intermediate, FAL ethers. The higher catalyst concentration resulted in the higher availability of Brønsted acid sites facilitating a faster consumption of furfuryl alcohol and rehydration of the intermediates to methyl levulinate.

One of the important process parameters was the substrate concentration, the effect of which on conversion and selectivity pattern was studied by systematically varying the furfuryl alcohol concentration from 5 to 15% and the results are shown in Fig. 4. With an increase in substrate concentration

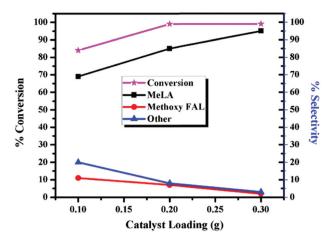


Fig. 3 Effect of catalyst dosage on the alcoholysis of furfuryl alcohol. Reaction conditions: furfuryl alcohol, 5% (w/w); solvent, MeOH, (95 mL); temperature, 130 °C; N_2 atm., catalyst, 0.15–0.3 g (acidic IL); reaction time, 2 h.

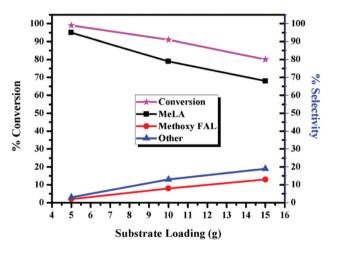


Fig. 4 Effect of substrate loading on the alcoholysis of furfuryl alcohol. Reaction conditions: furfuryl alcohol, 5-15% (w/w); solvent, MeOH, (95 mL); temperature, 130 °C; N_2 atm., catalyst, 0.3 g (acidic IL); reaction time, 2 h.

from 5 to 15%, both the conversion of furfuryl alcohol and the Me-LA selectivity decreased significantly. At higher substrate concentration, the accumulation of higher concentration of the first step alcoholysis products *viz.* FAL ethers on the active sites retarded further rehydration to Me-LA. The substrate concentration of 5% was the optimum to obtain complete conversion and suppression of methoxy FAL intermediates. This minimum substrate concentration can be compensated for by higher productivity as our catalyst system was found to show more than three reuses as discussed later.

Encouraged by the results on modified ILs for efficient alcoholysis of furfuryl alcohol to Me-levulinate, we thought it most desirable to obtain GVL directly from furfuryl alcohol in a single pot synthesis. For this purpose, a combination of acidic ILs and metal catalyst was used in a tandem synthesis of GVL. We therefore screened several combinations of various supported noble metals and the ILs selected from Table 1. All the combinations studied in this work were indeed very successful showing an excellent activity in terms of furfuryl alcohol conversion >99% (see Table 2). The selectivity to GVL varied depending on the noble metal used for the hydrogenation of the intermediate Me-LA. It is very interesting to note that under hydrogenation conditions, selectivity to GVL was only 58% and to the intermediate ester was also only 12% while almost all the remaining (26%) byproduct was (entry 2, Table 2) tetrahydrofurfuryl alcohol (THFAL). THFAL was formed due to the ring hydrogenation of furfuryl alcohol and it was found to be a very stable product as observed from the conversion/selectivity vs. time profile in Fig. 5. A novel strategy adopted by us involved conducting the initial alcoholysis reaction under an N2 atmosphere for 2 h after which N2 was replaced by H2. This time period of changeover was arrived at from the optimum time of alcoholysis as studied previously (Table 1). This approach worked very well to completely suppress the ring hydrogenation product, THFAL (entry 2, Table 2), enhancing the selectivities to the desired products such as MeLA and GVL. Hence, further studies were carried

Table 2 Screening of catalysts for alcoholysis^a/hydrogenation^b of furfuryl alcohol

				Selectivit	Selectivity (%)			
Entry	Catalyst	Additive	Conversion (%)	MeLA	GVL	4-HMeLA	FAL ethers	Others
1	5% Ru/C	H_2SO_4	99	47	31	9	13	<0.01
2	5% Ru/C	[BMIm-SH][HSO ₄]	99	24	68	8	< 0.01	< 0.01
3	5% Ru/C	BMIm-SH HSO ₄ b	99	12	58	1	3	26
4	5% Rh/C	BMIm-SH HSO ₄	99	92	2	2	4	< 0.01
5	5% Re/C	BMIm-SH HSO ₄	99	85	9	2	4	< 0.01
6	5% Pd/C	BMIm-SH HSO ₄	99	94	< 0.01	< 0.01	6	< 0.01
7	5% Ir/C	BMIm-SH HSO ₄	99	65	6	26	3	< 0.01
8	10% Ag/C	BMIm-SH HSO ₄	99	84	8	2	4	< 0.01
9	$10\% \text{ Ag/ZrO}_2$	BMIm-SHI HSO4	99	81	9	3	7	< 0.01
10	5% Ru/C+	Amberlyst-15	99	76	14	6	14	< 0.01
11	5% Ru/C+	SO_4 - ZrO_2	99	79	18	1	2	< 0.01

^a Reaction conditions: furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; N₂ atm. + H₂ pressure, 500 psi; catalyst, 0.3 + 0.5 g; reaction time, 2 h + 3 h. ^b Reaction conditions: furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; H₂ pressure, 500 psi; catalyst, 0.3 + 0.5 g; reaction time, 5 h.

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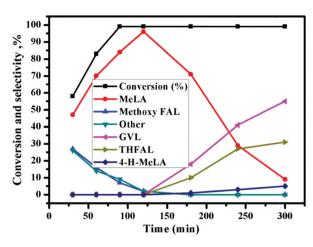


Fig. 5 CT profile for direct hydrogenation of furfuryl alcohol. Reaction conditions: furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 403 K; $\rm H_2$ pressure, 500 psi; catalyst, 0.3 (acidic IL) + 0.75 g (5% metal catalyst); reaction time, 5 h.

out initially under N_2 and then replacing it by H_2 . Under these conditions, among several noble metal catalysts, 5% Ru/C showed the highest selectivity to GVL (68%) in combination with IL [BMIm-SH][HSO₄]. For the same IL, other metals gave GVL selectivity in the range of 2–9%, which was in accordance with our earlier results.²⁸

The GVL selectivity is important not only from the process point of view but also it is necessary to dissolve the unwanted humin associated with cellulose hydrolysis.²⁹

The best performance of our Ru/C + [BMIm-SH][HSO $_4$] catalyst system for the direct conversion of FAL to GVL could be distinctly visible when compared with the performance of Ru/C in combination with the best solid acids chosen from Table 1 (entries 10 and 11, Table 2). Ru/C with both amberlyst and SO $_4$ -ZrO $_2$ gave <20% selectivity to GVL, as the major product was Me-LA. Our catalyst showed ten times higher activity (TOF, 160 h $^{-1}$) than the reported catalysts such as Ru/C + H $_2$ SO $_4$ for the synthesis of GVL (ESI, Table 2 †). This was because of deactivation of Ru catalyst due to sulfur leaching from H $_2$ SO $_4$, which was evidenced by an intense peak at 169.3 eV of S(2p) (ESI, Fig. 2 †).

Since both acid as well as metal sites are important for the direct conversion of FAL to GVL, the effect of compositions of 5% Ru/C + ILs was also studied. For this purpose, loading of 5% Ru/C was varied from 0.25 g to 0.75 g at a constant loading IL of 0.3 g. Fig. 6 shows that for all the loadings of Ru, the conversion of FAL remained constant at >99% while the product selectivity was significantly affected. With an increase in 5% Ru/C catalyst loading from 0.25 to 0.75 g, the selectivity to hydrogenation product GVL gradually increased from 35 to 83% at the cost of Me-LA indicating that an optimum Ru catalyst loading was necessary to achieve the highest selectivity to GVL. In another control experiment, IL loading was decreased to 0.15 g which resulted in significant lowering of the furfuryl alcohol conversion to 80%. More importantly, Me-LA selectivity was also minimum (10%) which

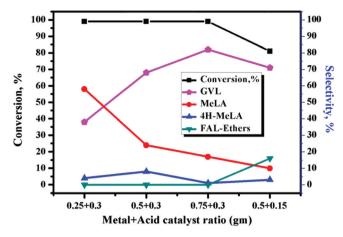
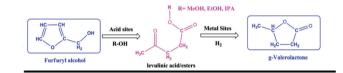


Fig. 6 Effect of the catalyst ratio on the hydrogenation of furfuryl alcohol to GVL. Reaction conditions: furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 403 K; H_2 pressure, 500 psi; catalyst, 0.15-0.3 g (acidic IL) + 0.25-0.75 g (5% metal catalyst); reaction time, 5 h.



Scheme 2 Direct conversion of furfuryl alcohol to GVL

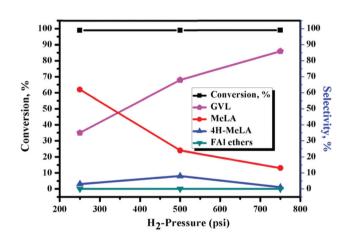


Fig. 7 Effect of hydrogen pressure on the hydrogenation of furfuryl alcohol to GVL. Reaction conditions: furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; H_2 pressure, 250–750 psi; catalyst, 0.3 g (acidic IL) + 0.5 g (5% metal catalyst); reaction time, 5 h.

in turn adversely affected the selectivity to GVL. This study suggests that the direct conversion of furfuryl alcohol to GVL involves acid catalyzed first step alcoholysis of furfuryl alcohol to Me-LA followed by its metal catalyzed hydrogenation to 4-hydroxy methyl levulinate and subsequent cyclization to GVL (Scheme 2). During the cyclization, R-O is released as the corresponding alcohol, methanol in this case.

In order to maximize the selectivity to GVL, hydrogen pressure was varied from 250 to 750 psi and the results are shown in Fig. 7. A complete conversion of furfuryl alcohol was

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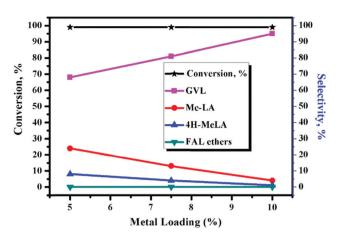


Fig. 8 Effect of metal loading on the hydrogenation of furfuryl alcohol to GVL. Reaction conditions: furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; H_2 pressure, 500 psi; catalyst, 0.3 g (acidic IL) + 0.5 g (5–10% metal catalyst); reaction time, 5 h.

achieved over the entire range of $\rm H_2$ pressures studied in this work. The $\rm H_2$ pressure effect was very positive to enhance the selectivity to GVL from 35 to 85% with complete disappearance of FAL ethers. However, even at the highest $\rm H_2$ pressure of 750 psi, marginal Me-LA and 4-MeLA remained unreacted indicating that rather than higher $\rm H_2$ concentration, a higher extent of metal sites would be necessary for complete hydrogenation of the intermediates to GVL. Therefore, the effect of active metal (Ru) loading on carbon was varied in the range of 5–10% with a constant amount of IL. As can be seen from Fig. 8, the conversion of the intermediate methyl LA increased from 76 to 95% with an increase in selectivity to GVL up to 94% for the active metal (Ru) loading of 10% on the carbon support. Thus, the availability of active metal content plays an important role in hydrogenation of methyl levulinate to GVL.

The role of acidic and metal sites could be further understood for the direct single pot conversion of furfuryl alcohol to GVL under a nitrogen and a hydrogen atmosphere. Fig. 9 shows the conversion and selectivity vs. time pattern for a single pot conversion of furfuryl alcohol to GVL over acidic as well as metal sites. Initially under an N2 atmosphere, Brønsted acid sites of IL gave complete formation of methyl levulinate within the first 2 h of the reaction with complete conversion of furfuryl alcohol while changeover from N2 to H2 facilitated the hydrogenation of MeLA to 4-hydroxy MeLA followed by its cyclization to GVL. However, under only hydrogenation conditions, the ring hydrogenation product THF alcohol was obtained to the extent of 25-31% which remained stable, affecting the selectivity to GVL (entry 3, Table 2). The mechanistic pathway for alcoholysis of furfuryl alcohol to methyl levulinate in alcoholic medium involves first the formation of methoxy FAL followed by ring hydration in the form of 1,4addition to cyclic oxonium (ESI, Scheme 1†). The cyclic oxonium compound then undergoes deprotonation to form cyclic diene followed by its isomerisation in acidic medium to give the final product, methyl levulinate.

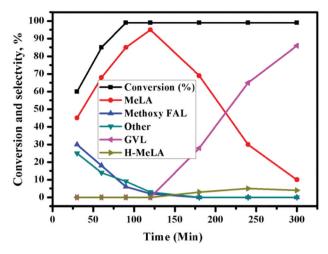
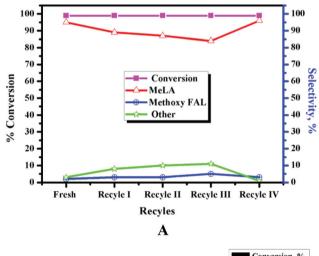


Fig. 9 CT profile for furfuryl alcohol alcoholysis and hydrogenation. Reaction conditions: furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; N_2 atm. + H_2 pressure, 500 psi; catalyst, 0.3 (acidic IL) + 0.75 g (5% metal catalyst); reaction time, 2 h + 3 h.



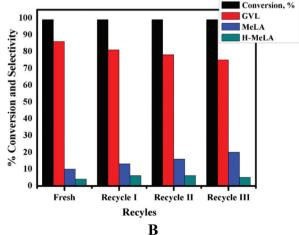


Fig. 10 Recycle study of (A) rehydration of furfuryl alcohol to methyl levulinate and (B) direct hydrogenation of FAL to GVL. Reaction conditions: (a) furfuryl alcohol, 5% (w/w); solvent, MeOH (95 mL); temperature, 130 °C; N_2 atm., catalyst, 0.3 g; reaction time, 2 h. (b) H_2 pressure, 500 psi; catalyst, 0.75 g.

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The recycle experiments for [BMIm-SH][HSO₄] catalyst were also carried out at 130 °C. After completion of the reaction, methanol was evaporated using a rotavapour. To this concentrated solution, 80 mL of ethyl acetate was added and the IL was extracted with three portions 40 mL each of distilled water, in a separating funnel. After evaporation of the aqueous layer, IL catalyst was recovered for its reuse in the subsequent alcoholysis experiment. This procedure was repeated up to the third recycle of the catalyst which showed the consistent activity (Fig. 10A). A decrease in selectivity to methyl levulinate from 99 to 83% associated with the corresponding increase in intermediate selectivity was observed due to handling loss from time to time extraction. This was confirmed by adding a make up amount (~20%) of the catalyst after the third recycle due to which the original selectivity to methyl levulinate was regained in the fourth recycle. The results of a catalyst recycle study for single pot conversion of furfuryl alcohol to GVL are also shown in Fig. 10B. Both the activity and selectivity were consistent for 5% Ru/C in combination with [BMIm-SH][HSO₄] up to three recycles, confirming the stability of our catalyst system under reaction conditions. GC analysis of the organic layer showed GVL with 100% purity while the aqueous layer did not show any GVL (ESI, Fig. 6A and B[†]). This confirms the easy protocol of solvent extraction for the recovery of pure product (GVL).

Conclusions

A novel approach for direct conversion of furfuryl alcohol to GVL via the alcoholysis/hydrogenation sequence using sulfonic acid-functionalized ionic liquids (SO3H-ILs) and 5% Ru/C catalyst system has been demonstrated. Furfuryl alcohol conversion as high as 99% could be achieved with ILs modified with HSO₄ and Cl-HSO₃ anions in the alcoholysis reaction. The catalyst could be further tuned by increasing the alkyl chain of IL 1-methyl imidazole with 1,4-sultone to give an enhanced selectivity of 95% to methyl levulinate. Combining furfural alcoholysis with a subsequent hydrogenation of Me-LA in a single pot synthesis using our catalyst system comprising [BMIm-SH][HSO₄] + 5% Ru/C successfully resulted in the formation of GVL with 68% selectivity and complete conversion of furfuryl alcohol. Under the hydrogenation conditions, the ring hydrogenation to THFAL is a competing reaction adversely affecting the GVL selectivity; hence, the first stage alcoholysis can be carried out under N2 and then changeover to H2 eliminates the THFAL formation. Among the various parameters studied in this work, an increase in Ru loading from 5 to 10% dramatically enhanced the GVL selectivity from 68 to 94%, indicating that the availability of active metal sites is more significant in the tandem reactions of alcoholysis and hydrogenation of methyl levulinate. 5% Ru/C in combination with IL could be satisfactorily recycled three times with consistent performance, confirming its stability under reaction conditions.

Experimental

Materials

Furfuryl alcohol (99%), methyl levulinate metal salts, 1-methyl imidazole and 1,4-butane sultone were purchased from Sigma-Aldrich, Bangalore, India, while methanol (>99.9%) was purchased from Rankem. Hydrogen (>99.99% purity) was obtained from Inox, India.

Catalyst preparation

1-Methylimidazole and 1,4-butane sultone (0.2 mol) were charged into a 100 mL round bottomed flask. The mixture was then stirred at 40–80 °C for 1 h. The solid zwitterion was recovered by filtration and washed with diethyl ether to completely remove the unreacted reactants and then dried under vacuum overnight. A stoichiometric amount of respective sulfonic acid was subsequently added dropwise to the respective zwitterion and the mixture was again stirred at 80 °C for 6 h. The viscous liquid thus obtained was washed with diethyl ether and dried under vacuum overnight. All the prepared sulfonic acid functionalized ionic liquids were confirmed by $^1\mathrm{H}$ NMR (200 MHz) in $\mathrm{D}_2\mathrm{O}$ at 25 °C.

Supported Ru, Pd, Re, Pd and Ag catalysts were prepared by the impregnation method. In a typical procedure, 2 g of the support, carbon, was suspended in aqueous medium containing a calculated amount of the respective metal precursor under stirring for 1 h. It was subsequently reduced using 5 mL of NaBH₄ (1 mol). The catalyst was then filtered and dried at $110~{\rm ^{\circ}C}$ for $12~{\rm h}$.

Hydrogenation experiment and analysis

Single pot furfuryl alcohol alcoholysis and hydrogenation were carried out in a 300 mL capacity autoclave (Parr Instruments Co., USA) at a stirring speed of 1000 rpm. The typical reaction conditions were: temperature, 130 °C; furfuryl alcohol concentration, 5 wt%; solvent, 95 mL; total volume, 100 mL; catalyst loading, 0.3 g (acidic IL) + 0.5 g (supported metal catalyst); substrate: catalyst mole ratio (10:1); and hydrogen pressure, 500 psi. Liquid samples were withdrawn periodically and analyzed by GC (Thermo-Trace-700) having an HP-5 column with a FID detector.

Abbreviations

GVL γ-Valerolactone

LA Levulinate or levulinic acid

MeLA Methyl levulinate

4-MeLA 4-Hydroxy methyl levulinate
[MIm] 1-Methyl imidazolium
[NMP] N-Methyl 2-pyrollidonium

[BMIm-SH] 1-Butyl sulfonic acid, 3-methyl imidazolium

[MMT] Montmorillonite

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