Supplementary Material (ESI) for Green Chemistry

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### **Electronic Supplementary Information (ESI)**

# Single pot conversion of furfuryl alcohol to levulinic esters and γ-valerolactone over sulfonic acid functionzed ILs with metal catalysts

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#### General procedure for the synthesis of ionic liquid by quaternization method

1-methylimidazole (0.2 mol) was placed in a two necked flask which was equipped with a magnetic stirred and cooled in an ice water bath. Small amount of water was added slowly with stirring and equimolar quantity of acid (0.2 mol) was added to the reaction mixture was stirred for an additional period of 2then water from the reaction crude was evaporated with a rotary evaporator at 70  $^{\circ}$ C and thus a courless liquid product was obtained with 95 % yield.

#### Experimental

The software program X-Pert High Score Plus was employed to subtract contribution of copper K $\alpha$ 2 line prior to data analysis. X-ray photoelectron spectra were recorded using an ESCA-3000 (VG Scientific Ltd. England) with a 9 channeltron CLAM4 analyzer under vacuum better than 1 x 140-8 Torr, using MgK $\alpha$  radiation (1253.6 eV) and a constant pass energy of 50 eV. The binding energy values were charge-corrected to the C1s signal (284.6 eV).

### **GC-MS** Analysis

Liquid samples were withdrawn and analyzed by GC Shimadzu-74218 having HP-5 column with FID detector and mass sepectrometer, QP-2010 ultra EI, Shimadzu. positive chemical ionization PCI ion source was used for acquiring the mass spectra of the compounds of interest. Mass range 1.5 to 1090 m/z, maxiumum scan rate of 20000 amu/sec.



Scheme 1 Plausible mechanistic pathway for MeLA formation



Fig. 1 Recycle study for FAL to methyl levulinate using NMP[HSO<sub>4</sub>] catalyst



Fig. 2 XPS study of Used Ru/C catalysts

# Table 1. Comparison study of our Ru/C with other reported catalysts systems for synthesis of GVL

Entry	Catalysts	Substrate	Time (h)	Conversion (%)	Selectivity (GVL) (%)	TOF (h <sup>-1</sup> )
1	10%Ru/C+	Furfuryl alcohol	5	99	>95	$53^{a}(160)^{b}$
	[BMIm-SH][HSO <sub>4</sub> ]					
2	5%Ru/C	Levulinic acid	24	90	>99	$15^{\mathrm{a}}$
3	10% Ru/C + TFA	Fructose	8	99	62	$7^{\mathrm{a}}$
[a] The tot	al turnover frequency is cal	culated on the basis of	moles of	Ru on support [l	o]. Numbers in par	enthesis refer to
the TON e	stimated on the basis of dis	persion of Ru atoms				

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Fig. 3 GC spectra of furfuryl alcohol alcoholysis



Fig. 4 Mass spectra of methyl levulinate



Fig. 5 Mass spectra of methoxy FAL

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Method filename:	E:\solvent\LA\Cont 6.mth
Method name:	Amol
Analysed:	10-07-13 14:00
Printed:	11-Jul-13 11:13
Chromatogram filename:	E:\solvent\LA\Ethyl acetate GVL.dat



Fig. 6A GC spectra of extracted GVL

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Fig. 6B GC spectra of aqueous layer for GVL