Electronic Supporting Information

Recognizing soft templates as stimulators in multivariate modulation of tin phosphate and its application in catalysis for alkyl levulinate synthesis

Pandian Manjunathan [a,b] , Dhanush Y. Shanbhag [c], Ajayan Vinu [c] and Ganapati V. Shanbhag [a]*

[a] *Materials Science and Catalysis Division, Poornaprajna Institute of Scientific Research (PPISR),*

Bidalur Post, Devanahalli, Bengaluru-562164, Karnataka, India

[b] *Graduate Studies, Manipal Academy of Higher Education, Manipal-576104, Karnataka, India*

[c] *Global Innovative Center for Advanced Nanomaterials (GICAN), Faculty of Engineering and Built Environment, The University of Newcastle, Callaghan, NSW 2308, Australia*

E-mail addresses: shanbhag@poornaprajna.org, gvshanbhag@gmail.com

S1. General information

S1.1. Chemicals and Materials

Stannic chloride pentahydrate ($SnCl_4.5H_2O$), tetrapropylammonium bromide (TPABr), N-cetyltrimethylammonium bromide (CTAB) and 2,6-lutidine were purchased from Loba Chemie Pvt. Ltd, India. ortho-Phosphoric acid (H_3PO_4) and furfuryl alcohol were procured from SD Fine-Chem Ltd. Glycerol (GLY), ethylene glycol (EG), polyethylene glycol-400 (PEG-400), methanol, 1-propanol, 1-butanol, 25% aqueous ammonia and conc. sulfuric acid were purchased from Merck India Pvt. Ltd. Pluronic P123 (P123), tetraethylene glycol (TEG) and tetraethyl orthosilicate (TEOS) were purchased from Sigma-Aldrich. Absolute ethanol was obtained from Changshu Hongsheng Fine Chemical Co. Ltd. China. Amberlyst-15 and aluminium isopropoxide were procured from Alfa Aesar. NH_4-Beta (SAR = 25) was obtained from Nankai University Catalyst Co.

S1.2. Experimental section

S1.2.1. Synthesis of tin phosphate by template assisted and template-free method

The tin phosphate was synthesized using stannic chloride pentahydrate as tin precursor with various structure directing agents (SDA). In a typical procedure, H_3PO_4 (2.3 g, 20 mmol) was dissolved in 30 ml of distilled water and SDA (2 g) was added into it. The mixture was stirred in a 60 ml polypropylene bottle for 2 h to get a homogeneous solution and then stannic chloride pentahydrate (7 g, 20 mmol) in 10 ml of distilled H_2O was added dropwise. A white colloidal precipitate was formed slowly with continuous stirring for 4 h. It was then hydrothermally treated at 100 °C for 72 h under static condition. The obtained product was filtered, washed repeatedly with water and then methanol and dried at 50 °C. Finally, the material was calcined at

650 °C for 5 h with the ramp rate of 2 °C min^{-1} and denoted as SnPO-SDA (SDA = P123, CTAB, TPABr, GLY, EG, PEG, TEG).

The template free (TF) tin phosphate was synthesized by adopting the aforementioned procedure using ortho-phosphoric acid in absence of SDA. The obtained product was filtered, washed, dried and calcined at 650 °C and designated as SnPO-TF. The tin oxide was prepared by using pluronic P123 as SDA in absence of phosphate source by employing the same synthesis procedure.

Other catalysts namely Al-MCM-41 (SAR = 25) was synthesized from the reported literature [1]. Protonic form of zeolite was obtained by calcining them at 540 °C under static air for 4 h with the ramp rate of 5 °C min^{-1}.

S1.2.2. General procedure for catalytic experiments

Alcoholysis of furfuryl alcohol (hereafter FFAL) with 1-butanol was performed in a 25 ml glass batch reactor in liquid phase equipped with a reflux condenser. In general, the required amounts of FFAL and 1-butanol were taken along with pre-activated catalyst, and the reaction mixture was magnetically stirred at a desired temperature. The effect of substrate was studied using different alkyl alcohols with furfuryl alcohol. The alcoholysis reaction above 120 °C was performed in a 50 ml stainless steel stirred autoclave equipped with temperature controller and pressure gauge. The progress of reaction was monitored by gas chromatography and the products were confirmed by GC–MS analysis. Furfuryl alcohol was distilled out prior to the use in reaction medium. After the desired time, the reaction mixture was taken out and centrifuged to remove the catalyst from liquid phase. The obtained liquid was analyzed by gas chromatography (Agilent 7820A) equipped with a capillary column (HP-5, 30 m length, 0.25 mm I.D, 0.25 µm

thickness) and flame ionization detector. The reactant conversion, product selectivity and yield were calculated using the following formulae as shown below:

Furfuryl alcohol (FFAL) conversion (mol%) = $\frac{(Initial\ moles\ of\ FFAL) - (Final\ moles\ of\ FFAL)}{Initial\ moles\ of\ FFAL}\ X\ 100$

Product selectivity (mol%) = $\frac{moles\ of\ desired\ product\ formed}{Initial\ moles\ of\ FFAL}\ X\ 100$

Product yield (mol%) = $\frac{FFAL\ converted\ (mol\%)\ X\ desired\ product\ selectivity\ (mol\%)}{100\ (mol\%)}$

S1.2.3. Catalyst recycle experiment

After completion of the experiment, the catalyst was filtered, washed with methanol to remove the adsorbed species on the catalyst surface followed by drying at 100 °C and finally calcined at 650 °C for 2 h. The calcined catalyst was further used for the respective reaction with a fresh reaction mixture.

S1.2.4. Procedure for the chemisorption of 2,6-lutidine in SnPO-P123 catalyst

The SnPO–P123 catalyst was calcined at 650 °C for 1 h, later cooled to 250 °C and placed in a desiccator to maintain moisture free condition. Then the samples were saturated with 2,6-lutidine and heated at 150 °C for 1 h to remove physisorbed molecule. Later, it was used in the corresponding reaction medium as 2,6-lutidine-treated-SnPO-P123 catalyst.

S1.3. Characterization techniques

Powder X-ray diffraction of the catalysts was recorded with Bruker D2 phaser X-ray diffractometer using CuKα radiation (λ = 1.5418 Å) with high resolution Lynxeye detector. Nitrogen sorption measurements of catalysts were performed at 77 K using a Belsorp mini II

instrument. Prior to the experiments, the samples were pretreated at 400 °C for 2 h at vacuum pressure of 10^{-2} kpa. The specific surface area of samples was calculated by using Brunauer–Emmett–Teller (BET) method in the relative pressure (P/P$_0$) range of 0.05 to 0.25. The pore-size distribution of samples was determined by Barrett–Joyner–Halenda (BJH) method. The desorption branch of isotherm was used to calculate the BJH distribution. The total pore volume of sample was accumulated at a relative pressure of P/P0=0.99.

The nature of acidic sites viz, Brønsted and Lewis acidic sites in catalysts were investigated by pyridine adsorption study using FT-IR (Bruker α-T model) [2]. The self-supported wafers of the catalysts were prepared by a pellet press instrument. The wafer was then calcined at 650 °C for 1 h, later cooled to 250 °C and placed in a desiccator to maintain moisture free condition. Then the samples were saturated with pyridine at 1 atm pressure and heated at 150 °C for 1 h under nitrogen flow to remove physisorbed pyridine. FTIR spectra were recorded in absorbance mode in the wavenumber range from 1400 to 1600 cm^{-1}. The spectrum obtained after pyridine treatment was subtracted with spectrum of pyridine untreated sample to get peaks only due to pyridine–acid interaction.

The amount of acidity present in the catalysts were determined by ammonia-temperature programmed desorption technique using Belcat II instrument equipped with thermal conductivity detector. In all the experiments, the sample (100 mg) was calcined at respective calcination temperature for 1 h in helium gas flow (25 mL min^{-1}) and then cooled to 50 °C. Later, the sample was saturated with 10% of ammonia balanced with helium at 50 °C for 30 min. After the saturation of probe molecule, the sample was flushed with helium for 1 h at 50 °C to remove the physisorbed ammonia, and then desorption of ammonia was performed in

temperature ranging from 50 to 650 °C with the heating rate of 10 °C min^{-1} [3]. The amount of acidic sites in amberlyst-15 was determined by acid-base titration method [4].

^{31}P MAS NMR analysis was studied by ECX-JEOL 400(S), AVIII400(L) NMR spectrometer using standard procedure at the operating frequency of 202.5 MHz. The sample was placed in a 4 mm zirconia rotor and was spun at 12 kHz. The chemical shifts of ^{31}P was referenced to $NH_4H_2PO_4$. Thermogravimetric analysis was performed using NETZSCH TG 209 F1 Libra analyzer by heating the sample from 30 to 800 °C at the rate of 5 °C min^{-1} in the flow of air. Scanning electron microscopy (SEM) images of samples were recorded in Zeiss microscope to investigate the particle size and morphology. Elemental composition of tin phosphate catalysts was estimated by EDS (Energy Dispersive X-Ray Spectroscopy) analysis. The transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) patterns were recorded using TEM-JEOL-2010 instrument.

Characterization of catalysts
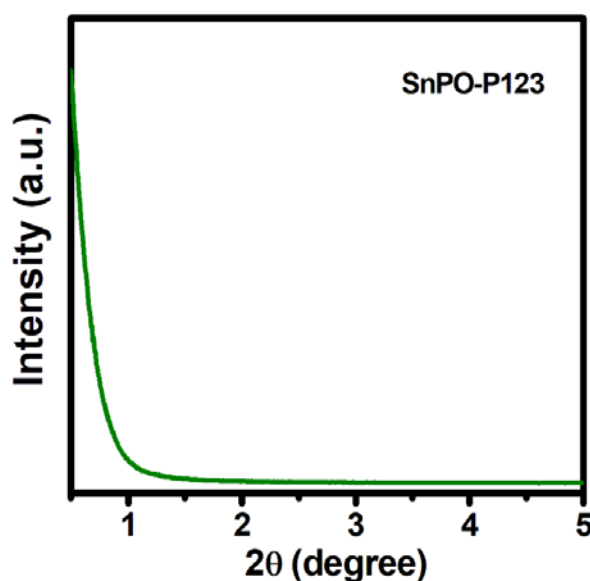
Fig. S1. Low angle XRD pattern of SnPO-P123.

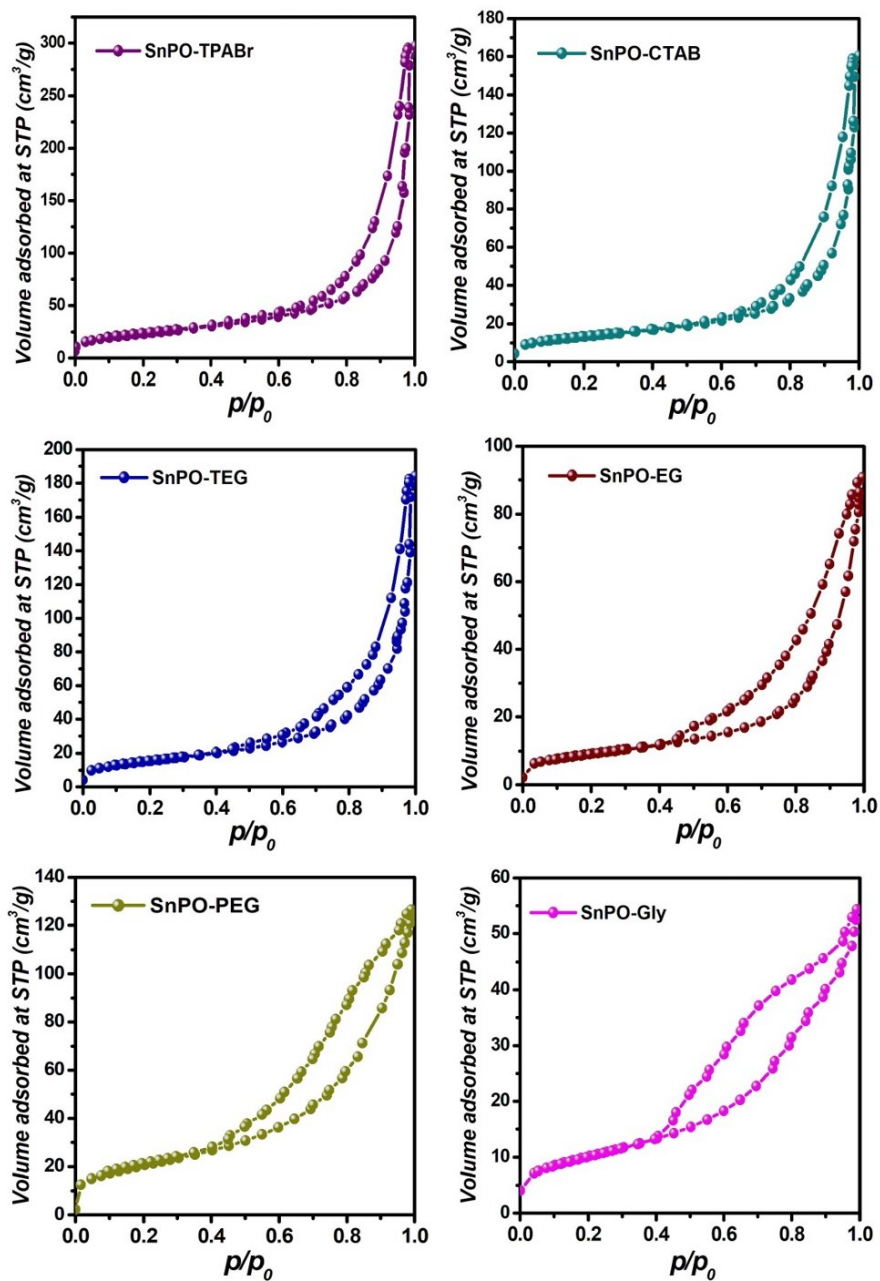**Fig. S2 .** Nitrogen sorption isotherms of different SnPO catalysts.

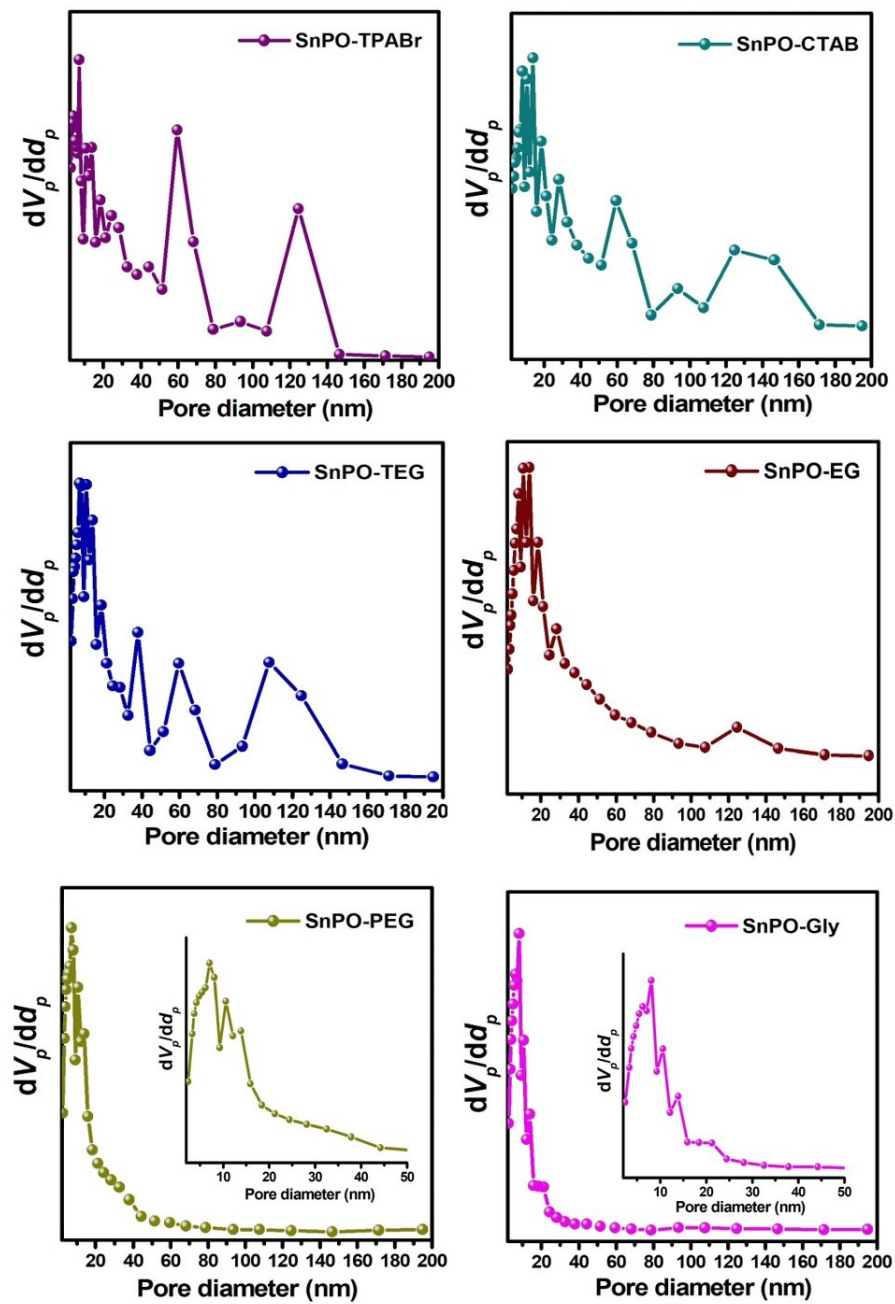**Fig. S3.** BJH pore size distribution of different SnPO catalysts.

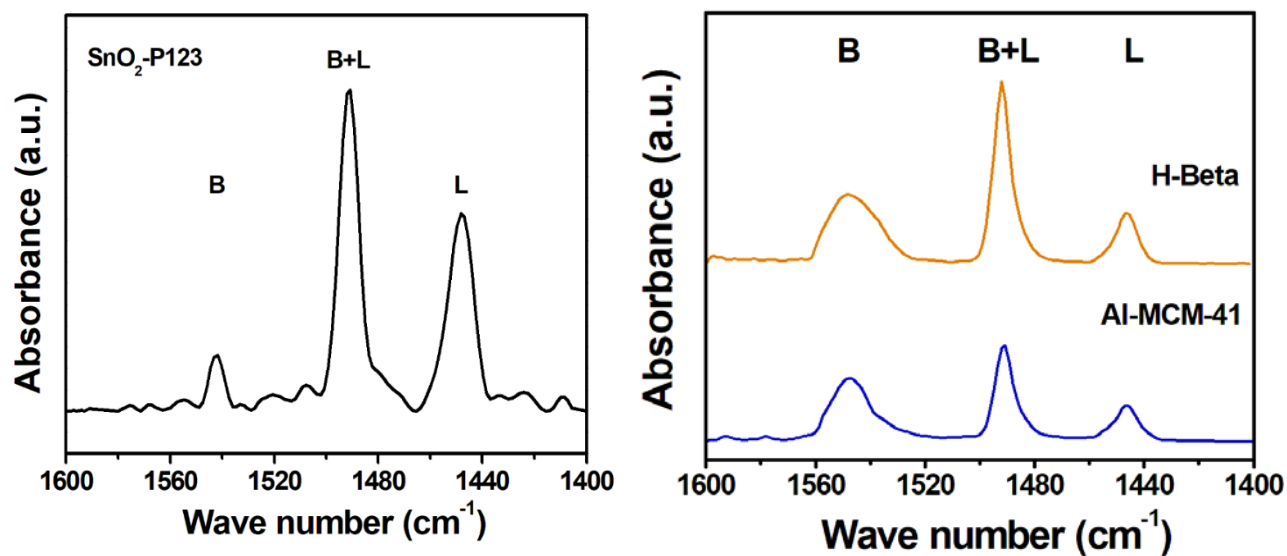**Fig. S4.** Pyridine-FTIR profile of tin oxide and aluminosilicates.

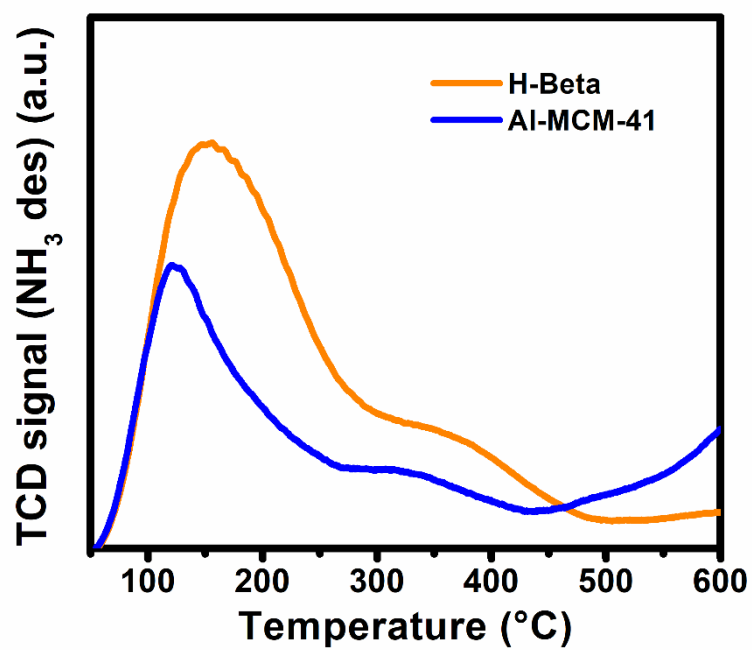

Fig. S5. NH$_3$-TPD profile of aluminosilicates catalysts
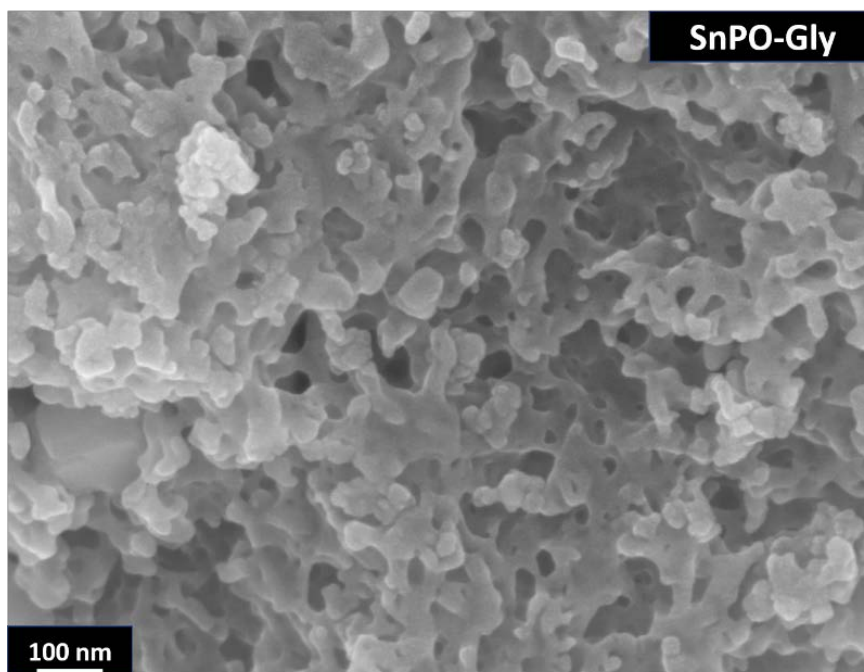
Fig. S6. SEM image of SnPO-Gly

Fig. S7. Bright field TEM image of SnPO-P123 **(a - e)**; and SAED images **(f)**.
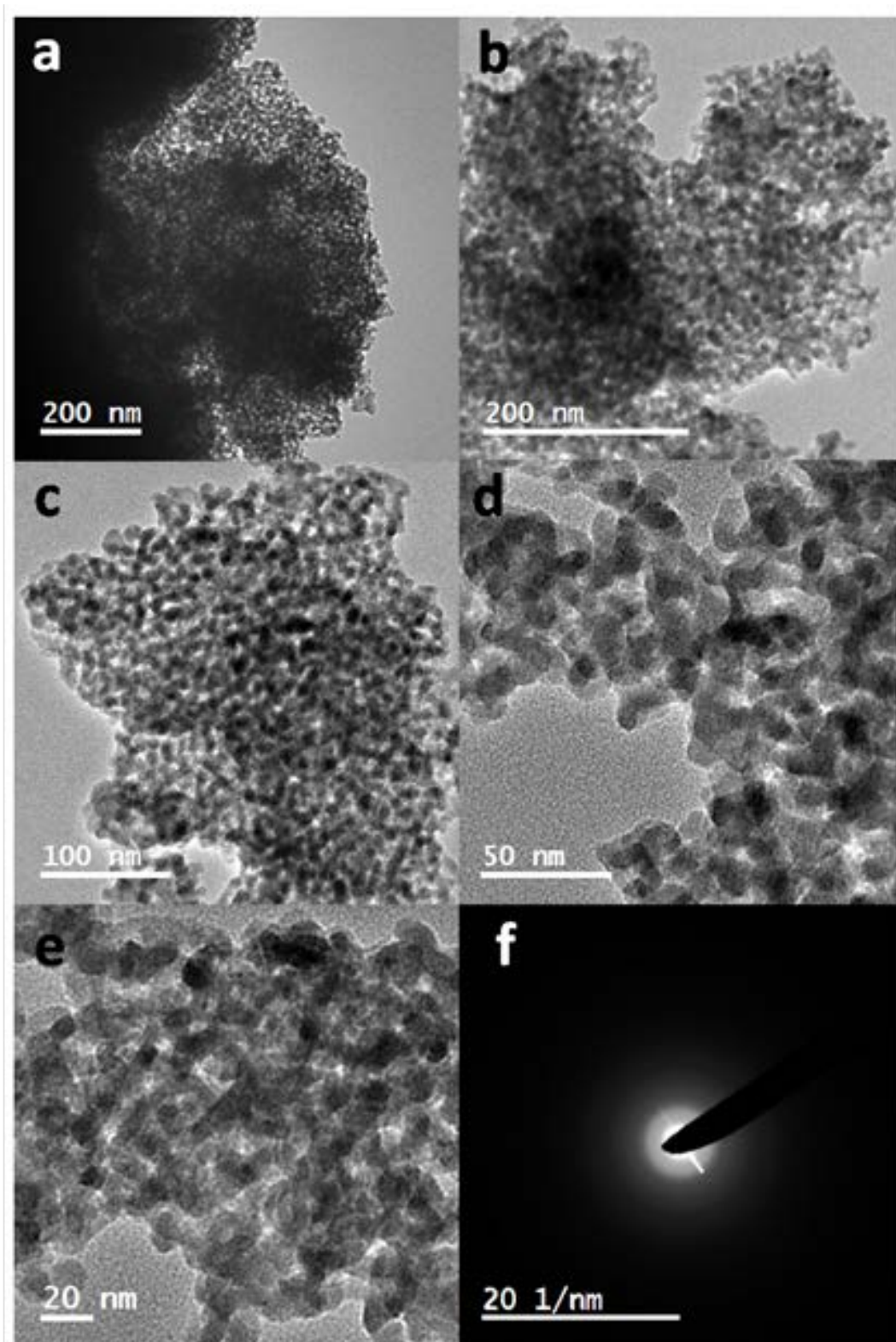
Fig. S8. Influence of time on the **c**atalytic activity of tin phosphates for butanolysis of furfuryl alcohol, **Reaction conditions:** Furfuryl alcohol (FFAL) (0.4 g, 4mmol), 1-butanol (3.1 g, 40 mmol), catalyst = 0.1 g (0.025 g_{cat}/mmol$_{FFAL}$), temperature = 120 °C, BMF = 2-(alkoxymethyl)furan, BuLv = butyl levulinate.
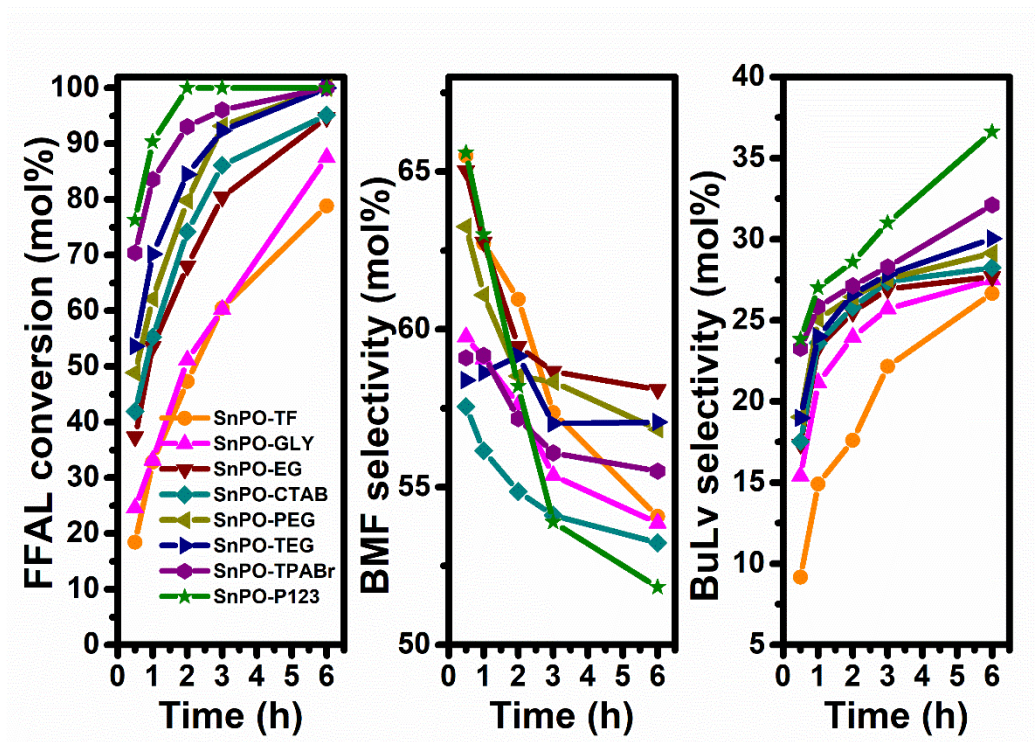
Fig. S9. Influence of reaction conditions on butanolysis of furfuryl alcohol over SnPO-P123 catalyst. **(a) Effect of reactant mole ratio.** Conditions: FFAL = 4 mmol (0.4 g), catalyst amount = 0.025 $g_{cat}/mmol_{FFAL}$, reaction temperature = 120 °C. **(b) Effect of catalyst amount.** Conditions: FFAL = 4 mmol (0.4 g), 1-butanol = 40 mmol (3.1 g), catalyst amount = $g_{cat}/mmol_{FFAL}$, reaction temperature = 120 °C. **(c) Effect of reaction temperature.** Conditions: FFAL = 16 mmol (1.6 g), 1-butanol = 160 mmol (12 g), catalyst amount = 0.10 $g_{cat}/mmol_{FFAL}$, reaction was carried out using autoclave.
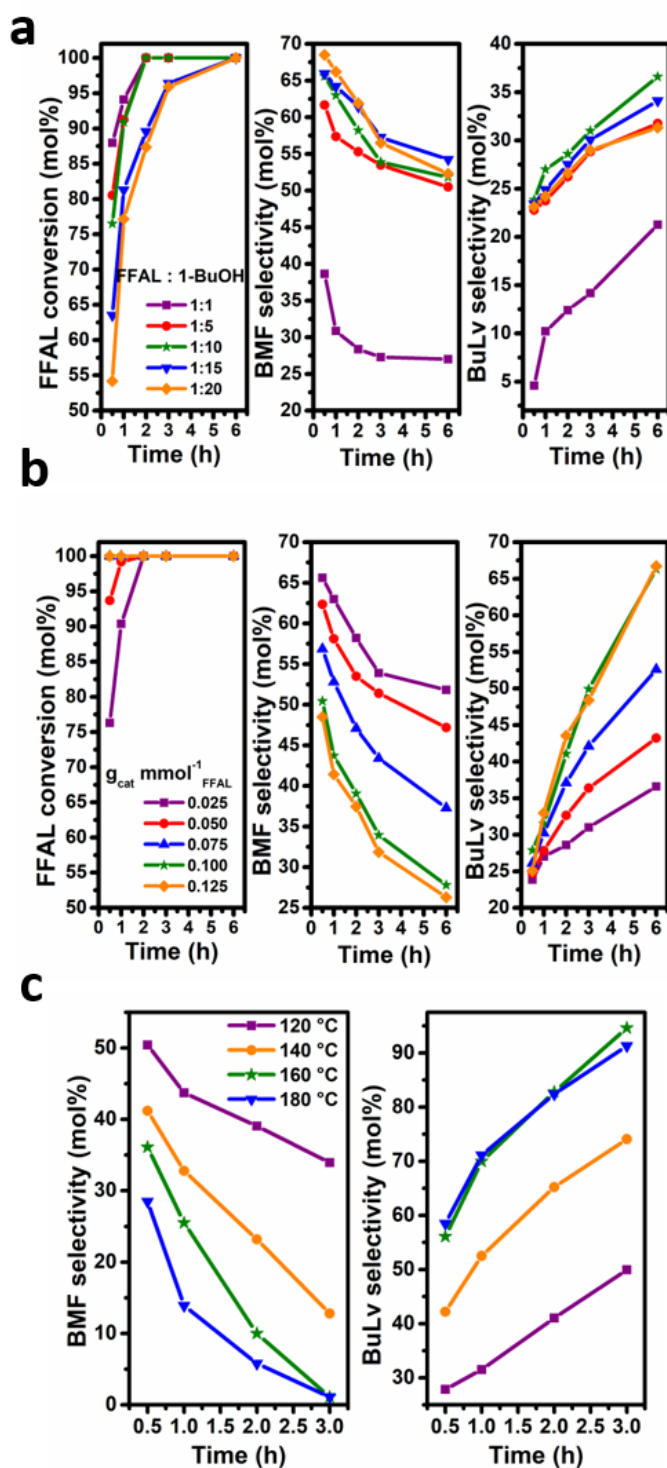
Fig. S10. Influence of reaction conditions on butanolysis of furfuryl alcohol over SnPO-P123 catalyst. **(a) Effect of reactant mole ratio.** Conditions: FFAL = 4 mmol (0.4 g), catalyst amount = 0.025 g_{cat}/mmol$_{FFAL}$, reaction temperature = 120 °C, time = 6 h. **(b) Effect of catalyst amount.** Conditions: FFAL = 4 mmol (0.4 g), 1-butanol = 40 mmol (3.1 g), catalyst amount = g_{cat}/mmol$_{FFAL}$, reaction temperature = 120 °C, time = 6 h. **(c) Effect of reaction temperature.** Conditions: FFAL = 16 mmol (1.6 g), 1-butanol = 160 mmol (12 g), catalyst amount = 0.10 g_{cat}/mmol$_{FFAL}$, time = 3 h, reaction was carried out using autoclave.
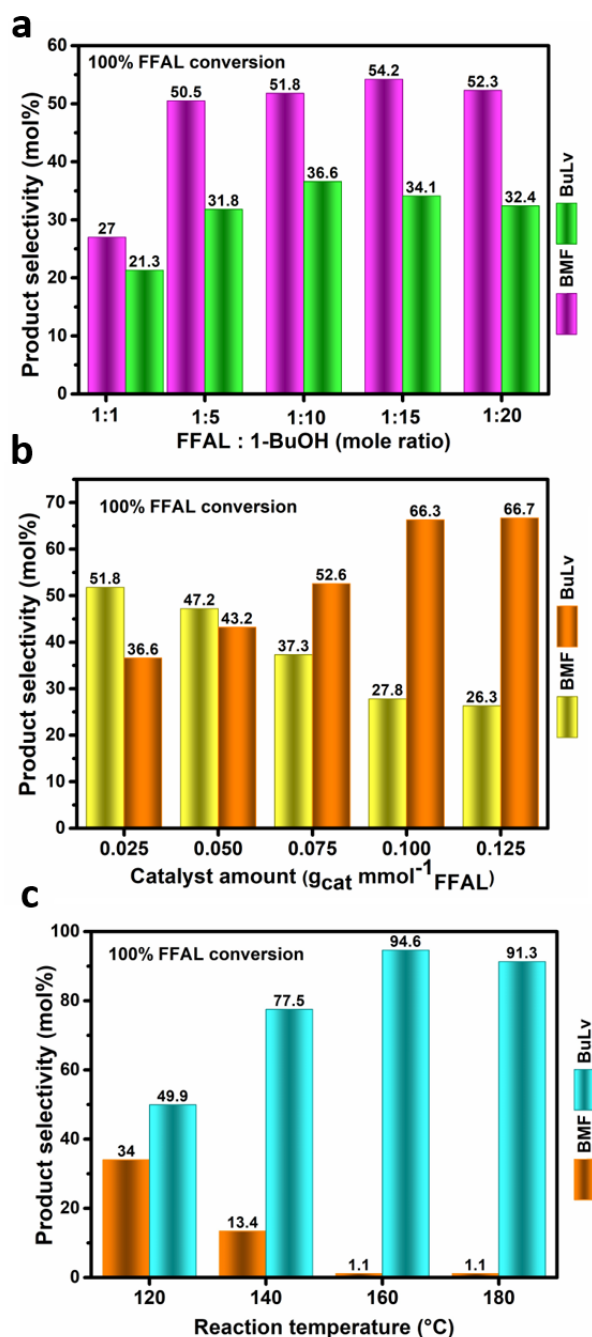
The reaction conditions play an important role in obtaining higher product yield and influence the catalyst performance. Thus, the alcoholysis of furfuryl alcohol was studied using different reactant mole ratio, catalyst amount and reaction temperature. The effect of reactant mole ratio was studied at 120 °C with FFAL (0.4 g) to 1-butanol mole ratio from 1:1 to 1:20 using SnPO–P123 and the influence of time on activity are depicted in ESI Fig. S9a. and ESI Fig. S10a. The progress of reaction proceeds faster with 1:1 mole ratio and gave 100% furfuryl alcohol conversion, however it fails to give higher yield to BMF (27%) and BuLv (21.3%) (total selectivity of 48.3% for 6 h). The lower selectivity to BMF and BuLv is due to the formation of other products by the polymerization of furfuryl alcohol at lower reactant mole ratio. Furfuryl alcohol converted 100% in 2 h by varying the reactant mole ratio from 1:5 to 1:10, whereas the selectivity to BMF and BuLv increased gradually. Further varying the mole ratio to 1:15 and 1:20 showed a slow progress in furfuryl alcohol conversion with marginal decrease in BuLv selectivity. This could be due to the dilution of reaction mixture with excess of 1-butanol which causes lower number of collisions between the molecules and preferential adsorption of 1-butanol on active sites resulting in difficulty in accessibility of active sites to BMF to further undergo transformation to form BuLv. Based on the above results, mole ratio of furfuryl alcohol to 1-butanol at 1:10 was selected for further studies.

Catalyst amount determines concentration of active sites in reaction medium and influences correspondingly the substrate conversion with product distribution. The effect of catalyst amount was studied using SnPO–P123 from 0.025 to 0.125 $g_{cat}/mmol_{FFAL}$ with FFAL to 1-BuOH mole ratio from 1:10 at 120 °C and the influence of time on activity is depicted in ESI Fig. S9b. and ESI Fig. S10b respectively. Furfuryl alcohol converts significantly (from 78 to 100%) within 0.5 h with increase in catalyst amount from 0.025 to 1.25 $g_{cat}/mmol_{FFAL}$ due to increase in availability of active sites. The increase in catalyst amount significantly increased the selectivity

of BuLv (36.6 to 66.7% for 6 h) with decrease of BMF (51.8 to 26.3% for 6 h) due to the availability of accessible acidic sites since the formation of BuLv from BMF are in requirement of greater amount of acidic sites. The reaction with 0.1 and 0.125 $g_{cat}/mmol_{FFAL}$ of catalyst amount showed a similar catalytic performance and hence 0.1 $g_{cat}/mmol_{FFA}L$ of catalyst amount was selected for further studies. It is worth noticing that BMF (major) was formed first, and then decreased with increase in reaction time for all experiments, whereas the yield of BuLv increased with decrease in BMF (intermediate).

Reaction temperature appears to have a profound effect on both reaction rates and products distribution. Therefore, a systematic study was conducted using SnPO–P123 catalyst to understand the effect of reaction temperature on alcoholysis of furfuryl alcohol from 120 to 180 °C with FFAL: 1-butanol mole ratio of 1:10 at 0.1 $g_{cat}/mmol_{FFAL}$ for 3 h is shown in ESI Fig. S9c. and ESI Fig. S10c. Furfuryl alcohol converted completely at 0.5 h, but selectivity towards the desired product varied drastically with respect to temperature. Increase of temperature from 120 to 160 °C resulted in decline of BMF selectivity from 34.0 to 1.1% at 160 °C, whereas the BuLv selectivity increased from 49.9 to 94.6%. The decrease of BMF is mainly due to the formation of BuLv via ether to keto-ester transformation reaction. Further increase of temperature to 180 °C resulted in decrease of BuLv yield (91.3%).

Plausible reaction mechanism for alcoholysis of furfuryl alcohol
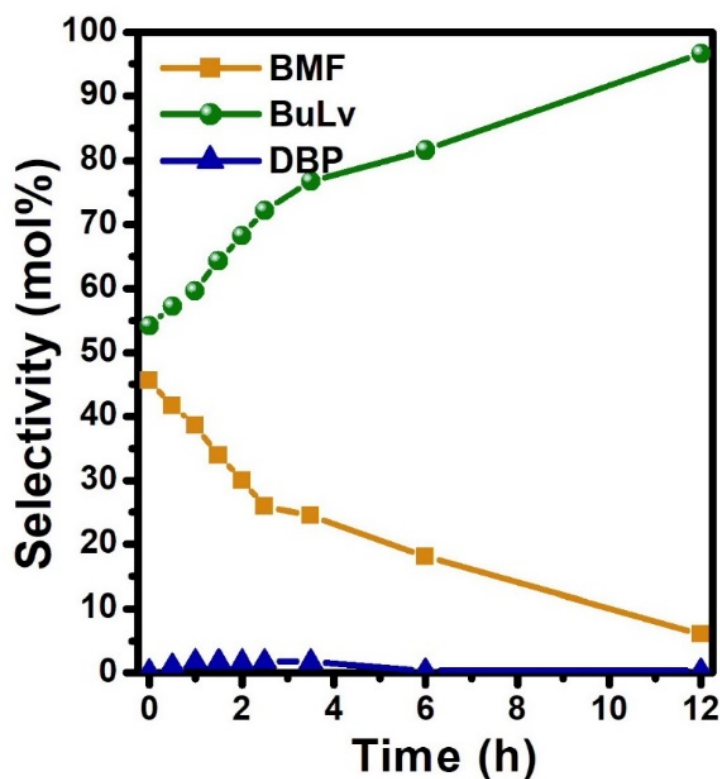
Fig. S11.

Fig. S10. Reaction of BMF and BuLv with 1-butanol. **Reaction conditions**: Mixture containing BMF and BuLv : 1-butanol = 1 : 5, catalyst = 0.025 g_{cat}/mmol$_{BMF}$, reaction temperature = 120 °C.

To confirm the reaction mechanism of alcoholysis of furfuryl alcohol, a reaction was conducted using a reaction mixture containing BMF (45.6%), BuLv (54.2%) and DBP (0.2%). To this mixture, a calculated amount of 1-butanol with 5:1 mole ratio corresponding to BMF was added along with SnPO–P123 catalyst. The reaction was carried out at 120 °C and the progress of reaction was monitored at regular interval of time and represented in ESI Fig. S11. In absence of catalyst, the reaction didn't proceed indicating that the transformation of BMF to BuLv requires a catalyst. In presence of a catalyst with increase in time, the concentration of BuLv increased from 54.2 to 93.6% with decrease in BMF from 45.6 to 6%. This indicates that the reaction takes place through the pathway were BMF acts as an intermediate to yield BuLv. Thus, a plausible mechanism is proposed and mentioned below.
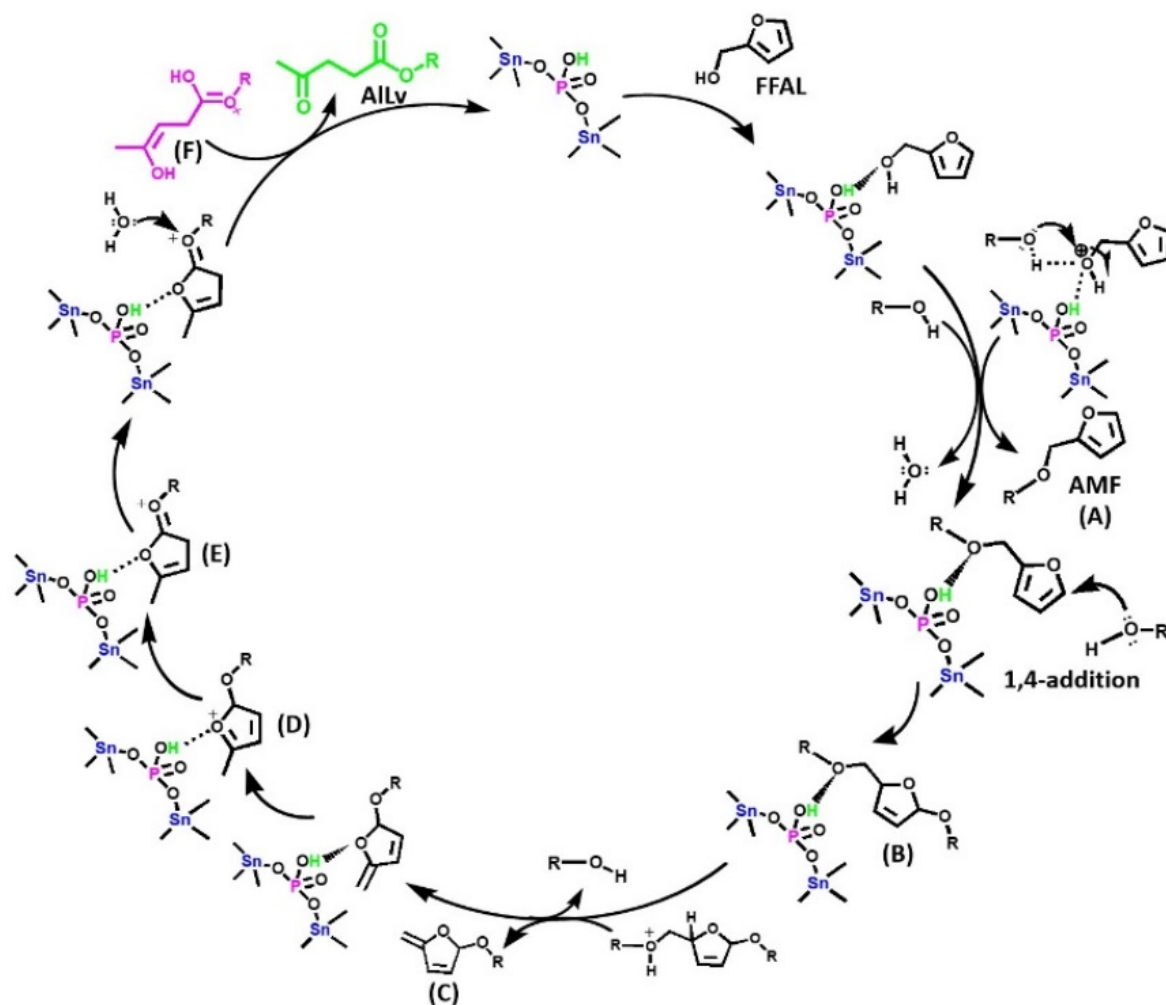
Scheme S1. Plausible mechanistic pathway of alcoholysis of furfuryl alcohol with alkyl alcohol.

According to an intermediate identified from the reaction and from the literature [5, 6, 7, 8, 9] and an active site responsible from 2,6-lutidine studies, a plausible reaction mechanism is proposed for the synthesis of alkyl levulinate from alcoholysis of furfuryl alcohol catalyzed by SnPO–P123 and depicted in ESI Scheme S1. In the initial step, hydroxyl group of furfuryl alcohol is adsorbed on acidic (H⁺) sites (P–O–H) resulting in the activation of furfuryl alcohol, then the alkyl alcohol attacks the activated furfuryl alcohol leading to the formation of 2–(alkoxymethyl)furan (species A) with elimination of water molecule. Subsequently, the formed 2–(alkoxymethyl)furan readily undergoes 1,4–addition with alcohol to form species B. Later, the species B is converted to species C (1,3–diene) with an elimination of alcohol molecule. Then

protonation of species C (diene) yields the cyclic oxonium (species D) and the formed species D undergoes electron-pair transfer to form exocyclic oxonium (species E). Further, species F is formed by the attack of water molecule resulting in ring-opening reaction, and finally species F is isomerized to form alkyl levulinate. Thus, it confirms that the reaction proceeds through 1,4–addition of 2–(alkoxymethyl)furan.

Fig. S12. Leaching and catalyst reusability studies of SnPO-P123 catalyst. **(a and b)** Conditions: FFAL : 1-butanol mole ratio = 1:10, catalyst amount = 0.1 g_{cat}/mmol$_{FFAL}$, reaction temperature = 160 °C, time = 3 h.
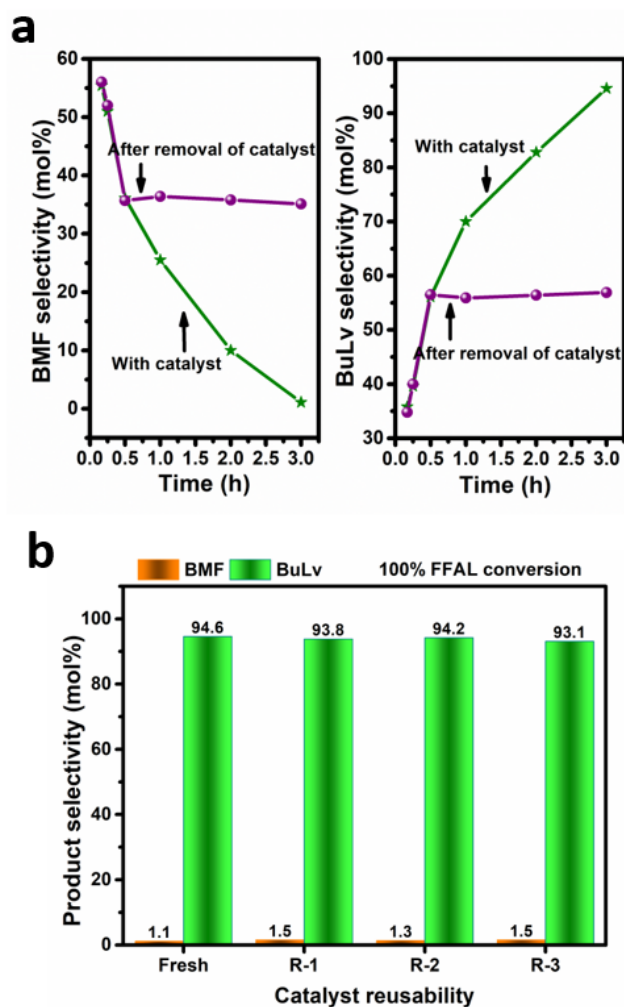
Fig. S13. FTIR spectra of fresh and spent SnPO-P123 catalyst.
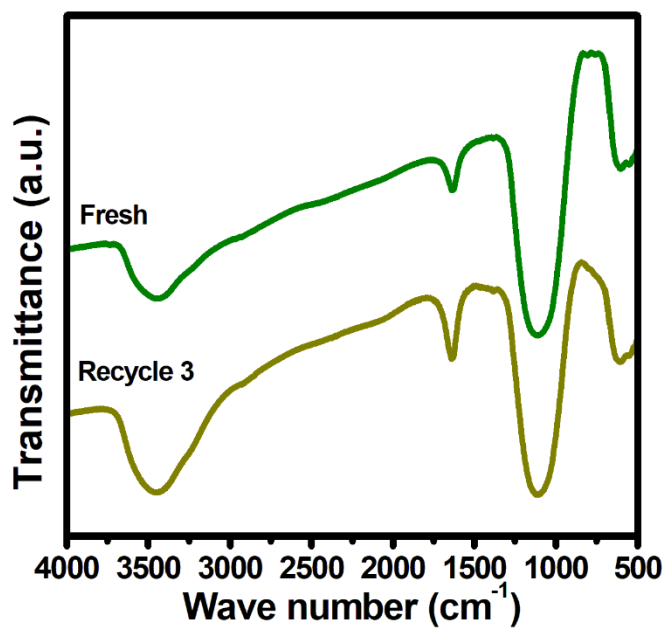
Fig. S14. XRD patterns of fresh and spent SnPO-P123 catalyst.
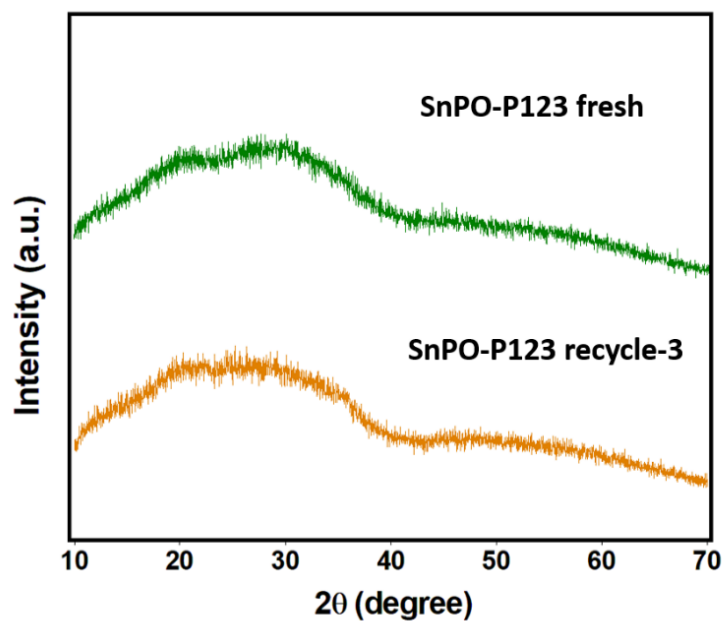
Fig. S15. Mass spectra of BuLv and DBP.
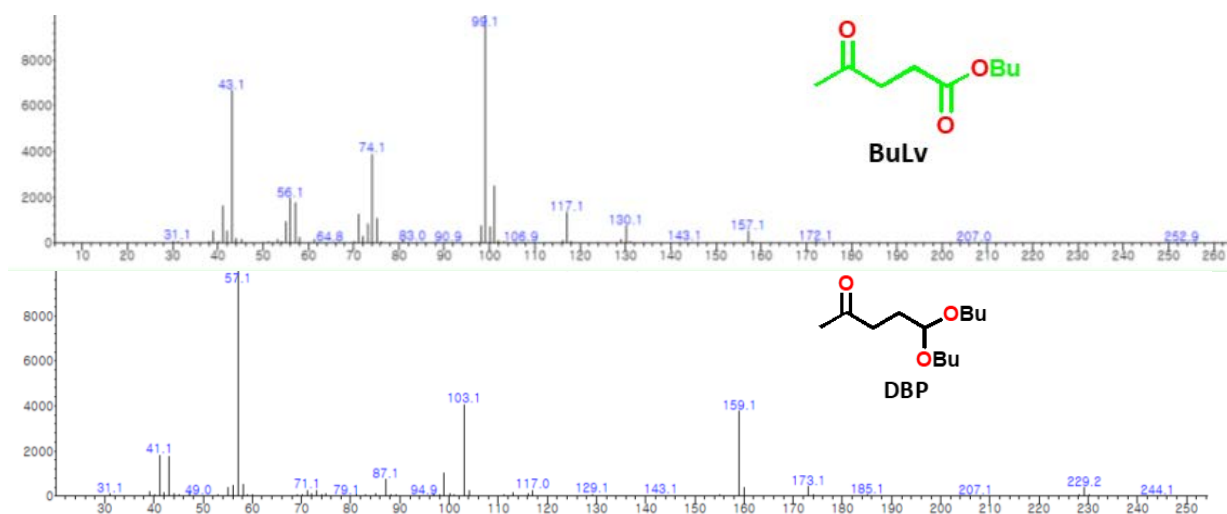
Table S1: Elemental composition of tin phosphate [a]		
Catalyst	**Elemental content (wt%)**	
	Sn	**P**
SnPO-TF	55.4	14.1
SnPO-Gly	55.6	15.5
SnPO-EG	53.5	16.3
SnPO-CTAB	57.0	15.6
SnPO-PEG	55.3	18.6
SnPO-TEG	52.1	14.8
SnPO-TPABr	50.4	16.8
SnPO-P123	50.7	15.3
[a] EDS elemental analysis		

Table S2. Catalytic activities of different catalysts for alcoholysis of furfuryl alcohol with 1-butanol.

Catalysts	B/L ratio	FFAL conv. (mol%)	Product selectivity (mol%)				BuLv yield (mol%)	TON (BuLv formed)
			BMF	DBP	BuLv	Others		
Blank*	-	0.1	100.0	0.0	0.0	0.0	0.0	-
H-beta	1.40	82.6	62.2	5.0	6.4	26.4	5.2	3.8
Al-MCM-41	1.72	90.3	57.4	9.9	6.2	26.6	5.6	4.1
Amberlyst-15	∞	50.7	30.4	17.9	26.8	24.9	13.6	9.9
SnPO–P123	**1.92**	**90.4**	**63.0**	**3.9**	**27.0**	**6.1**	**24.4**	**17.3**

Reaction conditions: Furfuryl alcohol (FFAL) (0.4 g, 4 mmol), 1-butanol (3.1 g, 40 mmol), catalyst = 55 µmoles of acidic sites taken, reaction temperature = 120 °C, time = 1 h, * time = 6 h, BMF = 2-(butoxymethyl)furan, BuLv = butyl levulinate, DBP = 5,5-dibutoxy-2-pentanone, TON (FFAL converted) (Turn over number) = moles of FFAL converted per mole of acidic sites, TON (BuLv formed) (Turn over number) = moles of BuLv formed per mole of acidic sites.

The catalytic performance of active catalyst SnPO–P123 was compared with other well-known conventional microporous and mesoporous catalysts, namely H-beta, Al-MCM-41 and amberlyst–15 by evaluating under identical amount of acidic sites (55 µmol of acidic sites for 4 mmol$_{FFAL}$) and the results are tabulated in Table S2. Among the catalysts screened, SnPO–P123 outperformed other catalysts by exhibiting higher BuLv yield 24.4% (27% selectivity) with 90.4% of furfuryl alcohol conversion. The conventional solid acid catalysts H-beta zeolite and Al-MCM-41 gave only 5.2 and 5.6% BuLv yield (6.4 and 6.2% selectivity) respectively. The difference in its catalytic behavior could be due to the difference in its structural properties and, nature and strength of acid sites in the catalyst. In other case, amberlyst-15 (sulfonic acid functionalized resin), a truly Brønsted acid catalyst gave only 50.7% furfuryl alcohol conversion with 13.6% BuLv

yield (26.8). The lower conversion of furfuryl alcohol by amberlyst-15 could be attributed to the presence of low specific surface area of 39 m^2/g. Further, 5,5-dibutoxy-2-pentanone, another intermediate to produce BuLv [7, 10] and other products were formed in significant quantity using Al-MCM-41 and amberlyst-15 as catalysts. The efficiency of catalyst was evaluated by comparing the turn over number (TON) and the BuLv yield. Among the catalysts screened, SnPO–P123 exhibited highest BuLv yield of 24.4% (27% selectivity) with TON for BuLv produced of 17.

Table S3. Comparison of SnPO-P123 with reported solid acid catalysts for butyl levulinate synthesis from butanolysis of furfuryl alcohol.

Entry	Catalysts	Amount (g_{cat}/mmol FFAL)	Temp (°C)	Time (h)	Mole ratio (FFAL: 1-BuOH)	BuLv yield (%)	Ref
1	[(HSO_3-p)$_2$im][HSO_4] Ionic liquid	0.012	120	2	1:22	93.0	11
2	SO_3H-SBA-15	0.025	110	4	1:35	96.0	12
3	[$BmimSO_3H$]$_3$$PW_{12}O_{40}$	0.180	120	12	1:48	88.0	8
4	Ti-KIT-6	0.306	110	5	1:60	94.0	13
5	Al-SBA-15	0.410	110	6	1:66	94.0	7
6	**SnPO–P123**	**0.100**	**160**	**3**	**1:10**	**94.6**	**PW**
		PW = Present work					

The catalytic efficiency of SnPO–P123 for furfuryl alcohol butanolysis was compared with other reported catalysts and tabulated in Table S3. The [(HSO_3-p)$_2$im][HSO_4] [11] ionic liquid and [$BmimSO_3H$]$_3$$PW_{12}O_{40}$ [8] exhibited greater yields for butyl levulinate. However, the steps involved in catalyst regeneration were tedious and complex. The [$BmimSO_3H$]$_3$$PW_{12}O_{40}$ catalyst showed a higher catalytic activity in first run, but it failed to retain its original activity and showed almost 30% loss in activity in first recycle attributed to catalyst deactivation due to the adsorption of some oligomeric products derived from furfuryl alcohol polymerization. Even though SO_3H-SBA-15 [12] showed 96% yield to butyl levulinate, the authors have not shown the

reusability result. Notably, sulfonic acid functionalized catalyst undergoes deactivation due to adsorption of oligomeric side products formed during reaction. The mesoporous catalysts namely Ti-KIT-6 [13] and Al-SBA-15 [7] exhibited 94% yield to butyl levulinate, however the catalyst quantity employed for the reaction was very high compared to the catalyst in this work. Most of the reports showed the use of higher mole ratio of FFAL to corresponding alkyl alcohols to inhibit the polymerization of furfuryl alcohol during the reaction. In this context, the performance of SnPO-P123 in the present study was at par with the reported best catalysts to yield higher butyl levulinate at lower alcohol concentration and proves to be a promising heterogeneous catalyst by retaining its activity in consecutive recycles.

Table S4. Physico-chemical properties of the spent catalysts.

SnPO-P123	Nitrogen sorption measurement			Acidity (μmol/g) [d]
	Surface area (m²/g) [a]	Pore volume (cm³/g) [b]	Pore size (nm) [c]	
Fresh	124	0.50	12.1	550
R-3-BuLv	126	0.50	12.1	530

[a] BET surface area, [b] Total pore volume, [c] BJH pore size analysis [d] NH_3-TPD

References

1. K. N. Tayade and M. Mishra, *Journal of Molecular Catalysis A: Chemical*, 2014, **382**, 114-125.
2. P. Manjunathan, S. P. Maradur, A. Halgeri and G. V. Shanbhag, *Journal of Molecular Catalysis A: Chemical*, 2015, **396**, 47-54.
3. P. Manjunathan, R. Ravishankar and G. V. Shanbhag, *ChemCatChem*, 2016, **8**, 631-639.
4. P. Manjunathan, M. Kumar, S. R. Churipard, S. Sivasankaran, G. V. Shanbhag and S. P. Maradur, *RSC Advances*, 2016, **6**, 82654-82660.
5. D. Song, S. An, B. Lu, Y. Guo and J. Leng, *Applied Catalysis B: Environmental*, 2015, **179**, 445-457.
6. B. Lu, S. An, D. Song, F. Su, X. Yang and Y. Guo, *Green Chemistry*, 2015, **17**, 1767-1778.
7. S. S. Enumula, K. S. Koppadi, V. R. B. Gurram, D. R. Burri and S. R. R. Kamaraju, *Sustainable Energy & Fuels*, 2017, **1**, 644-651.
8. Z. Zhang, K. Dong and Z. K. Zhao, *ChemSusChem*, 2011, **4**, 112-118.
9. G. M. G. Maldonado, R. S. Assary, J. A. Dumesic and L. A. Curtiss, *Energy & environmental science*, 2012, **5**, 8990-8997.

10. P. Neves, M. M. Antunes, P. A. Russo, J. P. Abrantes, S. Lima, A. Fernandes, M. Pillinger, S. M. Rocha, M. F. Ribeiro and A. A. Valente, *Green Chemistry*, 2013, **15**, 3367-3376.
11. G. Wang, Z. Zhang and L. Song, *Green Chemistry*, 2014, **16**, 1436-1443.
12. P. Demma Carà, R. Ciriminna, N. Shiju, G. Rothenberg and M. Pagliaro, *ChemSusChem*, 2014, **7**, 835-840.
13. J. N. Appaturi, M. R. Johan, R. J. Ramalingam, H. A. Al-Lohedan and J. J. Vijaya, *RSC Advances*, 2017, **7**, 55206-55214.