

Supplementary Information

Creation of Brønsted Acid Sites on Sn-based Solid Catalyst for the Conversion of Biomass

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Synthesis of SBA-15. As a typical run, 0.8 g of copolymer surfactant P123 was dissolved in 25 mL of water with 3 mL HCl (10M/L), followed by the addition of 2.4 mL TEOS. After stirring at 40 °C for 20 h, the mixture was transferred into an autoclave for further condensation at 100 °C for 24 h. The as-synthesized SBA-15 was collected after calcination of the sample for removing the surfactants.

Synthesis of S-Sn-Me and S-Sn-OH. As a typical run, 1.0 g of SBA-15 was heated at 100 °C for 2 h under vacuum in a 100 ml flask at first. After the addition of anhydrous toluene (20 ml) and dimethyldichlorostannane (63 mg), the mixture was stirred at room temperature for 0.5 h. Then, 5 mL of triethylamine was added, and the mixture was continuously stirred for another 2 h at room temperature. After filtrating, washing with toluene, and drying, the obtained sample was designated as S-Sn-Me. By treating S-Sn-Me at 600 °C for 3 h in air, S-Sn-OH was finally obtained. The Si/Sn ratios of S-Sn-Me and S-Sn-OH were 66.

Synthesis of conventional Sn-SBA-15. As a typical run, 1.5 g of P123 and 1.18 g of NaCl were dissolved in 70 g of water at 40 °C. Then, 4.2 g of TEOS was added, and the mixture was stirred for another 4 h. After the addition of 10 ml of SnCl₄ aqueous solution (0.76 mmol of SnCl₄), the mixture was continuously stirred at 40 °C for 24 h, and then hydrothermally treated at 90 °C for 24 h in an autoclave. After filtrating, washing, drying, and calcination at 500 °C for 4 h in air to remove the surfactants, Sn-SBA-15 with Si/Sn atomic ratio at 57 was finally obtained. For comparison, Al-SBA-15 (Si/Al atomic ratio at 5), Fe-SBA-15 (Si/Fe atomic ratio at 90) and Zr-SBA-15 (Si/Zr ratio at 50) were synthesized according to the literature.¹⁻³ The heteropolyacid of H₃PW₁₂O₄₀ and the zeolites of H-ZSM-5, H-USY, H-Beta (H-form zeolites with the Si/Al ratios being 25.0, 12.5, and 7.5, respectively) are commercially available.

Sample characterization. XPS spectra were performed on a Thermo ESCALAB 250 with Al K α radiation at $\theta=90^\circ$ for the X-ray sources, and the binding energies were calibrated using the C1s peak at 284.9 eV. Nitrogen sorption isotherms were measured using a Micromeritics ASAP 2020M system. The samples were outgassed for 10 h at 150 °C before the measurements. The pore-size distribution was calculated using the Barrett-Joyner-Halenda (BJH) model. Titan ChemiSTEM and FEI Tecnai G2 F20 microscopes equipped with an EDAX detector were employed to acquire TEM, HAADF-STEM images, and energy dispersive X-ray spectrum (EDS) elemental maps. The microscopes were operated at an accelerating voltage of 200 kV. The samples were ultrasonically dispersed in ethanol, and then a drop of the solution was deposited on a holey C/Cu TEM grid to be used for TEM characterization and elemental mapping. Powder X-ray diffraction patterns (XRD) were obtained with a Rigaku D/MAX 2550 diffractometer with CuK α radiation ($\lambda=0.1542$ nm). The UV-Visible spectra were

recorded on a Perkin-Elmer Lambda 20 spectrometer. The inductively coupled plasma (ICP) analysis was performed using a Perkin-Elmer plasma 40 emission spectrometer. The FTIR spectra of pyridine adsorption were recorded on a Bruker VERTEX70 spectrometer. The samples were pressed into self-supporting wafers containing material of 10 mg, and then the wafers were mounted inside a Pyrex vacuum cell and degassed at 250 °C for 1 h. Samples were allowed to cool down to RT, and then pyridine vapor was admitted into the cell and adsorption lasted for 1 h. Subsequently, the samples were heated up to 250 °C under vacuum and cooled down to RT for spectrum recording. All NMR experiments were conducted on a Varian Infinity Plus 400 spectrometer operating at a field strength of 9.39 T. A one pulse sequence was employed to record ^1H and ^{13}C magic-angle spinning (MAS) NMR spectra of the samples spun at 14.0 kHz using a 5 mm probe. The $\pi/2$ pulse widths and the recycle delays for ^1H and ^{13}C NMR were 2.5 μs and 5.0 s, and 2.8 μs and 5.0 s, respectively. The ^1H and ^{13}C chemical shifts were referenced to H_2O signal at 4.8 ppm and adamantane with the upfield methine peak at 29.5 ppm (relative to TMS).

Catalytic tests. The acetalisation of glycerol was performed in a 100-ml glass reactor with a magnetic stirrer (1200 rpm). Typically, the acetone, catalyst, and solvent were mixed in the reactor. Then the reaction system was heated to a given temperature (the temperature was measured with a thermometer in an oil bath) and glycerol was introduced. After the reaction, the product was taken out from the reaction system and analysed by gas chromatography (GC-14C, Shimadzu, using a flame ionization detector) with a flexible quartz capillary column coated with OV-17) using ethylbenzene as internal standard. The recyclability of the catalyst was tested by separating the catalyst solids from the reaction system by centrifugation, washing with large quantity of methanol and water, drying at 60 °C, then the catalyst was reused in the next reaction. The conversion of fructose was performed in a 40-ml high-pressure autoclave with a magnetic stirrer (1200 rpm). Typically, the fructose, catalyst, and solvent were mixed in the autoclave and stirred at room temperature for 1 h. Then N_2 was introduced and reaction system was heated to a given temperature (the temperature was measured with a thermometer in an oil bath, the N_2 pressure was 3.0 MPa at the reaction temperature). After the reaction, the product was taken out from the reaction system. The conversion of fructose was analyzed by high-pressure liquid chromatograph (HPLC, Bruker). The products were analyzed by gas chromatography (GC-14C, Shimadzu) using ethylbenzene as internal standard. The yields were calculated on the carbon basis in every product.

Table S1. Physicochemical characteristics of various samples.

Sample	Si/Sn ratio ^a	Acid type	S _{BET} (m ² /g)	Pore width (nm)
SBA-15	--	None	930	8.2
Sn-SBA-15	57	Lewis	834	7.1
S-Sn-Me	66	Lewis	677	7.5
S-Sn-OH	66	Brønsted and Lewis	635	7.5
S-Sn-C1 ^b	35	Lewis		
S-Sn-C2 ^c	>200	Undetectable in IR		

^a ICP analysis.

^b Synthesized from the calcination of S-Sn-Me (Si/Sn at 35) at 600 °C for 3 h.

^c Synthesized from the calcination of S-Sn-Me (Si/Sn at 66) at 800 °C for 3 h.

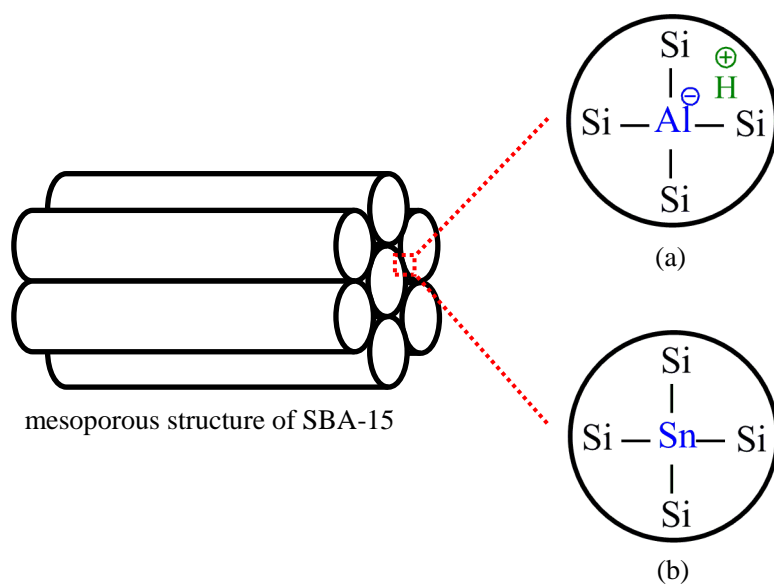
Table S2. Catalytic conversion of fructose over various catalysts.^a

Entry	Catalyst	Conv. (%)	Yield (%)			
			Route 1 ethyl lactate	Route 2 ethyl levulinate		ethoxy- methylfurfural
1 ^b	SBA-15	60.0	5.0	--	--	--
2 ^b	Sn-SBA-15	>99.0	23.9	--	--	--
3 ^b	S-Sn-Me	82.3	10.2	--	--	--
4 ^c	S-Sn-OH	>99.0	3.2	30.0	9.4	5.0

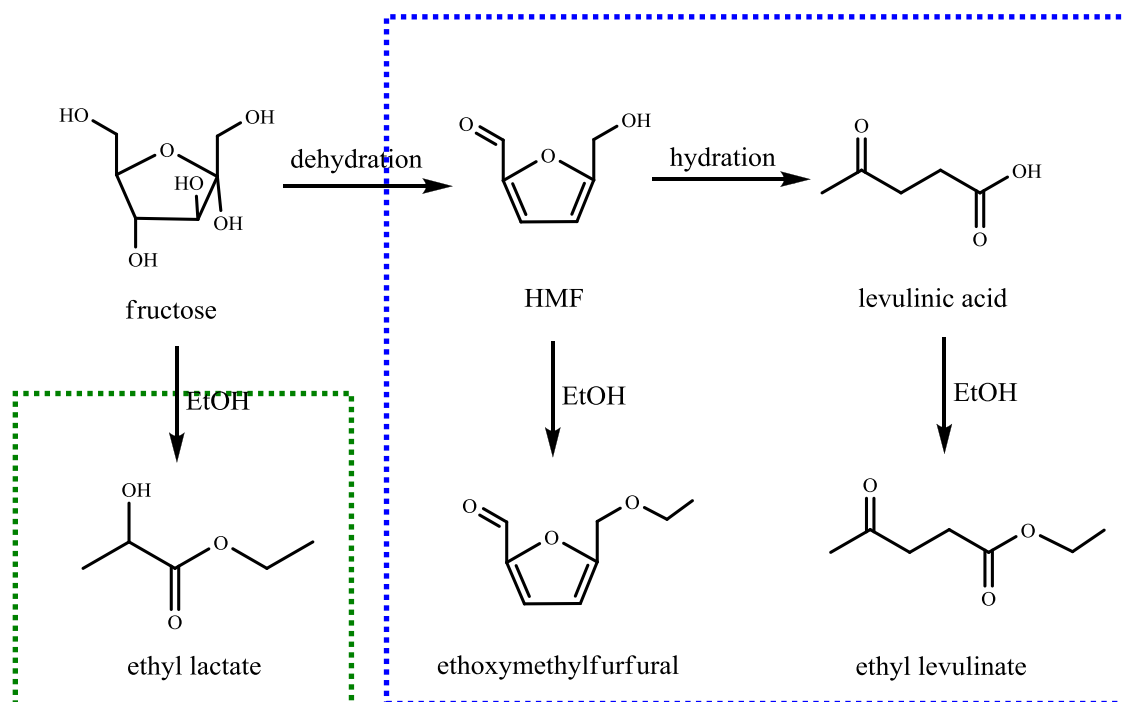
^a Reaction conditions: 230 mg of fructose, 90 mg of catalyst, 8 g of EtOH, 3.0 MPa of N₂, 16 h, the temperature of oil bath at 150 °C.

^b The by-products are mainly C₃ sugars such as glyceraldehyde and pyruvaldehyde, C₁ species such as formaldehyde, coke, and others.

^c The by-products are mainly furfural, 2-(ethoxymethyl)furan, lactic acid, C₃ sugars, coke, and others.



Scheme S1. The scheme of (a) conventional Al-SBA-15, and (b) conventional Sn-SBA-15.



Route 1

(Catalyzed by Lewis acid)

Route 2

(Catalyzed by

Brønsted acid or Brønsted & Lewis acid)

Scheme S2. Conversion of fructose through *Route 1* and *Route 2*.

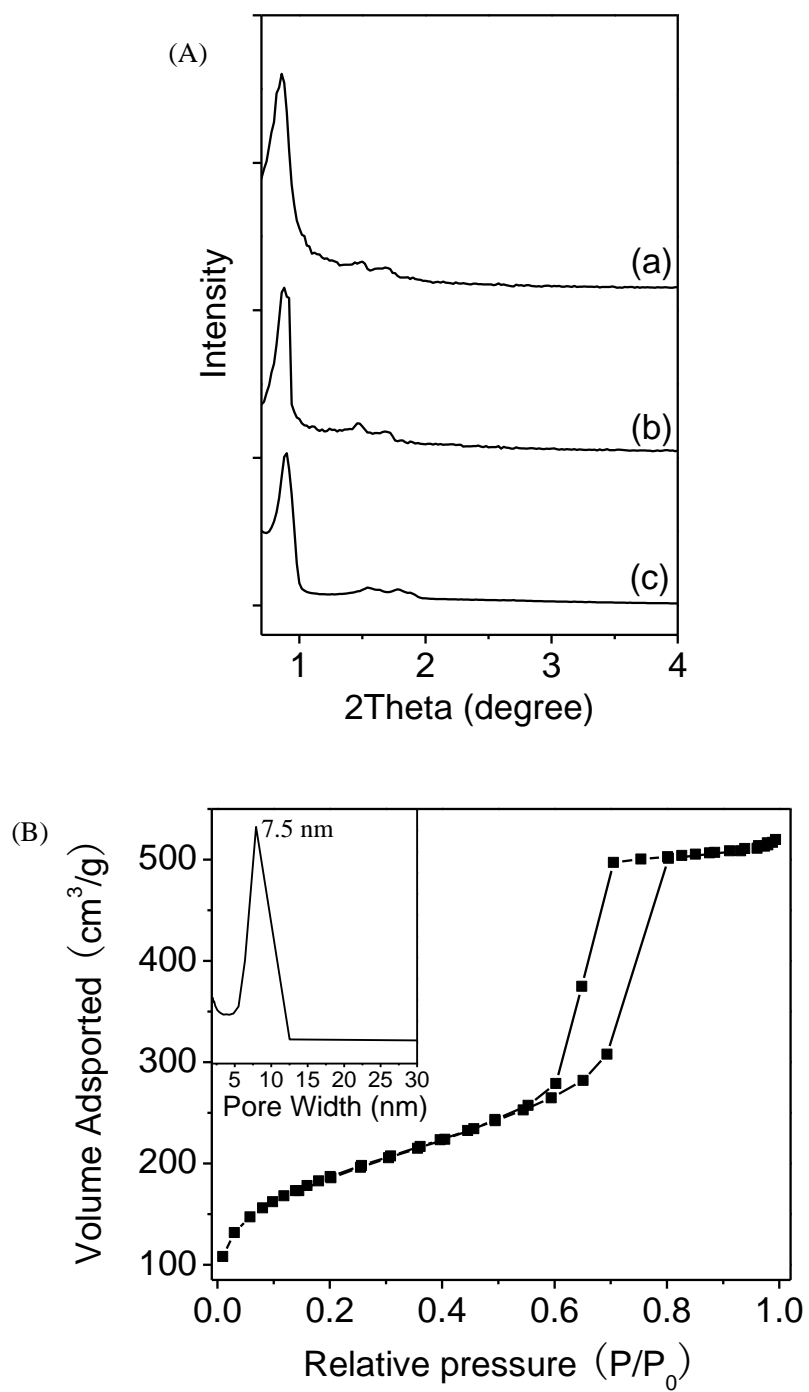


Figure S1. (A) Small-angle XRD patterns of (a) SBA-15, (b) S-Sn-Me, and (c) S-Sn-OH; (B) Nitrogen sorption isotherms of S-Sn-OH (Insert: Pore size distribution of S-Sn-OH).

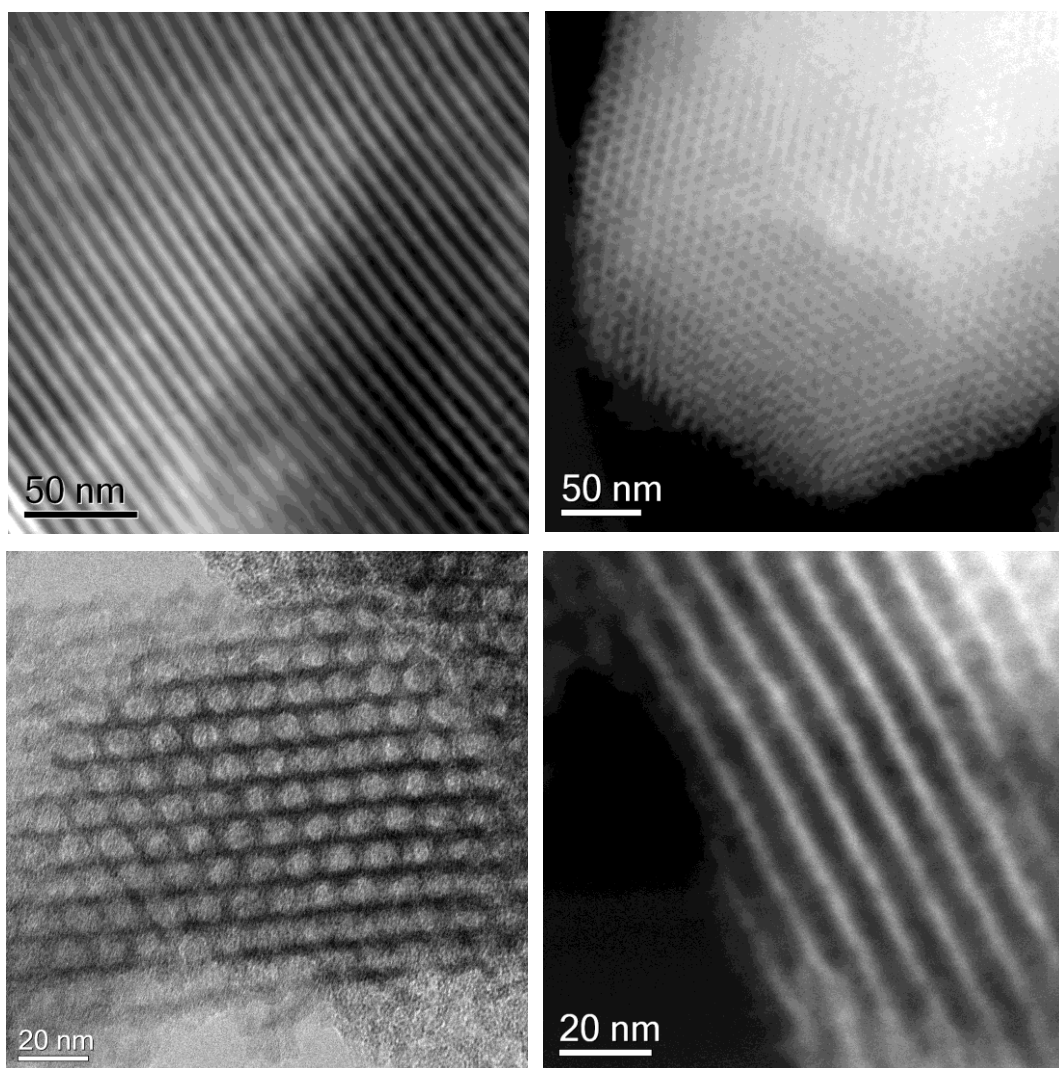


Figure S2. TEM images of randomly selected areas of S-Sn-OH.

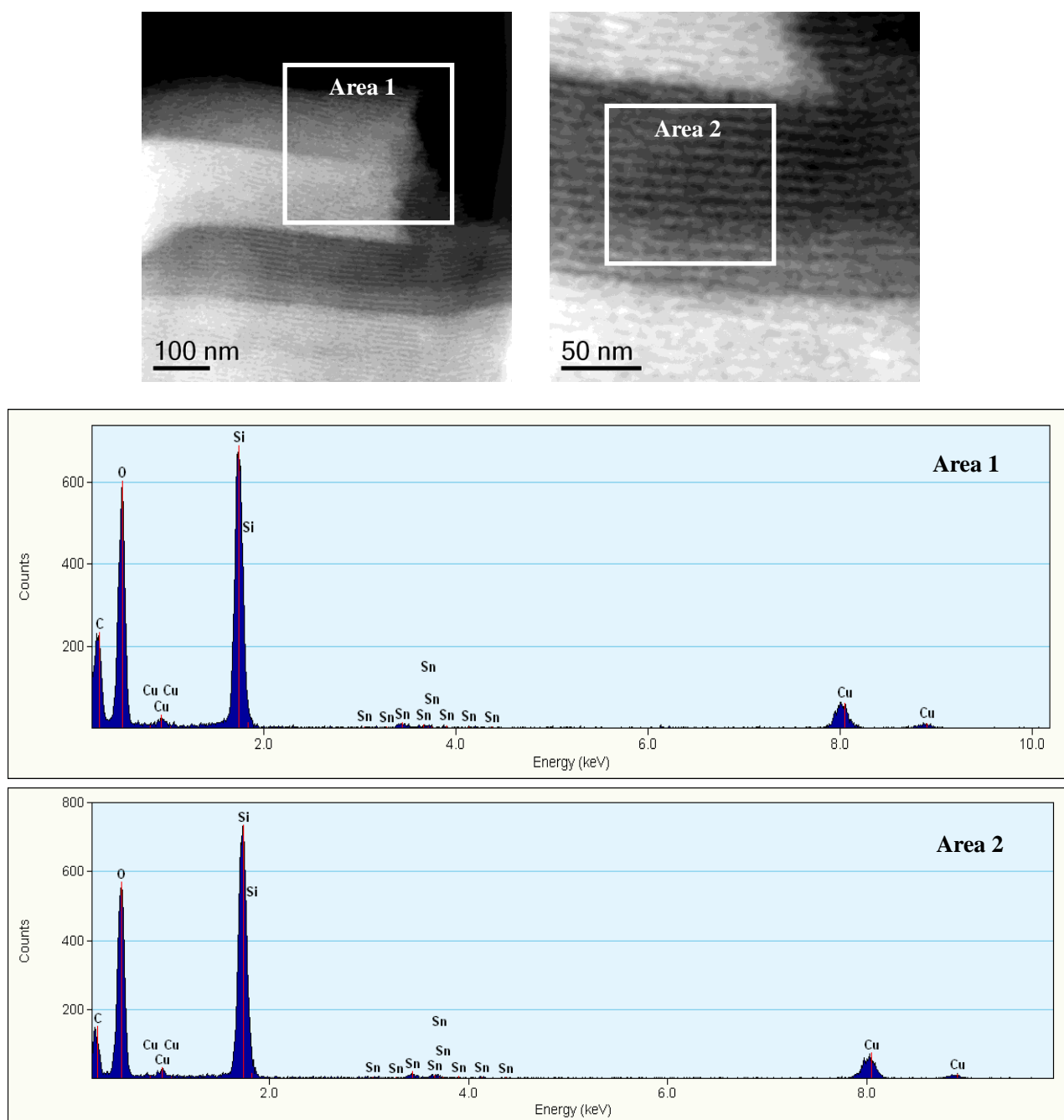


Figure S3. TEM images and corresponding EDX analysis of S-Sn-OH.

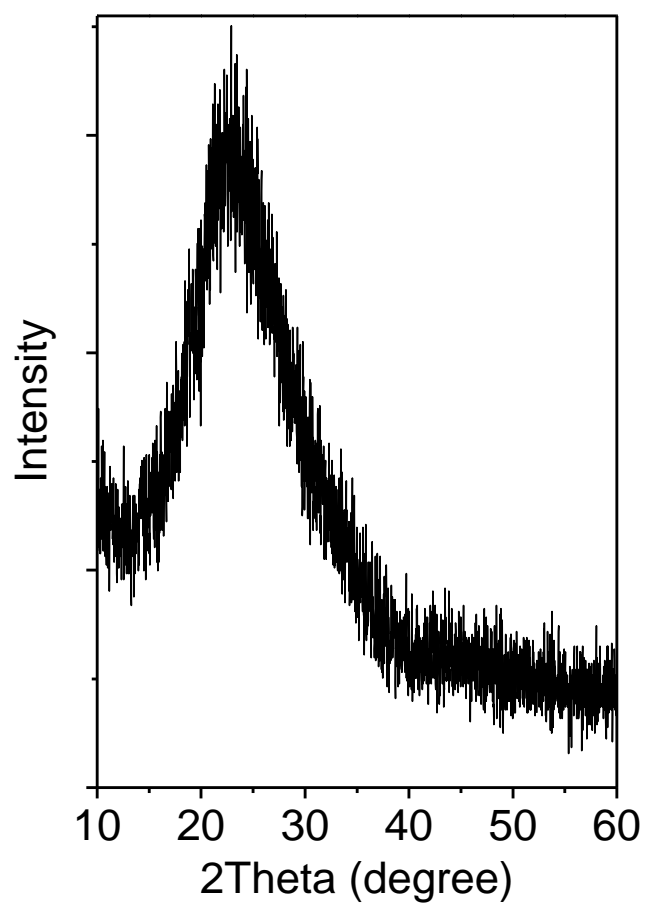


Figure S4. Wide-angle XRD pattern of S-Sn-OH.

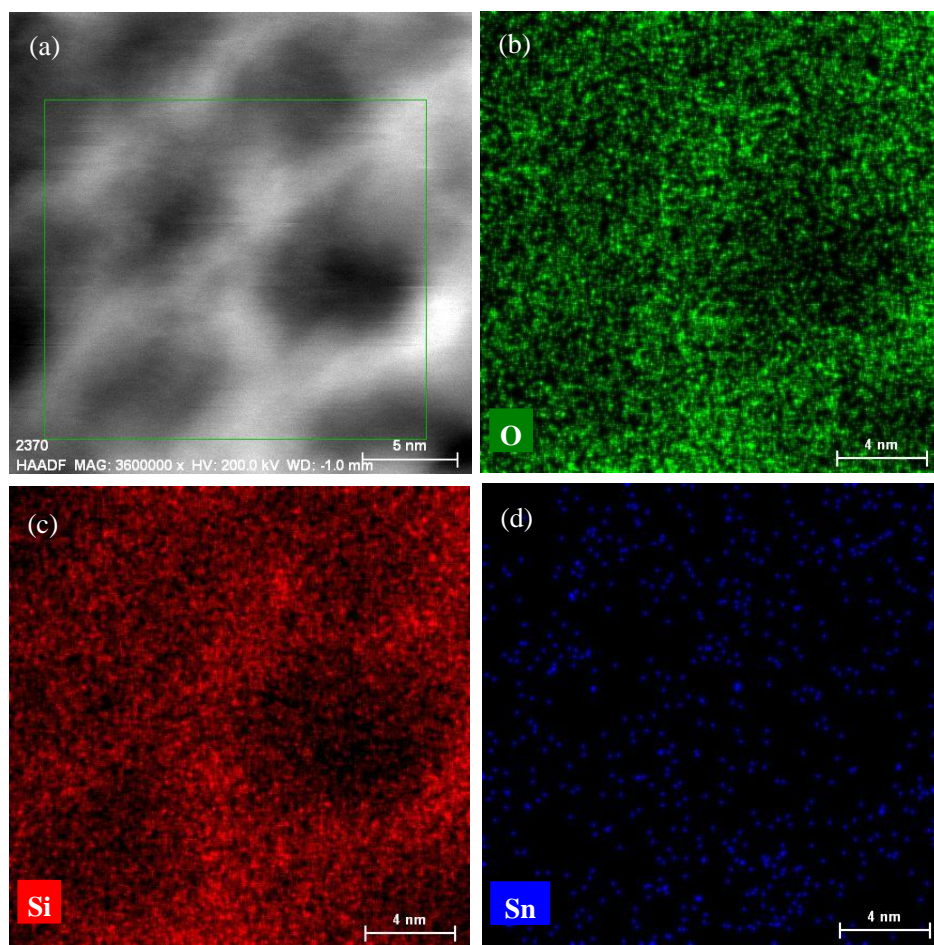


Figure S5. STEM image and the corresponding EDS elemental maps of randomly selected areas of S-Sn-OH.

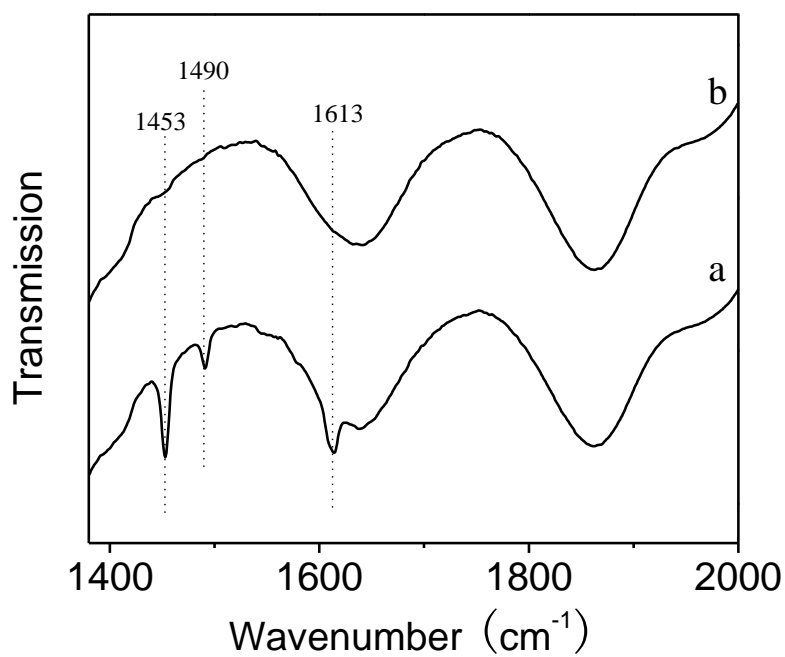


Figure S6. Pyridine-adsorption IR spectra of (a) S-Sn-C1 and (b) S-Sn-C2.

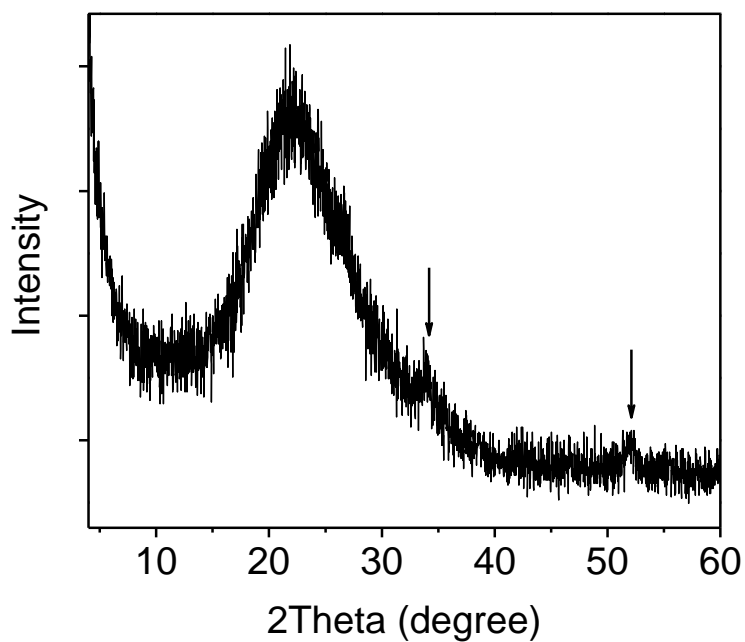


Figure S7. XRD pattern of S-Sn-C1.

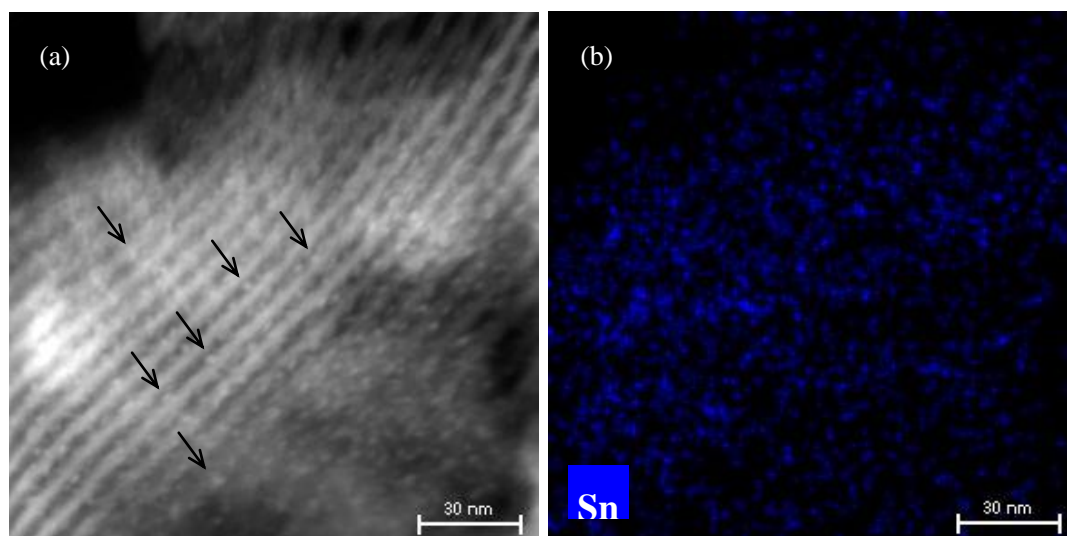


Figure S8. (a) STEM image and (b) the corresponding EDS elemental map of S-Sn-C1.

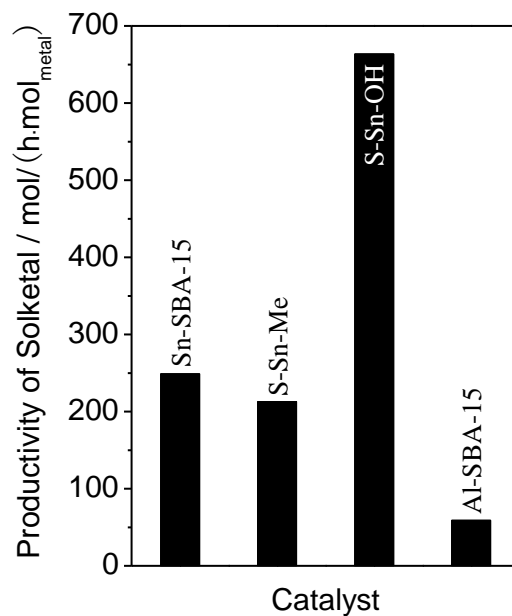


Figure S9. Productivity of solketal in acetalisation of glycerol with acetone to solketal. The productivity of solketal calculation was calculated from the amount of solketal produced per hour over per molar of metal sites in the reaction system.

References:

1. Y. Li, D. Pan, C. Yu, Y. Fan, X. Bao, *J. Catal.*, 2012, **286**, 124.
2. A. Vinu, D. P. Sawant, K. Ariga, K. Z. Hossain, S. B. Halligudi, M. Hartmann, M. Nomura, *Chem. Mater.*, 2005, **17**, 5339.
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