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# Catalytic transfer hydrogenation of levulinic acid to γ-valerolactone over Sn/BAL-SB Xiever Sinderolactone over Sn/BAL-SB Xiever Sinderolactone over Sn/BAL-SB Xiever Sinderolactone over Sinderolactone over

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#### ABSTRACT

Gamma valerolactone (GVL) is an important chemical feedstock from which several value-added fine chemicals, fuels & fuel additives are manufactured. GVL is the product obtained in the hydrogenation of levulinic acid (LA) which in turn is generally manufactured from several renewable resources such as pentoses and hexoses. The present work deals with the synthesis of SBA-15 and Sn loaded catalysts [x% Sn/Al-SBA-15 (x = Si/Sn=10, 25, 50, 50] 75 and 100 with Si/Al=25)) by hydrothermal In-situ method. A variety of both bulk and surface characterization techniques such as XRD, FT-IR, BET, FE-SEM, HR-TEM, XPS, TGA and UV-DRS were used to characterize bare and Sn/Al-SBA-15 catalysts. The characterization studies revealed the presence of Sn species well dispersed in the uniform pore channels of Al-SBA-15. All the synthesized catalysts were tested for the liquid-phase catalytic transfer hydrogenation of levulinic acid in atmospheric pressure under mild reaction conditions. Among them, Sn/Al-SBA-15 (Si/Sn= 25) catalyst showed remarkable conversion of levulinic acid (99 %) and with very high selectivity towards GVL (100 %). The various reaction parameters such as metal loading, reaction temperature, reaction time and catalyst weight were optimized to get maximum conversion of levulinic acid with high selectivity towards the desired product. The stability and reusability of the best catalysts was also tested upto five cycles and there was not much variation in the catalytic activity in terms of conversion.

Keywords: Hydrogenation, Levulinic acid, GVL, mesoporous catalyst, Sn/Al-SBA-15

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#### 1. Introduction

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A decision was taken at United Nations Climate Change Conference at Paris to reduce global warming to less than 2 °C from the year 2020 onwards <sup>1</sup>. Hence, the researchers devoted much of their time to find out newer and greener ways of producing fuels to mitigate over-dependency on fossil fuels. Renewable carbon can be obtained from non-edible biomasses such as lignocellulose<sup>2,3</sup>. United States Department of Energy identified 12 biomass-based compounds that may replace the fossil fuel-based chemical building blocks<sup>1,4-6</sup>. The sustainable production of value-added chemicals, intermediates, polymers, fuels, etc., through greener catalytic routes from one of the 12 identified biomasses is the need of the hour <sup>5,7</sup>.

Among the different non-edible, renewable carbon sources, levulinic acid (LA), which can be obtained by hydrolysis of the most abundant lignocellulose is an important feedstock for the production of fuels, fuel additives, value-added fine chemicals, flavoring agents, green solvents, polymer and resins <sup>8-12</sup>. It is expected that the global demand for levulinic acid may reach around 4000 tons by the end of the year 2020 <sup>5,13,14</sup>. Since levulinic acid possesses both keto and carboxylic acid groups it is the potential candidate from which umpteen number of other interesting compounds such as ethyl levulinates, gamma valerolactone (GVL), 1,4 pentane diol, MTHF derivatives, valeric esters, etc., can be obtained <sup>6,15-22</sup>. Among them the conversion of levulinic acid into GVL is the most essential process as the unique properties of GVL such as high boiling points, low toxicity, high energy density, etc., make GVL to be used as green fuels, fuel additives, green solvents, green polymer, resins, etc., 23-25. Hydrogenation followed by dehydration of levulinic acid can be effected either through liquid-phase and/or vapor phase using heterogeneous or homogeneous catalysts to obtain yvalerolactone (GVL) <sup>26,27</sup>. However, in most such conversions noble metals and gaseous hydrogen at high pressure are used and hence have several disadvantages such as high cost of noble metals, longer reaction time, usage of harmful gaseous hydrogen, etc.,<sup>23,28</sup>.

Hence, efficient production of GVL from LA without using noble metal catalyst and gaseous hydrogen is the need of the hour. Instead of gaseous hydrogen sources such as formic acid and 2-propanol were used for the catalytic transfer hydrogenation of levulinic acid <sup>29</sup>. But, in most of the reactions, they are catalyzed by using noble metals such as Ni/TiO<sub>2</sub> <sup>30</sup>, W/Ni-ZSM-5 <sup>31</sup>, Cu/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> <sup>32</sup>, Cu-ZrO<sub>2</sub> <sup>13</sup>, Ru/C <sup>33</sup>, Ni/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> <sup>34</sup>, Ru/Sn/C <sup>35</sup>, SnO<sub>2</sub>/SBA-15 <sup>29</sup>, Ru-Ni/OMC <sup>36</sup>, ZrO<sub>2</sub> <sup>37</sup>, Cu-Ni/SiO<sub>2</sub> <sup>38</sup>, Ru/Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> <sup>39</sup>, Ni/SiO<sub>2</sub> <sup>40</sup>, Ru/TiO<sub>2</sub> <sup>41</sup>, Ru/HAP <sup>42</sup>, Cu/ZrO<sub>2</sub> <sup>43</sup>, ZrO<sub>2</sub>/SBA-15 <sup>44</sup>, Ni/MgO-Al<sub>2</sub>O<sub>3</sub> <sup>45</sup> and Ru/H-ZSM-5 <sup>46</sup>

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The conversion of levulinic acid into GVL through liquid-phase catalytic transfered online hydrogenation has been reported elsewhere but at very high hydrogen pressure (5-100 bar) <sup>5</sup>. To the best of our knowledge, only a few reports were found for the catalytic transfer hydrogenation of levulinic acid at ambient H<sub>2</sub> pressure <sup>23</sup>. Hence, it is a challenge to develop an inexpensive catalytic system which can show high catalytic conversion and selectivity under mild reaction condition such as usage of ambient H<sub>2</sub> pressure and non-corrosive solvents for the production of GVL. The liquid-phase catalytic transfer hydrogenation of levulinic acid using highly dispersed Sn particles supported on Al-SBA-15 has not been reported so far.

In the present work, we report the synthesis of SBA-15 and Sn loaded catalysts [x% Sn/Al-SBA-15 (x = Si/Sn=10, 25, 50, 75 and 100 with Si/Al=25)]) by hydrothermal In-situ method. The characterization studies revealed the presence of Sn species well dispersed on in the uniform pore channels of Al-SBA-15. The catalyst exhibited both Lewis and Bronsted acidities which are essential for the conversion of levulinic acid. All the synthesized catalysts were tested for the liquid-phase catalytic transfer hydrogenation of levulinic acid in atmospheric pressure under mild reaction conditions. Among them, Sn/Al-SBA-15 (Si/Sn= 25) catalyst showed a remarkable conversion of levulinic acid (99 %) with very high selectivity towards GVL (100 %). Usage of noble metal-free catalysts possessing high recyclability and showing the highest conversion of levulinic acid and selectivity towards GVL under noncorrosive conditions are the attractive features of this work.

#### 2. Experimental

#### 2.1. Materials and method

SBA-15 was synthesized by using a triblock copolymer (Pluronic P-123) and a silicon source Tetraethylorthosilicate (TEOS), (Sigma Aldrich 98% purity). Aluminium isopropoxide Al(O-i-Pr)<sub>3</sub> purchased from Alfa Aesar and SnCl<sub>4</sub>.4H<sub>2</sub>O purchased from Sigma Aldrich were used as precursors for Al & Sn respectively. Levulinic acid (Sigma Aldrich 98% purity) was used for the catalytic transfer hydrogenation reactions. Hydrochloric acid (37 %, Sigma Aldrich) was used as received.

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### 2.2. Synthesis of mesoporous SBA-15, Al-SBA-15 & Sn-SBA-15 catalysts<sup>VieyArticle Online</sup> hydrothermal method

The mesoporous SBA-15 was synthesized according to the procedure previously reported  $^{47,48}$ . The mixture containing 4g of Pluronic P-123, 25 ml of concentrated HCl and 125 ml of water were taken in a polypropylene container and stirred for 4 h until transparent solution was obtained. 9 g silica source TEOS was added directly to the above reaction mixture and stirred for 24 h. The white suspension resulted was then subjected to hydrothermal treatment in a Teflon lined stainless steel autoclave for 24 h at 373 K. After cooling down to room temperature, the solid products were separated by centrifugation, thoroughly washed with deionized water to remove the unreacted soluble organics and inorganics and heated at 393 K for 12 h. The white mass obtained was finely grounded and fired at 823 K for 6 h to remove the template if any present. This procedure yielded mesoporous silica SBA-15. Al-SBA-15 (Si/Al = 25 and 50) and Sn-SBA-15 (Si/Sn=25 and 50) catalysts were also synthesized by following the above procedure by adding the calculated amounts of aluminium isopropoxide Al(O-i-Pr)<sub>3</sub> or SnCl<sub>4</sub>.4H<sub>2</sub>O along with TEOS.

## 2.3 Synthesis of Mesoporous Sn/Al-SBA-15 catalysts with different Si/Al and Si/Sn ratios by hydrothermal in-situ method

Sn/Al-SBA-15 catalysts with Si/Al of 25 and Si/Sn of 10, 25, 50, 75 & 100 were also synthesized as described above using Pluronic P-123 as surface directing agent, TEOS as silicon source, aluminium isopropoxide as Al source and SnCl<sub>4</sub>.4H<sub>2</sub>O as Sn source. For comparison purposes, other supported catalysts such as Sn/Al-SBA-16, Sn/Al-SBA-1, Sn/Al-KIT-5, Sn/Al-KIT-6, Sn/Al-MCM-41 and Sn/Al-MCM-48 were also synthesized by following the procedures reported in the literature <sup>49-54</sup>.

#### 2.4 Catalyst characterization

The purity and phase formation of all the synthesized catalysts were analyzed from the XRD pattern recorded using Rigaku, Mini Flex with Ni $\beta$  filter CuK<sub>a</sub> ( $\lambda$ =1.54 nm). FT-IR spectra were recorded to find out the functional groups present in all the synthesized catalysts using Thermo scientific NICOLET 4700 in the wavenumber range between 400 cm<sup>-1</sup> and 4000 cm<sup>-1</sup> using KBr pellet technique. The Lewis and Bronsted acidities of all the synthesized catalysts were determined from pyridine adsorbed FT-IR spectra in the wavenumber range between 1400 and 1800 cm<sup>-1</sup>. The surface area was calculated by the BET method (BEL

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SORP-mini, Bel-Japan analyzer) at -469 K. Pore volume and average pore size of the Manual Active Online

calculated by the BJH method. Prior to the adsorption measurement, the catalyst (100 mg) was evacuated at 150°C for 12 hr. The morphology studies of all the synthesized catalysts were carried out by using Field Emission Scanning Electron Microscope (Hitachi S-8230) and structure analysis was performed using energy-dispersive X-ray spectroscopy (EDS) analysis and elemental mapping. High-Resolution Transmission Electron Microscopic (HR-TEM) images of the mesoporous catalysts were taken by using a Hitachi H9500 microscope at an operating voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCA+, with the AlK<sub> $\alpha$ </sub> source (1486.6 eV) and a charge neutralizer. Thermal analysis of the most active catalyst was analyzed by Perkin Elmer, Diamond TG/DTD. The UV-Visible absorption spectra of the sample were recorded using JASCO V-650 UV-Vis spectrophotometer with BaSO<sub>4</sub> as reference

#### 2.5 Evaluation of catalytic activity

The liquid phase catalytic transfer hydrogenation of levulinic with 2-PrOH was carried out in the batch reactor at atmospheric pressure. The substrate, catalyst, and solvent were mixed in the reactor, then pure N<sub>2</sub> was introduced to remove the air. 100 mg of the catalyst was added to the mixture containing 1:4 mole ratio of levulinic acid and 2-propanol, the reaction temperature was varied from 373 K to 523 K and the reaction was conducted for 3 h under vigorous stirring. The reactor was cooled to room temperature and aliquots (0.5 ml) of the product were withdrawn in eppendorfs, centrifuged, filtered through a nylon membrane filter of 0.2µ microns and quantified by using gas chromatograph (Shimadzu GC-17A). An FFAP capillary column (30m × 0.32mm x 0.25 nm) and flame ionization detector (FID). The column temperature was raised from 40 °C to 250 °C at the heating rate of 3 °C and the sampling volume of 0.2 µL were used for the analysis. The % conversion of levulinic acid and selectivity towards GVL were determined by the following equations:

Conversion (%) =  $\frac{\text{Levulinic acid}_{\text{in}} - \text{Levulinic acid}_{\text{out}}}{\text{Levulinic acid}_{\text{in}}} \times 100$ 

Selectivity (%) =  $\frac{\text{GVL formed}}{\text{Sum of all the products}} \times 100$ 

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#### 3. Result and Discussion

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#### 3.1 X-ray diffraction (XRD)

The low angle XRD pattern of bare SBA-15 and Sn/Al-SBA-15 catalysts with different molar ratios were recorded to determine the structural order and shown in Figure 1 (A). Both SBA-15 and Sn/Al-SBA-15 catalysts exhibited one strong diffraction peak at  $2\theta$ = 0.9 ° (100) and two weak peaks at  $2\theta$ = 1.6 ° (110) and  $2\theta$ = 1.9 ° (200) which are characteristic of the 2D hexagonal mesoporous structure with space group (P6mm) symmetry <sup>55</sup>. These peaks confirm the presence of excellent textural uniformity <sup>48</sup>. The intensity of the peak decreased and move towards higher angle with decrease in Si/Sn ratio <sup>56</sup>. This is because the ionic radii of Al<sup>3+</sup> and Sn<sup>4+</sup> are larger than that of Si<sup>4+</sup> which leads to the lattice expansion <sup>57</sup>. This result clearly indicates that Al and Sn are present in the framework of SBA-15 materials. The increase in the d-spacing also confirmed the incorporation of Sn into the framework of SBA-15 without disturbing the mesoporous structure of SBA-15 <sup>58</sup>. The physicochemical properties of all the synthesized catalysts are given in Table 1.



Figure 1. (A) Low-angle and (B) high angle XRD patterns of (a) SBA-15, (b) Al-SBA-15 (25), (c) Sn-SBA-15 (25), (d) Sn/Al-SBA-15 (10), (e) Sn/Al-SBA-15 (25), (f) Sn/Al-SBA-15 (50), (g) Sn/Al-SBA-15 (75) and (h) Sn/Al-SBA-15 (100) catalysts.

	$d_{100}{}^{a}$	a <sub>0</sub> <sup>b</sup>	S <sub>BET</sub> <sup>c</sup>	$V_P^d$	$d_{P}^{e}$	SWT <sup>f</sup>
Catalyst	(nm)	(nm)	(m <sup>2</sup> /g)	(cm <sup>3</sup> /g)	(nm)	(nm)
SBA-15	9.80	11.31	1120	2.16	8.97	2.34
Al-SBA-15 (25)	9.70	11.20	980	1.88	8.51	2.69
Sn-SBA-15 (25)	9.59	11.07	830	1.68	7.68	3.39
Sn/Al-SBA-15 (10)	9.33	10.73	650	1.28	5.01	5.72
Sn/Al-SBA-15 (25)	9.39	10.48	710	1.41	5.49	4.99
Sn/Al-SBA-15 (50)	9.50	10.96	760	1.38	6.21	4.75
Sn/Al-SBA-15 (75)	9.59	11.07	810	1.64	6.91	4.16
Sn/Al-SBA-15 (100)	9.70	11.20	810	1.77	7.34	3.86

Table 1. Texture parameters of bare SBA-15, Al-SBA-15 and Sn/Al-SBA-15 catalyst We water Contine

 $^{a}d_{100}$  calculated from the x-ray diffraction pattern from (100) plane.

<sup>b</sup>Unit cell size calculated using the formula,  $a_0=2d_{100}/\sqrt{3}$ .

<sup>c</sup>S<sub>BET</sub> - Surface area calculated from BET equation at P/P<sub>0</sub> range of 0.05 to 0.3

 $^{d}V_{p}$  - Pore volume calculated at P/P<sub>0</sub> = 0.98.

<sup>e</sup>d<sub>p</sub>-Pore diameter calculated from the adsorption branch of the isotherm

<sup>f</sup>SWT- Single wall thickness calculated using,  $b = a_0 - d_P$ .

The wide-angle XRD pattern of bare SBA-15, Al-SBA-15 and Sn/Al-SBA-15 catalysts are shown in Figure 1(B). They all showed a strong and broad-band in the range of  $2\theta$ =20-30° due to amorphous silica walls of mesoporous material <sup>59</sup>. The wide-angle XRD patterns did not show any diffraction peaks to confirm the presence of Sn which indicates that the Sn species are homogeneously dispersed inside the framework of SBA-15 <sup>60</sup>. The presence of Sn and Al species is then confirmed by instrumental techniques such as SEM/EDX and XPS (discussed later). The increase Si/Sn molar ratio increased the peak intensity, which confirmed the incorporation of Sn into the framework of SBA-15. The decrease Si/Sn ratio decreased the peak intensity confirming the higher amount incorporation of Sn into the framework mesopores.

#### 3.2 FT-IR analysis

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Qualitative identification of functional groups present in bare SBA-15 and Sn/Al-SBA-15 catalysts was done by recording FT-IR spectra in the wavenumber region of 4000 to 500 cm<sup>-1</sup> and shown in Figure 2 (A). A broad peak at 3448 cm<sup>-1</sup> appears in the FT-IR spectra of all the catalysts due to the -OH stretching vibration of a water molecule <sup>61</sup>. The bending, symmetric stretching and asymmetric stretching of Si-O-Si vibration bands were observed in all the synthesized catalysts at 463, 802 and 1081 cm<sup>-1</sup> respectively <sup>62</sup>. The band around 962 cm<sup>-1</sup> corresponds to the asymmetrical stretching vibration of Si-OH group <sup>63</sup>. The peak around 960 - 980 cm<sup>-1</sup> is assigned to stretching vibration of Si-OH linkage and the change in its intensity may be attributed to the differential interaction of metal with Si-O linkage <sup>63</sup>. The peak intensity at about 1630 cm<sup>-1</sup> is attributed to O-H bending vibration of adsorbed water molecules and surface silanol groups <sup>64</sup>. IR peak at 970 cm<sup>-1</sup> was not observed to indicate the presence of Sn in Al-SBA-15 catalysts which indicates that Sn species were highly dispersed into the mesoporous framework of SBA-15 <sup>65,66</sup>.



Figure 2. (A) FT-IR and (B) Pyridine adsorbed FT-IR spectra of (a) SBA-15, (b) Al-SBA-15 (25), (c) Sn-SBA-15 (25), (d) Sn/Al-SBA-15 (10), (e) Sn/Al-SBA-15 (25), (f) Sn/Al-SBA-15 (50), (g) Sn/Al-SBA-15 (75) and (h) Sn/Al-SBA-15 (100) catalysts.

Figure 2 (B) shows the pyridine adsorbed FT-IR spectra of Al-SBA-15 (25) and Sn/Al-SBA-15 catalysts. All the synthesized catalysts exhibit bands at 1492 and 1546 cm<sup>-1</sup> corresponding to pyridine adsorbed on Lewis acid sites, both Lewis and Bronsted acid sites and the IR band around 1634 cm<sup>-1</sup> is attributed to Bronsted acid sites formed due to bridged hydroxyl groups.<sup>47.</sup> The presence of acidic sites in Sn-based catalysts was confirmed by pyridine adsorbed FT-IR spectra. Catalytic transfer hydrogenation of levulinic acid reaction requires high acidic sites to produce GVL with good selectivity and hence it is expected to

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59 60 play a key role in the conversion of LA. The incorporation of Sn provides enough\_acidic\_39768\_J01288B for CTH reaction.

#### 3.3 BET N<sub>2</sub> adsorption-desorption isotherms of bare SBA-15 & Sn/Al-SBA-15 catalysts

The N<sub>2</sub> adsorption-desorption isotherms for bare SBA-15 and Sn/Al-SBA-15 catalysts are shown in Figure 3 (A). High order mesoporous nature of the synthesized catalysts was confirmed by their type IV isotherm with H<sub>1</sub> hysteresis loop at (P/Po = 0.6-0.8) <sup>67</sup>. BET surface area, pore diameter, pore volume and wall thickness values were calculated for all the synthesized catalysts and given in Table 1. The type IV isotherm suggested that the incorporation of Sn and Al with framework of SBA-15 did not destroy its mesoporous structure. The specific surface area of bare SBA-15 was found to be the highest (1120 m<sup>2</sup>/g). However, when siliceous SBA-15 is converted into Al-SBA-15 the surface area reduced to 980 m<sup>2</sup>/g. Al-SBA-15 on further incorporation of Sn showed less surface area. However, with increase in Si/Sn ratio, the surface area increased gradually. The increase in Si/Sn molar ratio from 10 to 100 increases the BET surface area gradually. This result is in good agreement with XRD results. This behavior may be attributed to the presence of Sn and Al elements in the framework. However, the incorporation of Sn does not affect the mesoporous structure of SBA-15.



Figure 3. (A) Adsorption-desorption isotherms and (B) pore size distribution of (a) SBA-15, (b) Al-SBA-15 (25), (c) Sn-SBA-15 (25), (d) Sn/Al-SBA-15 (10), (e) Sn/Al-SBA-15 (25), (f) Sn/Al-SBA-15 (50), (g) Sn/Al-SBA-15 (75) and (h) Sn/Al-SBA-15 (100) catalysts.

The BJH pore size distribution curve of all the synthesized catalysts is shown in Figure 3 (B). All the catalysts show sharp peaks revealing, uniform regular porous structure. Pore diameter, pore volume and wall thickness of all the synthesized catalysts were

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calculated and given in Table1. Among the synthesized catalyst siliceous SBA-15\_bhowederfigicle Online highest pore diameter (8.97 nm) and the largest pore volume (2.16 cm<sup>2</sup>/g). These two values decreased when either Al or Sn or both is incorporated into the lattice. Thus Sn/Al-SBA-15 (Si/Sn=10) showed the pore diameter of 5.01 nm and pore volume of 1.28 cm<sup>2</sup>/g. However, these values increased gradually with increase in Si/Sn ratio from 10 to 100. The wall thickness increased from 2.34 nm to 3.86 nm. This result clearly indicates that the specific surface area, pore-volume, pore diameter, and silica wall thickness decreased with the decreasing Si/Sn molar ratio, due to the blockage of the mesopores in SBA-15<sup>68</sup>.

#### **3.4 XPS**

XPS is an important characterization technique used to determine the chemical composition and oxidation states. The high-resolution XPS survey spectrum and the core level spectra of the most active Sn/Al-SBA-15 (25) catalyst is shown in Figure 4. The survey scan spectrum [(Figure 4 (a)] shows the presence of dominant elements such as O (2s and 1s), Al (2p), Si (2p, 2s, and 1s), C (1s) and Sn (3d) in Sn/Al-SBA-15 (25) catalyst. The characteristic O 1s peak [(Figure 4 (b)] is located at 533.1 eV <sup>69</sup>. The peak located at 74.7 eV [(Figure 4 (c)] is attributed to Al 2p <sup>70</sup>. The core-level XPS spectra showed a strong spin-orbital doublet, (Sn  $3d_{3/2}$ ,  $3d_{5/2}$ ) at 494.61 and 485.32 eV which are attributed to Sn<sup>4+</sup> respectively <sup>71</sup>. This result suggests that Sn species were successfully incorporated into SBA-15 framework by hydrothermal in-situ method.

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Figure 4. (a) XPS survey spectrum and core-level spectra, (b) O 1s (c) Al 2p and (d) Sn 3d of the most active catalyst Sn/Al-SBA-15 (25).

#### **3.5 FE-SEM**

The FE-SEM images of bare SBA-15 and Sn/Al-SBA-15 catalysts are shown in Figure 5 (a-f). Figure 5 (a & b ) illustrates the FE-SEM image of bare SBA-15 and Al-SBA-15 catalysts which show a uniform cylindrical rod-like morphology <sup>47,48</sup>. Sn/Al-SBA-15 catalysts show similar rod-like morphology and long-range parallel mesochannels as shown in Figure 5 (c-f). The FE-SEM image of Sn/Al-SBA-15 (10) catalyst show small agglomerates on the small rod-like structure due to the presence of high Sn content in Al-SBA-15 mesoporous catalysts. However, when Sn content decreases (at higher Si/Sn ratio), the agglomerates were not formed. This indicates that Sn has been incorporated in the framework structure of Al-SBA-15 catalysts as shown in Figure 5 (d, f). The FE-SEM low and high magnification of the image of (Sn/Al-SBA-15 (25) catalyst) are shown in Figure 5 (d & e). The long mesochannels ranging from 500 to 850 nm were found in the Sn/Al-SBA-15 (25) rods. The Sn nanoparticles accelerate the self-assembly of P123 and TEOS, resulting in the formation of rods <sup>72,73</sup>. This observation is more clearly seen in HR-TEM image also.



Figure 5. FE-SEM image of (a) SBA-15, (b) Al-SBA-15 (25), (c) Sn/Al-SBA-15 (10), (d-e) high and low magnification image of Sn/Al-SBA-15 (25) and (f) Sn/Al-SBA-15 (50) catalysts.

The FE-SEM-EDX image of Sn/Al-SBA-15 (25) catalyst is shown in Figure 6 (a). The elemental mapping and line scanning were also performed to check the presence and distribution of all the elements present in the SBA-15. The wide-angle X-ray diffraction patterns of Sn/Al-SBA-15 (25) catalyst did not show clear evidence of presence of crystalline Sn within the framework of Al-SBA-15 catalyst. However, energy dispersive X-ray (EDX) mapping analysis confirms the presence of Sn particles evenly distributed within the framework of SBA-15. The line scanning EDX spectrum of Sn/Al-SBA-15 (25) is shown in Figure 6 (b) which indicates the presence of Sn, Si, and Al elements and well dispersion in the mesoporous structure. The SEM-EDX spectra show no other elements in the catalysts confirming the purity of samples.

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Figure 6. (A and B) FE-SEM micrographs, elemental mapping and EDX line-scanning spectra of the most active Sn/Al-SBA-15 (25) catalyst.

#### **3.6 HR-TEM**

HR-TEM image of bare SBA-15 and Sn/Al-SBA-15 catalysts are shown in Figure 7 (a-f). The hexagonal structure with honeycomb shape characteristic of 2D mesoporous is seen in the HRTEM images of bare and Sn/Al-SBA-15 catalyst. The HR-TEM image of Sn/Al-SBA-15 catalyst further confirmes the high dispersion of Sn within the framework of Al-SBA-15 <sup>60</sup>. The small agglomerates were formed on the surface of Sn/Al-SBA-15 (10) catalysts due to the high concentration of Sn (Figure 7 b). At lower concentration Sn in Sn/Al-SBA-15 (100) homogeneous dispersion of Sn nanoparticle takes place within the framework (Figure 7 f). The dark region in the HR-TEM images indicates the dispersion of Sn particles.

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Figure 7. HR-TEM images of (a) SBA-15, (b) Sn/Al-SBA-15 (10), (c) Sn/Al-SBA-15 (25), (d) Sn/Al-SBA-15 (50), (e) Sn/Al-SBA-15 (75) and (f) Sn/Al-SBA-15 (100) catalysts.

#### 3.7 UV-vis diffuse reflectance spectra of bare and Sn/Al-SBA-15 catalysts

UV-vis DRS was used to understand the chemical nature, coordination state and the presence of Sn in framework and extra-framework of SBA-15 catalysts. UV-vis diffuse reflectance spectra of Al-SBA-15 and Sn/Al-SBA-15 catalysts are shown in Figure 8 (a). The absorption peaks at 233 nm (strong) were observed. The peak is assigned to the ligand to metal charge transfer ( $O \rightarrow Sn^{4+}$ ) in tetrahedral coordination <sup>74</sup>. This peak is due to the presence of isolated Sn<sup>4+</sup> species dispersed in the mesoporous framework of SBA-15 <sup>75</sup>.



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Figure 8. (A) UV-Visible diffuse reflectance spectra (UV-DRS) image of (a) Al-SBA<sup>ieV</sup>S<sup>ticle Online</sup> (25), (b) Sn-SBA-15 (25), (c) Sn/Al-SBA-15 (10), (d) Sn/Al-SBA-15 (25), (e) Sn/Al-SBA 15 (50), (f) Sn/Al-SBA-15 (75), (g) Sn/Al-SBA-15 (100) catalysts and (B) TG (a) & DTA (b) thermograms of Sn/Al-SBA-15 (25) catalyst.

#### 3.8 Thermal stability of Sn/Al-SBA-15 (25) catalyst

TGA and DTA Thermograms of Sn/Al-SBA-15 (25) catalysts are shown in Figure 8 (B). The TGA analysis shows that the as-prepared mesoporous catalysts have high thermal stability. The two weight-losses, one below 150 °C is due to the physically adsorbed water and the minor and negligible loss in the wide temperature range between 300 and 1000 °C. The DTA thermogram also confirms the same.

#### 4. Catalytic Activities

#### 4.1 Effect of Si/Sn molar ratio on catalytic performance

The catalytic transfer hydrogenation of levulinic acid was carried out in a batch reactor using 2-PrOH as a solvent. Al-SBA-15 (Si/Al=25 & 50) and Sn-SBA-15 (Si/Sn=25 & 50) catalyst were evaluated for their catalytic conversion of levulinic acid and the results are given in Table 2. As far as the selectivity towards the desired product GVL is concerned Al-SBA-15 (Si/Al= 25, 50) catalysts show poor selectivity towards GVL and high selectivity towards angelica lactone (AL). The acidic sites of the catalyst initiate the dehydration of levulinic acid to intermediate product angelica lactone. Further angelica lactone hydrogenation leading to the formation of GVL does not occur due to the lack of metallic sites. Hence the presence of Sn is absolutely essential for obtaining very high conversion and high degree of selectivity towards GVL. The incorporation of Sn species increases the acidity of the catalyst, while the conversion increase with the incorporation of Sn in SBA-15, the selectivity towards GVL increased tremendously. Both conversion and selectivity increased with a decrease in Si/Sn molar ratio. Further increase in conversion and selectivity was observed when Sn was incorporated into Al-SBA-15. Hence, this study confirms that the presence of both Al & Sn are required to obtain high conversion with 100% selectivity towards GVL. Hence, further optimization studies were carried out using Sn/Al-SBA-15 (25) catalyst.

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Catalyst	Conversion	Selectivity (%)		
	(%)	GVL	4-HPA	AL
Al-SBA-15 (50)	38	1	-	85
Al-SBA-15 (25)	50	3	-	97
Sn-SBA-15 (50)	62	90	10	-
Sn-SBA-15 (25)	72	98	2	-
Sn/Al-SBA-15 (25)	99	100	-	-

Table 2. Effect of molar ratio on levulinic acid conversion

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{Reaction conditions: Weight of the catalyst 100 mg, reaction temperature 473 K, molar ratio of levulinic acid and 2-PrOH (1:4), reaction time 3 h}

#### 4.2 Effect of temperature on conversion and selectivity

The reaction temperature plays an important role in the catalytic transfer hydrogenation of levulinic acid. This study was conducted to identify the optimum reaction temperature and the most active catalyst among the various synthesized catalysts. The effect of reaction temperature on the conversion of levulinic acid was studied using a batch reactor by varying the reaction temperature between 373 to 523 K. All Sn/Al-SBA-15 the mesoporous catalysts with Si/Sn=10, 25, 50, 75, 100 and Si/Al=25 were evaluated for their catalytic activities in the above temperature range and the results are given in Table 3. These results clearly indicate that the conversion of levulinic acid increase with the increase in reaction temperature over all the catalysts. Gamma valerolactone (GVL) and 4hydroxypentanoic acid (4-HPA) were found to be the products. The decrease in Si/Sn ratio increased both the conversion of levulinic acid and selectivity towards GVL. As far as Sn/Al-SBA-15 catalysts are concerned, both conversion and selectivity increased with decrease in Si/Sn ratio upto 25 and further increase in Sn content (Si/Sn=10) decreased both conversion and selectivity while the increase in reaction temperature had pronounced effect of Sn/SBA-15 catalysts it had only a marginal effect on Sn/Al-SBA-15 catalysts. All the catalysts show maximum conversion of levulinic acid with high degree of selectivity at 473 K. Further increase in temperature to 523 K did not have any significant effect rather it decreased slightly the conversion and selectivity. Among the catalysts Sn/Al-SBA-15 (25) catalyst exhibited the maximum conversion of LA (99 %) with the highest selectivity towards GVL (100 %) at 473K. Hence, further optimization studies were carried out at 473 K.

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 Sn/Al-SBA-15 (10)

	Reaction	Conversion	Selecti	ivity (%)
Catalyst	Temperature (K)	(%)	GVL	4-HPA
	373	37	80	20
Sn/SBA-15 (50)	423	42	86	14
	473	62	90	10
	523	59	81	19
	373	47	95	5
Sn/SBA-15 (25)	423	52	96	4
	473	72	98	2
	523	68	96	4
	373	66	53	47
Sn/Al-SBA-15 (100)	423	71	62	38
	473	78	74	26
	523	81	60	40
	373	76	70	30
Sn/Al-SBA-15 (75)	423	80	77	23
	473	88	83	17
	523	86	79	21
	373	87	74	26
Sn/Al-SBA-15 (50)	423	90	79	21
	473	96	83	17
	523	94	84	16
	373	90	96	4
Sn/Al-SBA-15 (25)	423	95	98	2
	473	99	100	-
	523	98	100	-
	373	80	95	5

#### Table 3. Effect of reaction temperature on levulinic acid conversion.

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{Reaction conditions: Weight of the catalyst 100 mg, molar ratio of levulinic acid and 2-PrOH (1:4), and reaction time 3 h}

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#### 4.3 Effect of time on stream on conversion

The stability of the most active catalyst [Sn/Al-SBA-15 (Si/Sn=25)] has been examined by Time On Stream (TOS) studies. To study the effect of reaction time on the conversion of LA and selectivity towards GVL, the reaction was conducted for 6 h over 100 mg of Sn/Al-SBA-15 (25) catalyst at the optimized reaction temperature of 473 K. This reaction was conducted continuously for 6 h to identify the catalyst deactivation if any. The product was collected every hour, analyzed and the results are shown in Figure 9. The conversion of levulinic acid and selectivity of the desired product GVL increased slightly with increase in reaction time up to 3 h and after 3 h, again there was a marginal decrease in conversion and selectivity. Hence, the reaction time of 3 h was found to be the optimum.



Figure 9. Time on stream studies over Sn/Al-SBA-15 (25) catalyst.

{Reaction conditions: Weight of the catalyst 100 mg, reaction temperature 473 K, molar ratio of levulinic acid and 2-PrOH (1:4)}

#### 4.4 Effect of weight of catalyst on conversion of LA

To study the performance of weight of catalysts on conversion and selectivity, the weight of Sn/Al-SBA-15 (Si/Sn=25) was varied from 50 to 200 mg and the reaction was carried out at the optimized reaction conditions. The obtained results are shown in Figure 10. It was found that the catalytic conversion increased with the weight of the catalyst from 50 to 100 mg owing to the increase in the catalytically active sites with increase in the catalyst weight. 99 % conversion of levulinic acid obtained over 100 mg of Sn/Al-SBA-15 (25)

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catalyst. However, a further increase in the catalyst weight upto 200 mg decreased/ieufAgicle Online levulinic acid conversion and selectivity. Hence catalyst weight of 100 mg was used for further studies.





{Reaction conditions: weight of Sn/Al-SBA-15 (25) catalyst, reaction temperature 473 K, reaction time 3 h, molar ratio of levulinic acid and 2-PrOH (1:4)}

#### 4.5 Effect of alcohol molar ratio on conversion

In order to check the effect of the molar ratio of levulinic acid to GVL on conversion and selectivity of desired product, the catalytic transfer hydrogenation reaction was performed with different levulinic acid: 2-PrOH molar ratios varying from 1:2 to 1:10 under the optimized reaction conditions (Catalyst Sn/Al-SBA-15 (25), temperature 473 K, time 3 h) the product was collected after 3 h, analyzed and the results are illustrated in Figure 11. The figure clearly indicates that the molar ratio of LA:2-PrOH of 1:4 was found to be the best as it gives maximum conversion and selectivity of the desired product.

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Figure 11. Effect of the molar ratio over Sn/Al-SBA-15 (25) catalyst.

{Reaction conditions: weight of the catalyst 100 mg, reaction temperature 473 K and reaction time 3 h}

## 4.6 Effect of addition of alcohols (hydrogen donors) with the substrate (LA) on catalytic activity

The liquid phase hydrogenation at atmospheric pressure has not been reported so far. Catalytic transfer hydrogenation of levulinic acid can be affected with different alcohols hydrogen donors. The liquid phase catalytic transfer hydrogenation of levulinic acid was carried out by using different hydrogen donors such as MeOH, EtOH, 2-PrOH, 2-BuOH, and CyOH under the optimized reaction conditions over Sn/Al-SBA-15 (25) catalyst and the results are shown in Figure 12. Interestingly the catalyst shows the hydrogenation activity in the presence of all the alcohols but to different extents. The catalyst showed poor conversion and selectivity towards the desired product of GVL when MeOH and EtOH were used as hydrogen donors, but with 2-PrOH, a conversion of 99 % of levulinic acid was observed whereas with the other alcohols such as 2-BuOH, and CyOH the conversion decreased to 98% and 89% respectively. Figure 12 shows that secondary alcohols ((2-PrOH, 2-BuOH)) showed better conversion of LA than primary alcohols (methanol and ethanol), which may be related to their better reduction potentials <sup>37,80</sup> Hence, 2-propanol was found to be the best hydrogen donor for the present catalytic system.

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Figure 12. Effect of hydrogen donor on conversion and selectivity over Sn/Al-SBA-15 (25) catalyst

{Reaction conditions: Weight of the catalyst 100 mg, levulinic acid and alcohol molar ratio (1:4), reaction temperature 473 K and Reaction time 3 h}

#### 4.7 Catalytic transfer hydrogenation of other substrates over Sn/Al-SBA-15 (25) catalyst

As Sn/Al-SBA-15 (25) catalyst exhibit tremendous conversion of LA and selectivity towards GVL, it was evaluated for its catalytic activity with other substrates such as methyl levulinate and ethyl levulinate using 2-PrOH as hydrogen donor under the optimized reaction conditions and the results are shown in Figure 13. Interestingly, these substrates were also converted to the extents of 96 % and 97 % with 97 % and 98 % selectivities towards GVL.

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**Figure 13. Effect of different substrates on conversion over Sn/Al-SBA-15 (25) catalyst** {Reaction conditions: Weight of the catalyst 100 mg, alcohol molar ratio (1:4), reaction temperature 473 K and Reaction time 3 h}

#### 4.8 Effect of support on the catalytic conversion

In order to check the effect of support on the catalytic conversion of levulinic acid, Si & Al were incorporated into various supports such as SBA-15, SBA-16, SBA-1, KIT-5 & KIT-6 and their catalytic activities were evaluated and the results are summarized in Table 4. Among the different supports, SBA-15 showed not only the highest conversion of levulinic acid (99%) but also 100% selectivity towards the desired products (GVL). Hence further studies were carried out with SBA-15 support. The liquid phase catalytic transfer hydrogenation reaction was carried out by using different heterogeneous catalysts reported elsewhere, compared and given in Table S1. The results indicate that, in addition to several advantages such as noncorrosive conditions, short reaction time and easy work-up, our catalyst also shows outstanding conversion and high selectivity towards the desired product.

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Catalysts	Conversion	Selectivity (%)	
	(%)	GVL	4-HPA
Sn/Al-SBA-15 (25)	99	100	-
Sn/Al-SBA-16 (25)	88	80	20
Sn/Al-SBA-1 (25)	72	75	25
Sn/Al-KIT-6 (25)	79	70	30
Sn/Al-KIT-5 (25)	82	73	27
Sn/Al-MCM-41 (25)	85	78	22
Sn/Al-MCM-48 (25)	81	81	19

Table 4. Effect of the various supported catalyst

{Reaction conditions: Weight of the catalyst 100 mg, molar ratio of levulinic acid and 2-PrOH (1:4), reaction temperature (473 K) and reaction time 3 h}

# 4.9 The reaction pathways and mechanism in the conversion of levulinic acid over Sn/Al-SBA-15 catalyst

Based on the experimental results a possible reaction pathway is suggested. Levulinic acid is converted into GVL through 4-HPA (where the hydrogen donor secondary alcohol is converted into a ketone) as illustrated below:



# Scheme 1. Catalytic transfer hydrogenation (CTH) of levulinic acid using alcohol as a hydrogen donor.

In the case of 2-PrOH, acetone is the other product. Hence the reaction product was found to contain 4-HPA, GVL H<sub>2</sub>O, ketone and unreacted reactants such as levulinic acid and secondary alcohol. We propose a possible reaction mechanism (Scheme 2) based on the formation of the above different products. In step, I the acidic sites of the Sn species is responsible for the dehydration of the secondary alcohol and formation of alkoxide species on Sn sites.

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Step II illustrates the adsorption of levulinic acid on the same Sn site. Due to retain the online of electrons transfer of hydrogen atom from alkoxide part to the adsorbed levulinic acid occurs in step III and at the same time carbonyl compound is released from Sn sites (step IV). In step V the water removed in the first step converts the other alkoxide part on Sn site into 4-HPA (a thermally unstable compound) which then undergoes cyclization in step VI to form GVL and at the end, the catalyst is regenerated with a hydroxyl group on Sn atom.



Scheme 2. Proposed reaction mechanism of the catalytic transfer hydrogenation of levulinic acid over Sn/Al-SBA-15(25) catalyst using secondary alcohol.

#### 4.10 Reusability of Sn/Al-SBA-15 (25) catalyst.

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 The recyclability of Sn/Al-SBA-15 (25) catalyst was examined by performing the reaction at the optimized conditions [(Temperature=473 K), (weight=100 mg), (time=3 h) and molar ratio (1:4) of LA: 2-PrOH for five subsequent runs and the results are illustrated in Figure 14. After every catalytic cycle, the spent catalyst was removed from the reactor washed with water and dried to be reused for the next run. The catalyst retained almost the same performance with very small activity loss. These results prove that Sn/Al-SBA-15 (25) catalyst is stable. The morphology by HR-SEM, EDX, and HR-TEM of the used catalyst after five runs are shown in Figure 15 which also suggests the same observation. The results confirmed that the catalyst has not undergone any significant change in its structure and morphology. The HR-SEM/EDX images of the used catalyst clearly indicate that it is intact and has the same texture and morphology before and after the hydrogenation. The qualitative

analysis of Sn was made to check the leaching of Sn ions during the reaction<sub>D</sub> and it View Article Online indicated that there was no leaching of any metal ions in the product mixture



Figure 14. Recyclability of Sn/Al-SBA-15 (25) catalyst.

{Reaction conditions: Weight of the catalyst 100 mg, molar ratio of levulinic acid and 2-PrOH (1:4) and reaction temperature 473 K}

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Figure 15. (a) HR-SEM and (b) HR-TEM image and (c) FE-SEM/EDX elemental mapping of Sn/Al-SBA-15 (25) spent catalyst and overlay image.

#### 5. Conclusion

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Hydrothermal in-situ method were used successfully for the synthesis of Sn-SBA-15 and Sn/Al-SBA-15 catalysts with different molar ratios. The characterization studies revealed the presence of Sn and Al species and their well dispersion over SBA-15. The Sn/Al-SBA-15 (25) catalyst maintained the mesoporous structure even after the incorporation of Sn species. The presence of both Lewis and Bronsted acidic sites in Sn/Al-SBA-15 catalysts were confirmed by FT-IR. The HR-SEM/EDX and TEM images showed that Sn species were highly dispersed in the uniform pore channels of SBA-15. All the synthesized catalysts were tested for catalytic transfer hydrogenation of levulinic acid at ambient pressure and the different reaction parameters were optimized. Among them, Sn/Al-SBA-15 (25) exhibited the highest catalytic activity with 99% conversion of levulinic acid and 100% selectivity towards GVL. The recyclability test proved that the catalyst is recyclable. This noble metal-free catalytic route clearly proves a greener way for the production of GVL from levulinic acid which can easily be obtained from the most abundant lignocellulose.

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#### **Conflicts of interest**

There are no conflicts to declare.

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### **Graphical Abstract**



### Highlights

- ✓ Sn/Al-SBA-15 catalysts were synthesized by hydrothermal In-Situ method
- ✓ The HR-SEM/EDX and HR-TEM images revealed the high dispersion Sn in the uniform pore channels of SBA-15
- ✓ Sn/Al-SBA-15 catalysts exhibited both Lewis and Bronsted acidities
- ✓ The synthesized inexpensive catalysts show high catalytic transfer hydrogenation activity at ambient N₂ pressure under non-corrosive conditions
- ✓ Sn/Al-SBA-15 (25) catalyst exhibited the highest catalytic activity with 99 % conversion of levulinic acid and 100 % selectivity towards GVL