Supporting Information

Metal deficiency Tuned Charge Transfer in $Ni_{2-x}Sn$ (x = 0.37 - 0.65) Enhances Selective Conversion of Furfural to Furfuryl Alcohol Towards Theoretical Limit

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S.1.1. Materials

Tetraethyl orthosilicate (TEOS) (>99% GC, Sigma Aldrich), pluronic P123 (Mn~5800, Sigma Aldrich), HNO_3 (69% analytical grade, Merck Chemicals), H_2SO_4 (98% analytical grade, Merck Chemicals), nickel nitrate hexahydrate (98%, SDFCL) and Tin Chloride (98%, SDFCL).

S.1.2. Synthesis

SBA-15: The support material Santa Barbara Amorphous (SBA-15)[1] was synthesized by modifying an already reported method.[2] Four grams of pluronic P123 were dissolved in 105 mL of deionized water and 10.8 mL of 98% H_2SO_4 to act as a soft template. Then 9.063 mL of TEOS was added to the solution with a high, stirring rate for 3.5 hours at 313 K, followed by hydrothermal treatment at 373 K for 30 hours. The white powder was filtered, washed with deionized water, and dried at 373 K overnight. Lastly, it was calcined for 6 hours at 823 K.

$Ni_{2-x}Sn$/SBA-15: A typical method of incipient wetness impregnation was followed with slight modification to distribute the $Ni_{2-x}Sn$ system on SBA-15. Ni(II) and Sn(II) nitrates were dissolved in a 4 M HNO_3 solution. The nitrate salts were weighed to get 20% of metal loading with different ratio of Ni:Sn – 1.35:1 (($Ni_{1.35}Sn$)/SBA-15), 1.5:1 (($Ni_{1.5}Sn$)/SBA-15), and 1.63:1 (($Ni_{1.63}Sn$)/SBA-15). Metal nitrates were soaked with SBA-15 in the solution for an hour, which propels the solution impregnation into the channels by capillary action. The excess solution was dried at 60 ºC on a hotplate and in a vacuum oven at 120 ºC overnight. The precursor was reduced at 800 ºC under an H_2 atmosphere in a tubular furnace for 5 hrs. As a control Ni (23 wt%) was also loaded on SBA-15.
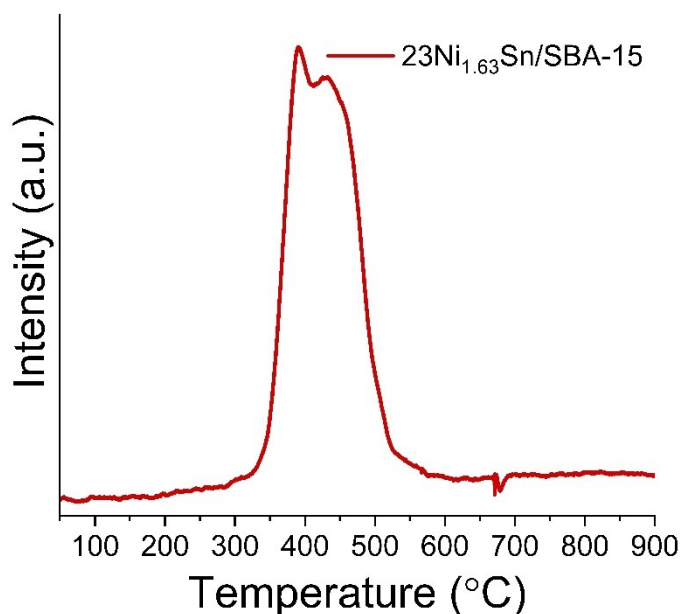
Figure S1. H_2-TPR profile if $23Ni_{1.63}Sn/SBA-15$.

S.1.3. Material Characterisation

ICP-OES: ICP-OES was performed using a Perkin Elmer Optima 7000 DV instrument. The samples were first digested in concentrated aqua regia prepared in the lab. Then samples were treated with 2-3 drops of HF to remove silica of SBA-15 and diluted with distilled water. In a typical experiment, 5 mg of the sample was dissolved in 3-5 ml aqua regia and heated at 333 K for digestion. The digested sample was then treated with 3-5 drops of HF and diluted to 10 ml volume with deionised water. From this, 1 ml was again taken and diluted to 10 ml. The solid particles were separated by thorough centrifugation before measurements.

Powder X-ray Diffraction (PXRD): The phase formation on SBA-15 was confirmed by X-ray diffraction (XRD) collected on a PANalytical X-ray diffractometer with Cu $K_{\alpha 1}$ radiation at 45 kV and 40 mA. The features of the PXRD patterns were compared with simulated patterns from Pearson Database.

N_2 Adsorption Measurement: The adsorption isotherms were studied by using N_2 at 77 K on the BelCat instrument. Before the measurements, the powders were treated for degassing at 423 K for 6 hours. The specific surface area was confirmed by Brunaur-Emmett-Teller (BET) method and pore size distribution by the classical BJH (Barrett, Joyner and Halenda) method.

X-ray Photoelectron Spectroscopy (XPS): XPS measurements were carried out using a Thermo K-alpha+ spectrometer using micro-focused and monochromated Al K-α radiation with energy 1486.6 eV. The pass energy for the spectral acquisition was kept at 50 eV for individual core levels. The electron flood gun was utilized for providing charge compensation during data acquisition. Further, the individual core-level spectra were checked for charging using C1s at 284.6 eV as standard and corrected

if needed. The peak fitting of the individual core levels was done using CasaXPS software with a Shirley-type background.

X-ray Absorption Spectroscopy (XAS): Ni and Sn K-edge XAS measurements of the catalyst on SBA-15 were carried out in transmittance and fluorescence mode at PETRA III, P64 beamline of DESY, Germany. Pellets for the measurements were made by homogeneously mixing the sample with an inert cellulose matrix to have an X-ray absorption edge jump close to 1. The XAS data processing was done using the ATHENA software.[3] The multiple data were collected and averaged before proceeding to the background correction. The averaged data were smoothed out using the standard kernel size of 11. The weak spline was used for background correction in the pre-edge region. All the data were normalized for the standard data analysis procedure and were used to extract the extended X-ray absorption fine structure (EXAFS) signal from the measured absorption spectra. Theoretical EXAFS models were constructed and fitted to the experimental data in ARTEMIS. To obtain the value of amp factor and E_0 for respective elemental K-edge, all the oxides were fit using the crystallographic information file (CIF). The obtained amp factor and E_0 were used for EXAFS data fitting of the compounds. The EXAFS data were fitted with $Ni_{2-x}Sn$ (x = 0.37, 0.50, 0.65) and the second phase of Ni_3Sn_2. The CIF files for $Ni_{1+\delta}Sn$ were modified before the F_{eff} calculations. Initially, both Ni positions were rendered fully occupied, followed by removing several Ni atoms per synthesised Ni occupancy in the system. Data were fitted in R-space between 1 and 4.2 Å for all the samples. The fitting parameters consist of bond length change between atoms (ΔR), change in energy scale between data and theory (ΔE_0), and mean-square displacement of the bond length (σ^2). The coordination numbers (C. N.) were taken from the respective crystal structures and varied until a low R-factor was achieved.

S 1.4 .Catalyst Screening Test

Batch-mode hydrogenation of furfural and recycling of the catalyst

Ten milligrams of catalyst were weighed and transferred into the quartz vial, filled with 5 ml of IPA solvent. The catalyst was dispersed into the solution using small magnetic beads. The vials were closed with rubber septa, and a syringe needle was used to feed gas enters the vials in a controlled fashion. The vials were put inside the Parr vessel, and the remaining empty space was filled with glass wool to support the vials. The vessel was flushed 3 times using the feed gas (H_2) to flush out the oxygen gas from the vessel. The vessel was pressurized to 40 bar with the feed gas and put inside the preheated oil bath at 150 °C. An external temperature indicator was attached to the Vessel's thermocouple to monitor the inside temperature throughout the course of the experiment. Upon completion of the experiment, the product solution was removed from vials and centrifuged to remove the catalyst.

Supplementary Figures and Tables
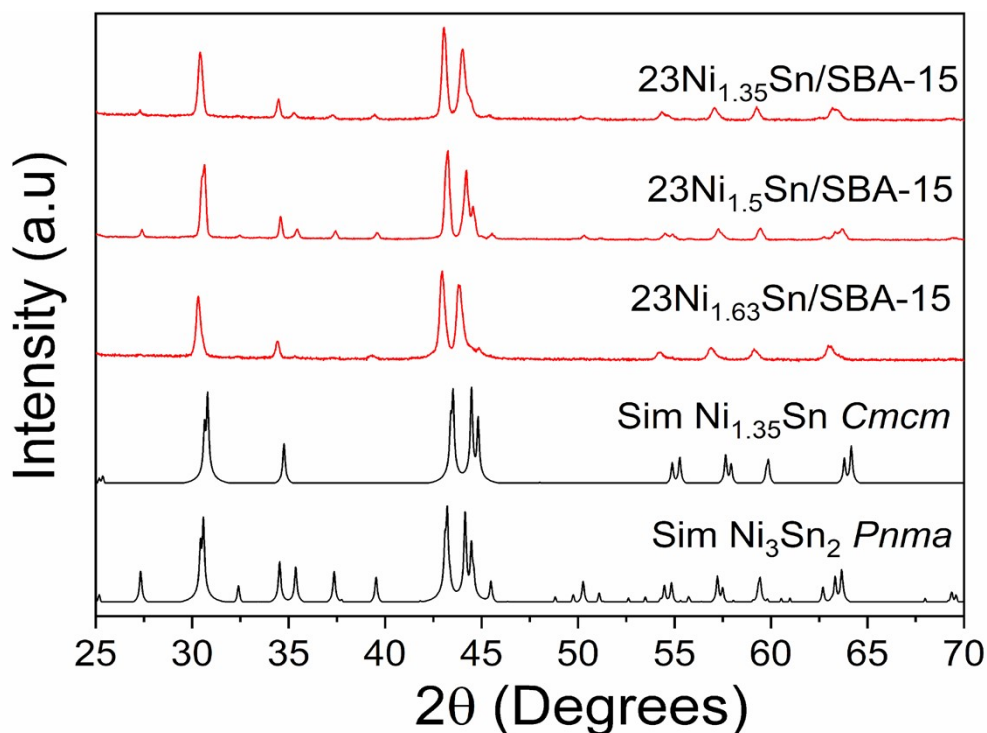
Figure S2. Powder XRD of various $Ni_{2-x}Sn$ (x = 0.35, 0.35, 0.63) intermetallic compounds supported on SBA-15.

Table S1. ICP-OES data of different $In_2(Ni_xCo_y)$/SBA-15 catalysts.

Catalyst	Metal Conc. from ICP-OES (moles)		Stoichiometric Ratio (Ni/Sn)		
	Ni	Sn	Expected	ICP-OES	Rietveld Refinement
$23Ni_{1.35}Sn$/SBA-15	0.07752	0.05633	1.35	1.38	1.40
$23Ni_{1.5}Sn$/SBA-15	0.0862	0.05621	1.5	1.53	1.5
$23Ni_{1.63}Sn$/SBA-15	0.0911	0.05464	1.63	1.67	1.85
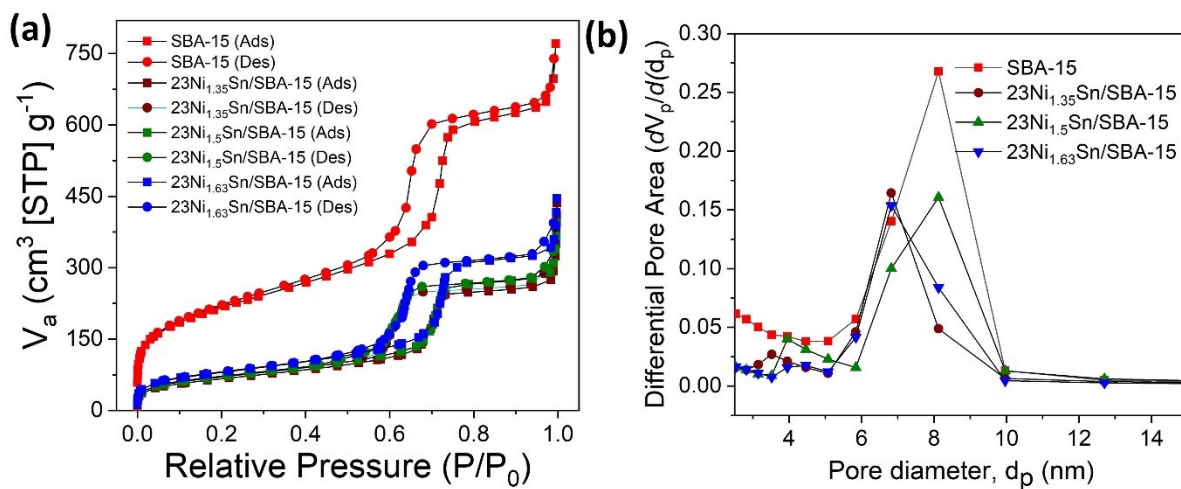
Figure S3. BET plots and BJH data for all samples.

Table S2. Textural Properties

	Surface Area (m²/g)	Pore Diameter (nm)
SBA-15	762	7.50
23Ni$_{1.35}$Sn/SBA-15	284	7.25
23Ni$_{1.5}$Sn/SBA-15	251	7.14
23Ni$_{1.63}$Sn/SBA-15	249	6.65
Spent 23Ni$_{1.63}$Sn/SBA-15	237	6.8

Table S3. EXAFS fitted data parameter for Ni$_{1.35}$Sn

Name	Coordination Number (C. N.)	σ²	R$_{CIF}$	R$_{EXAFS}$
Ni$_3$Sn$_2$_Ni	0.896(1)	-0.00790	2.55030	2.49329
Ni$_3$Sn$_2$_Sn	0.896(1)	-0.00561	2.60390	2.45272
Ni$_3$Sn$_2$_Ni	2.688(2)	0.02252	2.64610	2.79186
Ni$_3$Sn$_2$_Sn	1.792(2)	0.07619	2.66410	2.37181
Ni$_3$Sn$_2$_Ni	0.896(1)	-0.01808	2.69320	2.84464
Ni$_3$Sn$_2$_Sn	1.792(1)	0.00363	2.70850	2.75772
Ni$_3$Sn$_2$_Sn	0.896(1)	-0.01605	2.89260	2.80607
Ni$_{1.35}$Sn_Sn	0.896(1)	0.00589	2.32570	2.25807
Ni$_{1.35}$Sn_Sn	1.792(2)	0.00081	2.36210	2.43529
Ni$_{1.35}$Sn_Sn	1.792(2)	0.01431	2.58090	2.68809
Ni$_{1.35}$Sn_Ni	3.584(2)	0.00363	2.65710	2.63193
Ni$_{1.35}$Sn_Ni	1.792(2)	-0.00256	2.72850	2.76921

Table S4. EXAFS fitted data parameter for Ni$_{1.50}$Sn.

Name	Coordination Number (C. N.)	σ²	R$_{CIF}$	R$_{EXAFS}$
Ni$_3$Sn$_2$_Ni	1.792(2)	-0.00412	2.55030	2.49243
Ni$_3$Sn$_2$_Sn	0.896(1)	0.02324	2.60390	2.62543
Ni$_3$Sn$_2$_Ni	2.688(3)	0.01846	2.64610	2.76290
Ni$_3$Sn$_2$_Sn	1.792(2)	0.00211	2.66410	2.46897
Ni$_3$Sn$_2$_Ni	0.896(1)	0.00014	2.69320	2.62454
Ni$_3$Sn$_2$_Sn	1.792(2)	0.00737	2.70850	2.70039
Ni$_3$Sn$_2$_Sn	0.896(1)	0.00653	2.89260	2.92997
Ni$_{1.35}$Sn_Sn	0.896(1)	0.02677	2.32570	2.29036
Ni$_{1.35}$Sn_Sn	1.792(2)	0.03861	2.36210	2.04238
Ni$_{1.35}$Sn_Sn	1.792(2)	0.01831	2.58090	3.22423
Ni$_{1.35}$Sn_Ni	3.584(2)	0.02189	2.65710	3.02962
Ni$_{1.35}$Sn_Ni	1.792(2)	0.01282	2.72850	2.78678

Table S5. EXAFS fitted data parameter for $Ni_{1.63}Sn$.

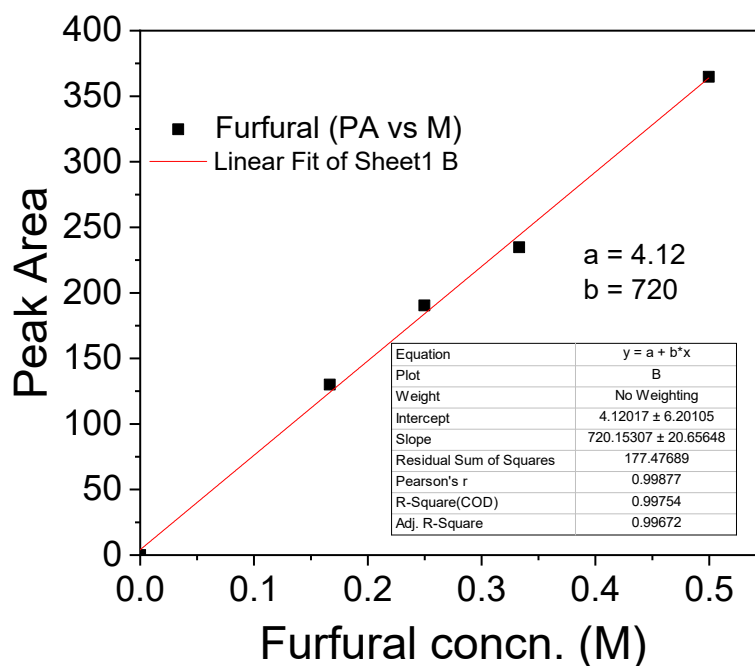| Name	Coordination Number (C. N.)	σ^2	R_{CIF}	R_{EXAFS}
$Ni_3Sn_2\_Ni$	1.792(2)	-0.01132	2.55030	2.49056
$Ni_3Sn_2\_Sn$	1.792(2)	0.00964	2.60390	2.07358
$Ni_3Sn_2\_Ni$	2.688(3)	0.00393	2.64610	2.67529
$Ni_3Sn_2\_Sn$	1.792(2)	0.00547	2.66410	2.67289
$Ni_3Sn_2\_Ni$	0.896(1)	0.00607	2.69320	2.80761
$Ni_3Sn_2\_Sn$	1.792(2)	0.01963	2.70850	2.79564
$Ni_3Sn_2\_Sn$	0.896(1)	0.00856	2.89260	3.30072
$Ni_{1.35}Sn\_Sn$	0.896(1)	-0.00914	2.32570	2.44591
$Ni_{1.35}Sn\_Sn$	1.792(2)	0.03204	2.36210	2.97080
$Ni_{1.35}Sn\_Sn$	1.792(2)	0.01381	2.58090	2.40989
$Ni_{1.35}Sn\_Ni$	3.584(4)	0.03428	2.65710	2.84601
$Ni_{1.35}Sn\_Ni$	1.792(2)	0.01687	2.72850	2.41419

Table S6. Summary of Ni 2p and Sn 3d XPS spectrum of $Ni_{1.35}Sn/SBA-15$, $Ni_{1.5}Sn/SBA-15$ and $Ni_{1.63}In/SBA-15$.

Peak Area	$Ni_{1.35}Sn/SBA-15$		$Ni_{1.5}Sn/SBA-15$		$Ni_{1.63}Sn/SBA-15$	
	B.E (eV)	Peak Area	B.E (eV)	Peak Area	B.E (eV)	Peak Area
Ni^0	852.8	921	852.7	1260	852.8	1876
Ni^{2+}	855.6	3076	856.1	3229	856	3951
Ni^0/Ni^{2+} (Peak Area Ratio)		**0.3**		**0.4**		**0.47**
Sn^0 (Peak Area)	485.1	4088	485.5	4316	485.4	7222
Sn^{2+} (Peak Area)	487.2	11754	487.7	9668	487.2	12037
Sn^0/Sn^{2+} (Peak Area Ratio)		**0.35**		**0.45**		**0.6**

Activity Calculations

Response factor of GC-FID (RF):

The response factor of Furfural aldehyde with FID GC is obtained by the calibration curve **figure S4.**

Figure S4 plot: Peak Area vs Furfural concn. (M)

Inset table:

Equation	$y = a + b*x$
Plot	B
Weight	No Weighting
Intercept	4.12017 ± 6.20105
Slope	720.15307 ± 20.65648
Residual Sum of Squares	177.47689
Pearson's r	0.99877
R-Square(COD)	0.99754
Adj. R-Square	0.99672

a = 4.12
b = 720

Figure S4: GC Calibration curve for Peak area Vs Furfural concentration (Furfural in IPA as solvent).

Thus, the unknown furfural concentration after reaction = Peak Area/Response factor (1)

From the calibration curve the R.F(Furfural) for FID is 720.

23Ni$_{1.5}$Sn/SBA-15

Reaction Conditions:

Furfural Aldehyde = 100 µL

IPA = 5 ml

TEMP = 150 °C

Pressure = 40 B & Time of Reaction 6 h

Peak area of Furfural after reaction = 2.8

$$Concn.\,of\,Furfural\,after\,reaction = \frac{2.8}{720} = 0.00389\,Molar$$

From eqn (1)

Thus, the moles of Furfural left after reaction = 3.89 mM × 5 ml = 0.01945 millimoles

100 µL Furfural corresponds to 1.2 millimoles.

$$Conversion\,\% = \frac{Initial\,moles\,of\,Furfural - Moles\,of\,Furfural\,after\,reaction}{Initial\,moles\,of\,furfural} \times 100$$

$$Conversion\,\% = \frac{1.2 - 0.01945}{1.2} \times 100$$

Furfural Conversion % = 98.38 %

Activity calculation

Amt of Ni-Sn in 10 mg 23 % Ni$_{1.5}$Sn/SBA-15 = 2.3 × 10^{-3} g

Amount of Furfural Converted = 98.38 % of 1.2 mmoles = 1.18056 mmol

Therefore in 6 h,

$Activity\ per\ gNiSn = (1.1856 \times 1000\ \mu mol)\ /(6 \times 60 \times 60 \times 0.0023)$

$$= 23.76\ \mu mol/g_{Ni}.s$$

23Ni$_{1.35}$Sn/SBA-15

Reaction Conditions:

Furfural Aldehyde = 100 µL

IPA = 5 ml

TEMP = 150 °C

Pressure = 40 B & Time of Reaction 6 h

Peak area of Furfural after reaction = 100.8

$Concn.\ of\ Furfural\ after\ reaction = \dfrac{100.8}{720} = 0.14\ Molar$ From eqn (1)

Thus, the moles of Furfural left after reaction = 0.14 M × 5 ml = 0.7 millimoles

100 µL Furfural corresponds to 1.2 millimoles.

$Conversion\ \% = \dfrac{Initial\ moles\ of\ Furfural - Moles\ of\ Furfural\ after\ reaction}{Initial\ moles\ of\ furfural} \times 100$

$Conversion\ \% = \dfrac{1.2 - 0.7}{1.2} \times 100$

Furfural Conversion % = 41.66 %

Activity Calculation

Amt of Ni-Sn in 10 mg 23 % Ni$_{1.5}$Sn/SBA-15 = 2.3 × 10^{-3} g

Amount of Furfural Converted = 41.66 % of 1.2 mmoles = 0.5 mmol

Therefore in 6 h,

$Activity\ per\ gNiSn = (0.5 \times 1000\ \mu mol)\ /(6 \times 60 \times 60 \times 0.0023)$

$$= 10.06\ \mu mol/g_{Ni}.s$$

Leaching and Recycling Test

23Ni$_{1.63}$Sn/SBA-15 was chosen as the catalyst for the leaching and the recycling tests. Only 5 mg of the catalyst was loaded as obtaining almost complete conversion using 10 mg of the catalyst would not have given us unambiguous conclusions owing to saturated conversion. Furfural hydrogenation was

performed at 150 °C and 40 bar hydrogen pressure. Centrifugation separated the solution mixture from the catalyst following the 6-hour reaction. The supernatant was then transferred to a new vial, sealed with a septum, and given a 40-bar H_2 purge. The reaction was continued for an additional 6 hours. Every hour, aliquots were obtained and measured by GC.
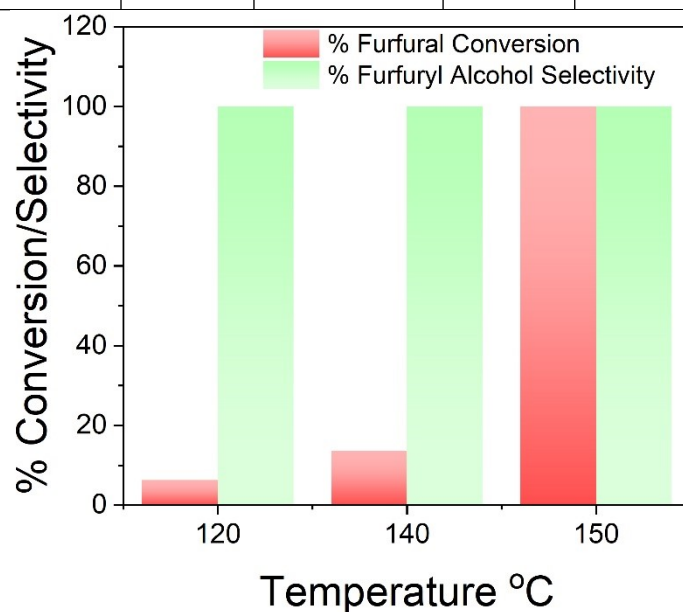
Recycling Test

For the recycling tests, we used 5 mg of the catalyst again but each cycle was run for a longer duration of 10 hours with a conversion of 70%. The catalytic mixture was carefully centrifuged and the supernatant was collected for analysis. The catalyst was then transferred to a fresh vial. Following this fresh IPA and furfuryl alcohol (100 μL) were added to carry out furfural hydrogenation. This cycle was repeated for an additional 4 times.

Table S7. Summary of catalytic activity of Ni-Sn catalyst for furfural aldehyde reduction at different reaction condition.

Catalyst	Reaction Condition	Conversion (%)	Furfuryl Alcohol Selectivity (%)	Selectivity other (%)	Furfuryl Alcohol Yield (%)	Activity $(\mu mol/g_{Ni-Sn}^{-1}s^{-1})$
$23Ni_{1.35}Sn/SBA-15$	40 B, 150 °C, 6 h	41.7	100	-	41.7	10.1
$23Ni_{1.5}Sn/SBA-15$	40 B, 150 °C, 6 h	98.4	100	-	98.4	23.8
$23Ni_{1.63}Sn/SBA-15$	40 B, 150 °C, 6 h	100	100	-	100	24.1
$23Ni_{1.63}Sn/SBA-15$	40 B, 120 °C, 6 h	6.3	100	-	6.3	1.5
$23Ni_{1.63}Sn/SBA-15$	40 B, 140 °C, 6 h	13.7	100	-	13.7	3.3
23Ni/SBA-15	40 B, 150 °C, 6 h	100	0	100 (THFA)	0	0
23Sn/SBA-15	40 B, 150 °C, 6 h	0	0	-	0	-
Pt_n/CoAl-MMOs[4]	8 B, 120 °C, 5 h	98.7	100	-	98.7	-
Pt/CoAlO$_x$[5]	1 B, R.T, 24 h	99	100	-	99	-
Cu-Pt@TMS[6]	10 B, 110 °C, 3 h	99.5	100	-	99.5	-
Ru_3C_{100}[7]	1 B, 120 °C, 4 h	100	100	-	100	-
Cu_3Co_1/MgAlO$_x$[8]	20 B, 110 °C, 2 h	99.9	100	-	99.9	-

| Ni@OMC[9] | 30 B, 180 ºC, 4 h | 98.0 | 100 | - | 98.0 | - |

Figure S5. Furfural hydrogenation @ 40 Bar at different reaction temperature for 23% by wt Ni$_{1.63}$Sn/SBA-15.
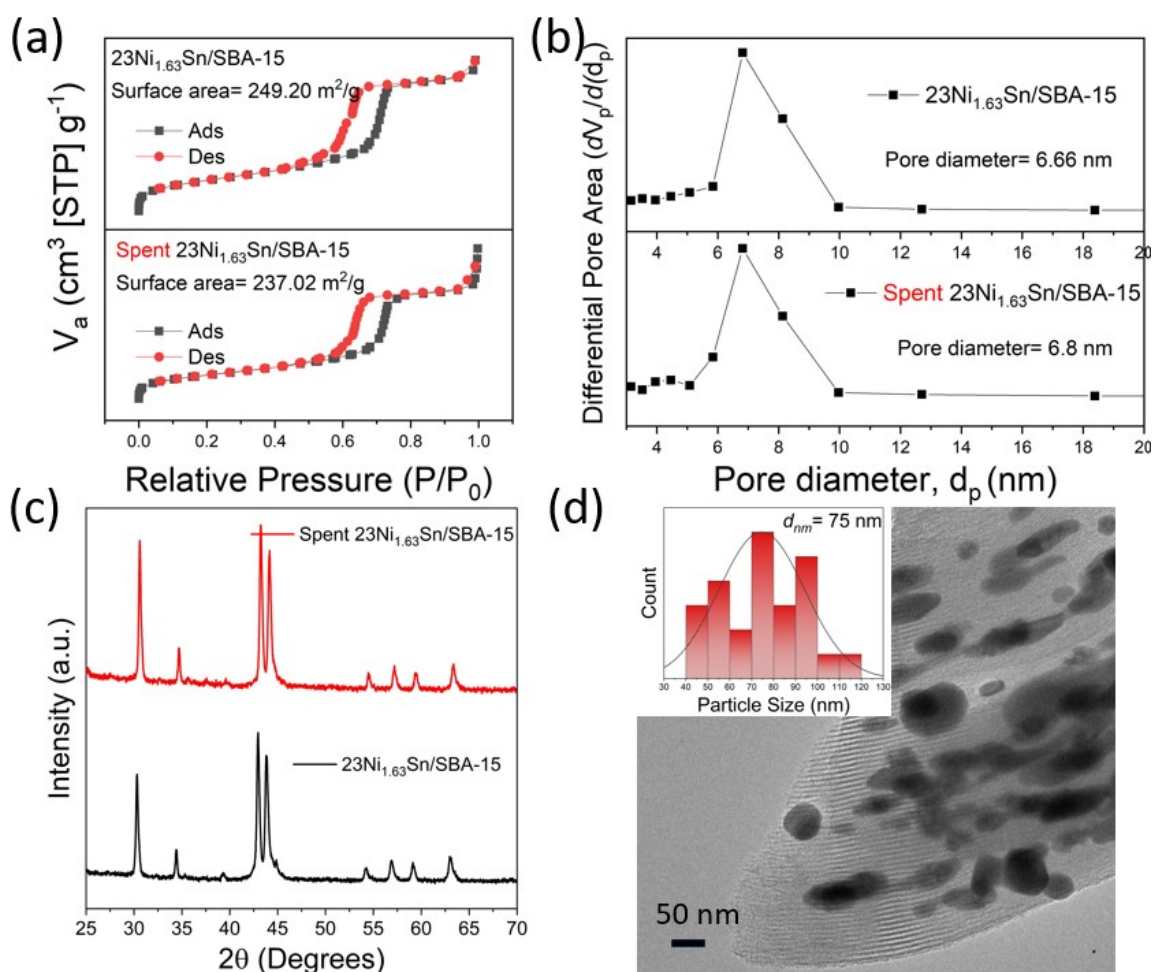
Figure S6. Spent catalyst (a) nitrogen adsorption-desorpion isotherm, (b) pore size distribution, (c) powder XRD and (d) TEM image.

Reference

1. D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024-6036.
2. E. M. Björk, *J. Chem. Educ.*, 2017, **94**, 91-94.
3. B. Ravel and M. J. J. o. s. r. Newville, 2005, **12**, 537-541.
4. Y. Zhang, S. Wang, Y. Yang, L. Wang, E. Xu, Q. Hou, S. Zhao, T. Liu, S. Hong, L. Zheng, F. Li, X. Zhang and M. Wei, *Applied Catalysis B: Environment and Energy*, 2024, **346**, 123719.
5. E. Xu, H. Feng, L. Wang, Y. Zhang, K. Liu, S. Cui, H. Meng, G. Wang and Y. Yang, *ACS Applied Nano Materials*, 2023, **6**, 14991-15001.
6. S. Wang, Y. Lv, J. Ren, Z. Xu, Q. Yang, H. Zhao, D. Gao and G. Chen, *ACS Catalysis*, 2023, **13**, 8720-8730.
7. Y. Wang, T. Gao, Y. Lu, Y. Wang, Q. Cao and W. Fang, *Green Energy & Environment*, 2022, **7**, 275-287.
8. H. Zhao, X. Liao, H. Cui, M. Zhu, F. Hao, W. Xiong, H. Luo, Y. Lv and P. Liu, *Fuel*, 2023, **351**, 128887.
9. Y. Tang, M. Qiu, J. Yang, F. Shen, X. Wang and X. J. G. C. Qi, 2021, **23**, 1861-1870.