

Electronic Supplementary Information for

Unravelling the one-pot conversion of biomass-derived furfural and levulinic acid to 1,4-pentanediol catalysed by supported RANEY® Ni-Sn alloy catalysts

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1. Experimental sections

1.1. Materials

Raney Ni–Al was purchased from Kanto Chemical Co. Inc. (50%wt Ni+ 50%wt Al = 50:50). Tin dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), NaOH (97%), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (99.9%), ethylene glycol (99.5%), ethanol (99.5%), and 2-methoxyethanol (99.8%) were purchased from WAKO Pure Chemical Co. and used as received. Furfuraldehyde (98%), furfuryl alcohol (97%), 2-methylfuran (98%), tetrahydrofurfuryl alcohol (99%), levulinic acid (98%), and γ -valerolactone (99%) were purchased from Tokyo Chemical Industry Co. All organic chemical compounds were purified using standard procedures prior to use. Active carbon (AC, $S_{\text{BET}} = 815 \text{ m}^2\text{g}^{-1}$), and aluminium hydroxide (*c*-AlOH) were purchased and used as received from WAKO Pure Chemical Industries, Ltd. unless otherwise stated. SiO_2 ($S_{\text{BET}} = 200 \text{ m}^2\text{g}^{-1}$) and $\gamma\text{-Al}_2\text{O}_3$ ($S_{\text{BET}} = 100 \text{ m}^2\text{g}^{-1}$) were purchased from Japan Aerosil Co. Lithium-taenolite (TN), sodium-Bentonite (BNT), lithium- hectorite (HT) and smectite SA (SMT) were donated by Kunimine Industries Co. Ltd.

1.2. Catalyst preparation

RANEY® Ni. Typical procedure for the synthesis of the conventional RANEY® Ni is described as follows:^{1–3} RANEY Ni-Al alloy powder (1.0 g) was slowly added to an aqueous solution of NaOH (6 M, 10 mL) at 363 K under gentle stirring and was kept on stirring for 30 min for further alkali leaching. The precipitated was washed by distilled water until the supernatant became neutral and then stored under water for activity test.

Supported RANEY® Ni. Typical procedure for the synthesis of the supported RANEY® Ni is described as follows:^{2,3} RANEY Ni-Al alloy powder (1.0 g) was slowly added to an aqueous solution of NaOH (6 M, 10 mL) at 363 K under gentle stirring and was kept on stirring for 30 min for further alkali leaching, then washed with deionized water and ethanol until the filtrate was neutralized then the clay or active carbon (AC) was added slowly and stirred for overnight at room temperature. The mixture was transferred into a sealed-Teflon autoclave reactor for hydrothermal treatment at 423 K for 2 h. The solvent was removed by simple centrifugation then dried under vacuum for overnight. Prior to safety use (pyrophoricity), the supported RANEY® Ni/AC was examined by heating up under air and it was found to be nonpyrophoric. In the case of RANEY® Ni, the catalyst was stored in H_2O and used as slurry to prevent the oxidation with air during handling. In addition, metal oxides or acidic co-catalysts were added by simple mixing at room temperature without further treatment.

Synthesis of supported RANEY® Ni–Sn (1.5) catalysts. Typical procedure for the synthesis of the supported Raney® Ni-Sn/AC is described as follows:^{2,3} Supported RANEY® Ni/AC that was obtained from the above procedure was mixed with an ethanol solution that contained 2.30 mmol $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (to keep the Ni/Sn molar ratio of approximately 1.5) at room temperature and stirred for 2 h. The mixture was then placed into a sealed-Teflon autoclave reactor for the hydrothermal treatment at 423 K for 2 h. The resulting precipitate was filtered, washed with distilled water until the filtrate was neutralized, and then stored in water. The catalyst was reduced with H_2 at 673 K for 1.5 h prior to catalytic reaction.

Synthesis of RANEY® Ni/AlOH. Typical procedure of the synthesis of Raney nickel supported on aluminium hydroxide catalyst (denoted as RANEY® Ni/AlOH or RNi/AlOH) is described as follows:⁴ RANEY® Ni-Al alloy powder (1.0 g) was slowly added to a dilute aqueous solution of NaOH (0.31 M, 8 mL) at room temperature. The temperature was raised to 363 K and 1 mL of 3.1 M NaOH solution was subsequently added and stirred for 30 min. The mixture was placed into a sealed-Teflon autoclave reactor for hydrothermal treatment at 423 K for 2 h. The resulting precipitate was filtered, washed with distilled water until filtrate was neutralized, and then stored in water. The catalyst was dried under vacuum before the catalytic reaction.

Synthesis of RNi–Sn(x)/AlOH and RNi–Sn(x)AA. Typical procedure of the synthesis of RANEY® nickel-tin alloy supported on aluminium hydroxide (denoted as RNi-Sn(3.0)/AlOH; 3.0 is Ni/Sn molar ratio (Sn loading amount = 1.04 mmol) is described as the follows:^{5,6} RANEY® Ni/AlOH that was obtained from the above procedure was mixed with an ethanol solution that contained 1.04 mmol $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ at room temperature and stirred for 2 h. The mixture was then placed into a sealed-Teflon autoclave reactor for the hydrothermal treatment at 423 K for 2 h. The resulting precipitate was filtered, washed with distilled water until the filtrate was neutralized, and then stored in water. The catalyst was dried under vacuum before the catalytic reaction. The RNi–Sn(x)/AlOH was reduced with H_2 at 673–873 K for 1.5 h and produced RNi–Sn(x)/AA (AA = amorphous alumina).

1.3. Catalyst characterisation

XRD measurements were recorded on a Mac Science M18XHF instrument using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). The XRD was operated at 40 kV and 200 mA with a step width of 0.02° and a scan speed of 4° min^{-1} ($\alpha_1 = 0.154057 \text{ nm}$, $\alpha_2 = 0.154433 \text{ nm}$). The formation of Ni-Sn alloy for every sample was confirmed by JCPDS card. The mean crystallite sizes of Ni–Sn was calculated from the full width at half maximum (FWHM) of the Ni–Sn alloy

diffraction peak according to the Scherrer equation. $\text{Ni}_3\text{Sn}_2(110)$ phase at $2\theta = 30.37^\circ$. ICP measurements were performed on an SPS 1800H plasma spectrometer of Seiko Instruments Inc. (Ni: 221.7162 nm and Sn:189.898 nm). The BET surface area (S_{BET}) and pore volume (V_p) were measured using N_2 physisorption at 77 K on a Belsorp Max (BEL Japan). The samples were degassed at 473 K for 2 h to remove physisorbed gases prior to the measurement. The amount of nitrogen adsorbed onto the samples was used to calculate the BET surface area via the BET equation. The pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of approximately 0.995 according to the Barrett–Joyner–Halenda (BJH) approach based on desorption data.⁷

The ammonia-temperature programmed-desorption (NH_3 -TPD) was carried out on a Belsorp Max (BEL Japan). The samples were degassed at elevated temperature of 373–473 K for 2 h to remove physisorbed gases prior to the measurement. The temperature was then kept at 473 K for 2 h while flushed with He gas. NH_3 gas (balanced NH_3 , 80% and He, 20%) was introduced at 373 K for 30 min, then evacuated by helium gas to remove the physisorbed also for 30 min. Finally, temperature programmed desorption was carried out at temperature of 373–1073 K and the desorbed NH_3 was monitored by TCD.

The H_2 uptake was determined through irreversible H_2 chemisorption. After the catalyst was heated at 393 K under vacuum for 30 min, it was treated at 673 K under H_2 for 30 min. The catalysts were subsequently cooled to room temperature under vacuum for 30 min. The H_2 measurement was conducted at 273 K, and H_2 uptake was calculated according to the method described in the literatures.^{8,9}

1.4. Catalytic reaction

FFald to 1,4-PeD. A typical reaction of furfuraldehyde was carried out in the following manner. Furfural (1.2 mmol) in an ethanol/ H_2O 1.5/2.0 v/v (3.5 ml) solvent, decalin (0.25 mmol) as an internal standard, were placed into an autoclave reactor system of TAIATSU Techno (a Pyrex tube was fitted inside of a sus316 jacket to protect the vessel from corrosion in acidic media). After H_2 was introduced into the reactor (initial pressure of H_2 was 3.0 MPa) at room temperature, the temperature of the reactor was raised to 433 K for 12 h. After the reaction, the autoclave was cooled, the gas released slowly, the mixture was centrifuged, and the filtrate was analyzed by using gas chromatography (GC) with *trans*-decahydronaphthalene as an internal standard.

LA to GVL and 1,4-PeD. A typical reaction of levulinic acid was carried out in the following manner. Levulinic acid (1.2 mmol) in an H_2O (3.5 ml) solvent, decalin (0.25 mmol) as an internal standard, were placed into an autoclave reactor system of TAIATSU Techno (a Pyrex tube was fitted inside of a sus316 jacket to protect the vessel from corrosion in acidic media). After H_2 was introduced into the reactor (initial pressure of H_2 was 4.0 MPa) at room temperature, the temperature of the reactor was raised to 503 K for 12 h. After the reaction, the autoclave was cooled, the gas released slowly, the mixture was centrifuged, and the filtrate was analysed by using gas chromatography (GC) with *trans*-decahydronaphthalene as an internal standard.

1.5. Product analysis

GC analyses were performed by a Shimadzu GC-8A with a flame ionization detector equipped with Silicone OV-101 packing (3 m). GC-MS was performed by a Shimadzu GC-17B with a thermal conductivity detector equipped with an RT-bDEXsm capillary column. ^1H NMR and ^{13}C NMR spectra were obtained on JNM-AL400 at 400 MHz in chloroform- d_1 or D_2O with TMS as an internal standard. Products were confirmed by the comparison of their GC and GC-MS retention time, mass, ^1H NMR and ^{13}C NMR spectra with the literatures, except for 2H2MeTHF due to the limitation of commercial availability.

2. Results of catalyst characterisation

Table S1. The bulk composition of the catalysts, H₂ uptakes, average Ni(111) crystallites sizes, specific surface area (S_{BET}), and the amount of acids sites.⁶

Entry	Catalyst ^a	Composition ^a (mmol g ⁻¹)			H ₂ uptake ^b ($\mu\text{mol g}^{-1}$)	D_{Ni} ^c (nm)	S_{BET} ^d (m ² g ⁻¹)	Amount of acid site ^e ($\mu\text{mol g}^{-1}$)
		Ni	Al	Sn				
1	Raney®Ni	3.98	0.63	-	121	8.6	66	195 ¹⁰
2	Raney® Ni/AlOH	3.46	3.80	-	104	8.8	151	474
3	RNi-Sn(14.7)/AlOH	3.82	3.66	0.26	103	7.0	90	477
4	RNi-Sn(7.9)/AlOH	3.58	3.44	0.45	101	6.2	77	487
5	RNi-Sn(3.7)/AlOH	3.77	3.52	0.76	94	5.9	76	488
6	RNi-Sn(3.0)/AlOH	3.13	4.91	1.04	110	5.3	145	491
7	RNi-Sn(1.4)/AlOH	3.01	3.48	2.14	103	4.8	76	489
8	RNi-Sn(1.0)/AlOH	3.54	3.71	3.96	98	4.6	72	490
9	$\gamma\text{-Al}_2\text{O}_3$	-	-	-	-	-	100	180 ¹¹

^aValues in the parenthesis are Sn loading amount, the bulk compositions are determined by ICP-AES. ^bBased upon total the H₂ uptake at 273 K (after corrections for physical and chemical adsorption). ^cAverage Ni(111) or Ni-Sn crystallite sizes were calculated from the full width at the half maximum (FWHM) of the Ni(111) diffraction peak according to the Scherrer's equation. ^dDetermined by N₂ adsorption at 77 K. ^eAmount of acidic sites ($\mu\text{mol. g}^{-1}$) was derived from the NH₃-TPD spectra.

Table S2. Physico-chemical properties of synthesized RNi–Sn(*x*)/AA catalysts (*x* = Ni/Sn molar ratio; 3.0, 1.4, and 1.0) after reduction with H₂ at different temperature of 673–873 K for 1.5 h.¹²

Entry	Catalysts ^a	$S_{\text{BET}}^{\text{b}}$ (m ² g ⁻¹)	V_{p}^{b} (cm ³ g ⁻¹)	$d_{\text{pore}}^{\text{b}}$ (nm)	H ₂ uptake ^c (μmol.g ⁻¹)	S_{Ni}^{c} (m ² g ⁻¹ cat)	D^{d}/nm
1	RNi–Sn(3.0)/AA 673 K	42	0.079	2.8	81	35.2	nd
2	RNi–Sn(3.0)/AA 773 K	72	0.065	3.6	67	31.8	nd
3	RNi–Sn(3.0)/AA 873 K	122	0.098	3.2	53	22.7	nd
4	RNi–Sn(1.4)/AA 673 K	50	0.065	3.2	45	13.6	14.7
5	RNi–Sn(1.4)/AA 773 K	27	0.063	9.3	32	9.4	16.6
6	RNi–Sn(1.4)/AA 873 K	26	0.073	11.2	17	5.1	28.4
7	RNi–Sn(1.0)/AA 673 K	26	0.040	4.9	66	32.1	nd
8	RNi–Sn(1.0)/AA 773 K	61	0.086	5.7	59	24.4	nd
9	RNi–Sn(1.0)/AA 873 K	126	0.079	5.6	56	21.3	nd

^aThe value in the parenthesis is Ni/Sn molar ratio. The composition was determined by using ICP-AES.

^bDetermined by N₂ adsorption at 77 K. ^cBased on total H₂ uptake at 273 K (noted after corrected for physical and chemical adsorption). ^dAverage crystallite sizes of Ni₃Sn₂(101) alloy phases at 2θ = 30.37°, calculated by using Scherer equation; n.d. = not determined.

Table S3. Results of catalytic conversion of FFald to 1,4-PeD over various bimetallic RANEY® Ni-based supported on aluminium hydroxide (AlOH) catalysts

Entry	Catalyst	Conv. ^a (%)	Yield ^b (%)							
			1,4-PeD	1,2-PeD	1,5-PeD	FFalc	THFalc	2H2MeTHF	2-MeTHF	Others ^c
1	RNi-Fe/AlOH	100	0	2	3	0	80	0	15	0
2	RNi-Co/AlOH	100	0	0	0	0	100	0	0	0
3	RNi-In/AlOH	100	0	0	0	99	1	0	0	0
4	RNi-Ag/AlOH	100	0	0	0	0	98	0	2	0
5	RNi-Ga/AlOH	100	0	0	0	99	0	0	1	0
6	RNi-Zr/AlOH	100	0	0	0	0	87	0	13	0
7	RNi-V/AlOH	100	0	0	0	0	99	0	1	0
8	RNi-Nb/AlOH	100	0	0	0	0	98	0	2	0

Reaction conditions: catalyst, 44 mg; substrate, 1.2 mmol; solvent, ethanol/H₂O, 3.5 ml (1.5 : 2.0 volume ratio); initial H₂ pressure, 3.0 MPa, 433 K, 12 h. ^aConversion of FFald was determined by GC analysis using an internal standard technique. ^bYield of product was determined by GC and GC-MS analyses using an internal standard technique. ^cIt may be the dimerization product of FFalc according to GC and GC-MS data. **FFald** = furfuraldehyde. **PeD** = pentanediol. **FFalc** = furfuryl alcohol. **THFalc** = tetrahydrofurfuryl alcohol. **2H2MeTHF** = 2-hydroxy-2-methyl tetrahydrofuran. **2-MeTHF** = 2-methyl tetrahydrofuran.

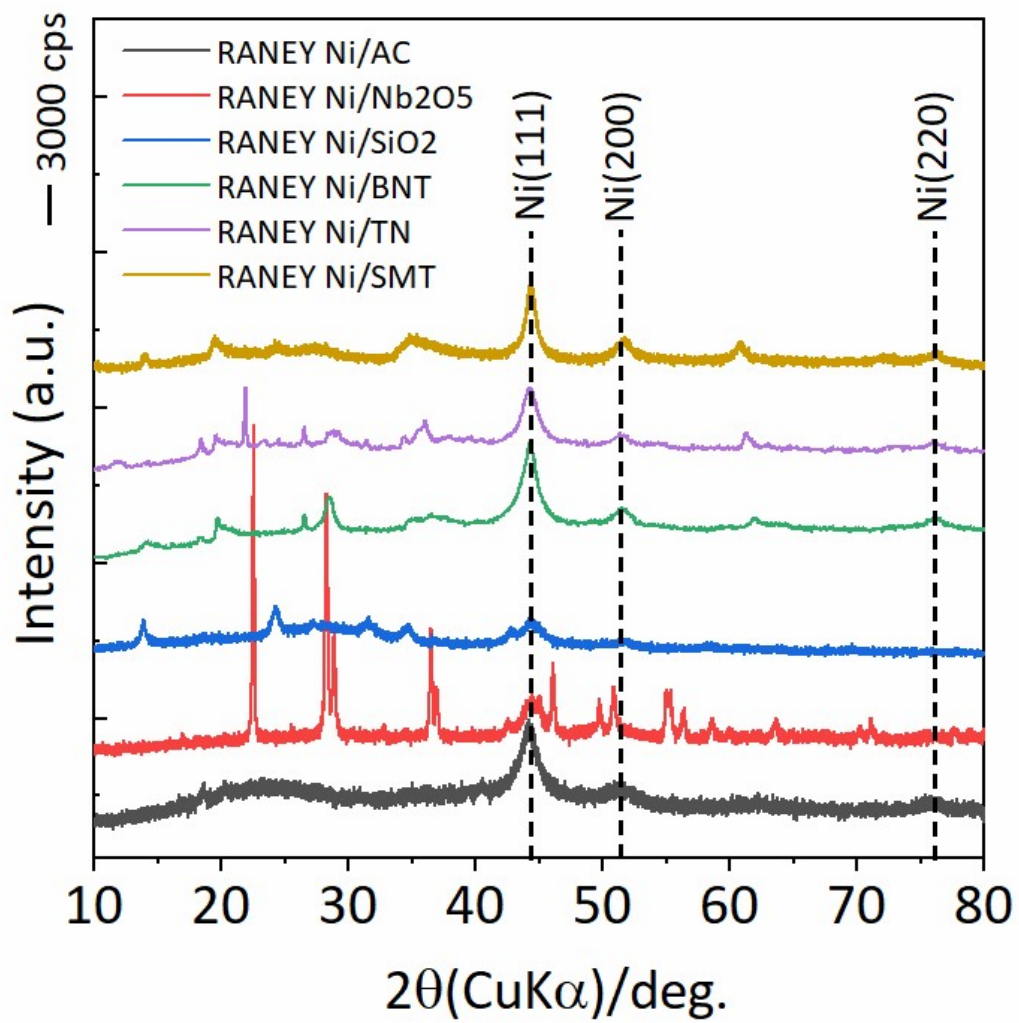


Fig. S1 XRD patterns of various supported RANEY® Ni catalysts.

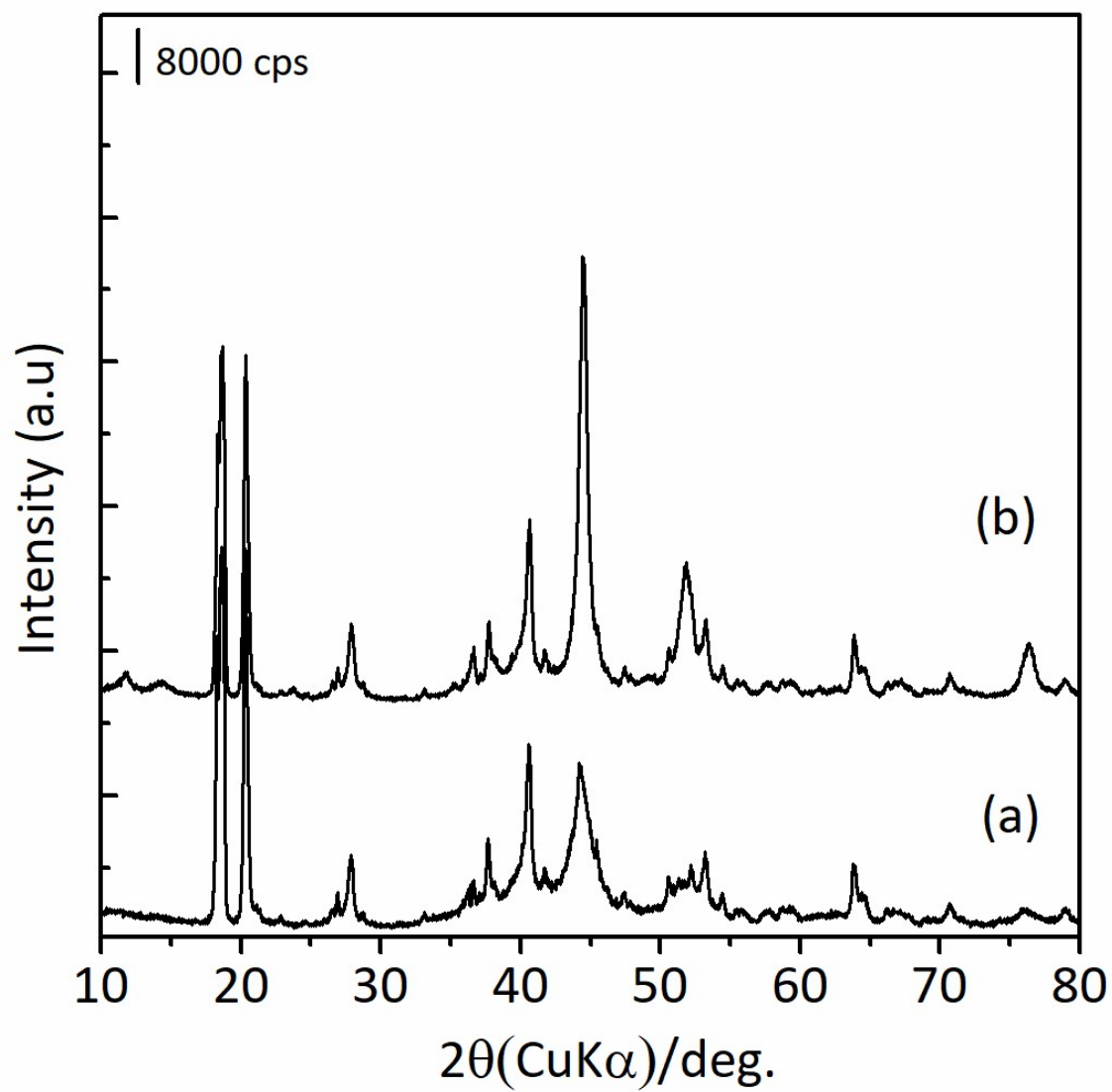


Fig. S2 XRD patterns of the as-prepared RANEY® Ni/AlOH catalyst (a) without and (b) with hydrothermally treated at 423 K for 2 h.

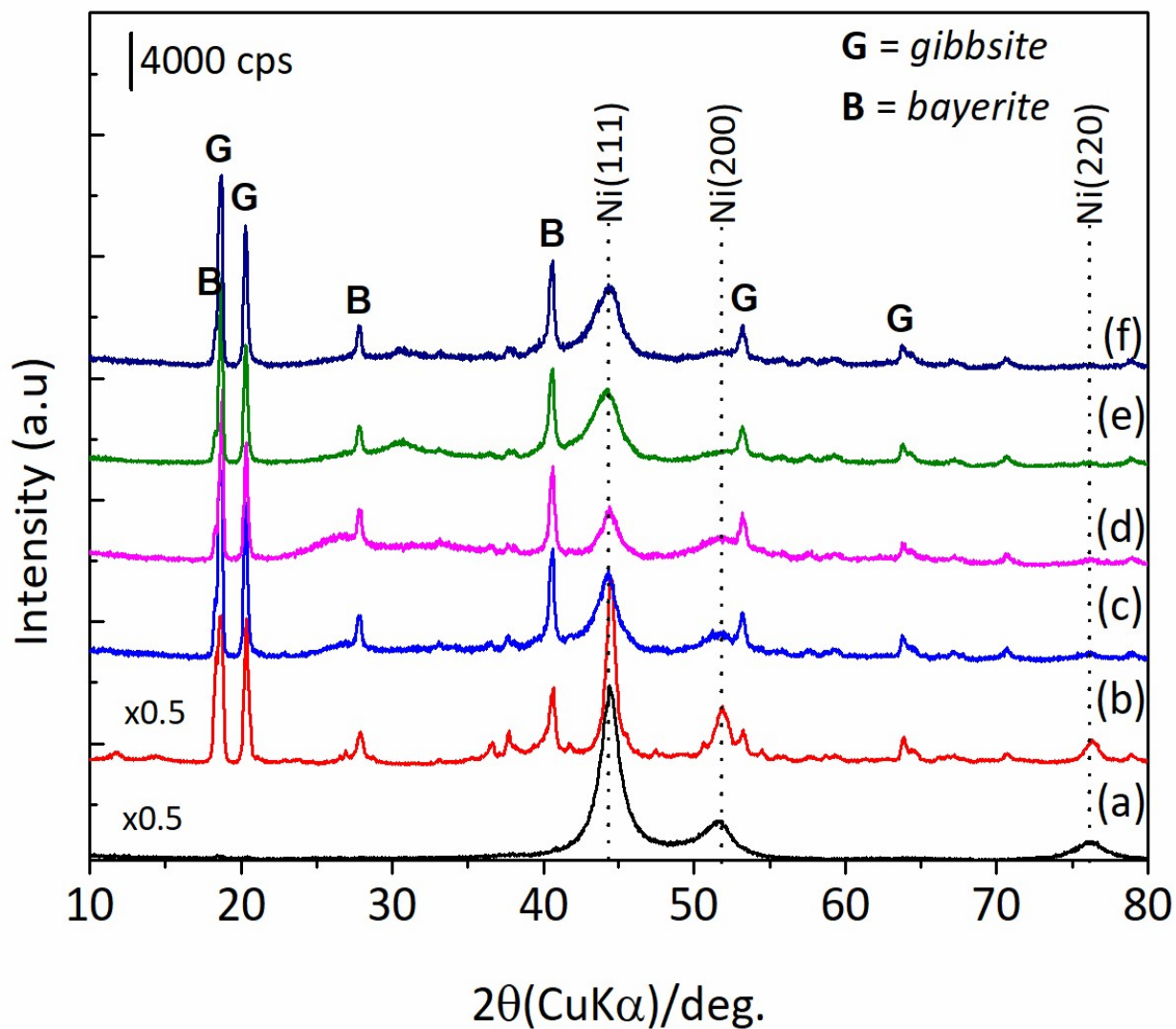


Fig. S3. The XRD patterns of (a) RANEY®Ni, (b) RNi/AlOH, and RNi-Sn(x)/AlOH with different Ni/Sn molar ratio Sn loading amount of (c) 3.7, (d) 3.0, (e) 1.4, and (f) 1.0 obtained after hydrothermal synthesis at 423 K for 2 h.

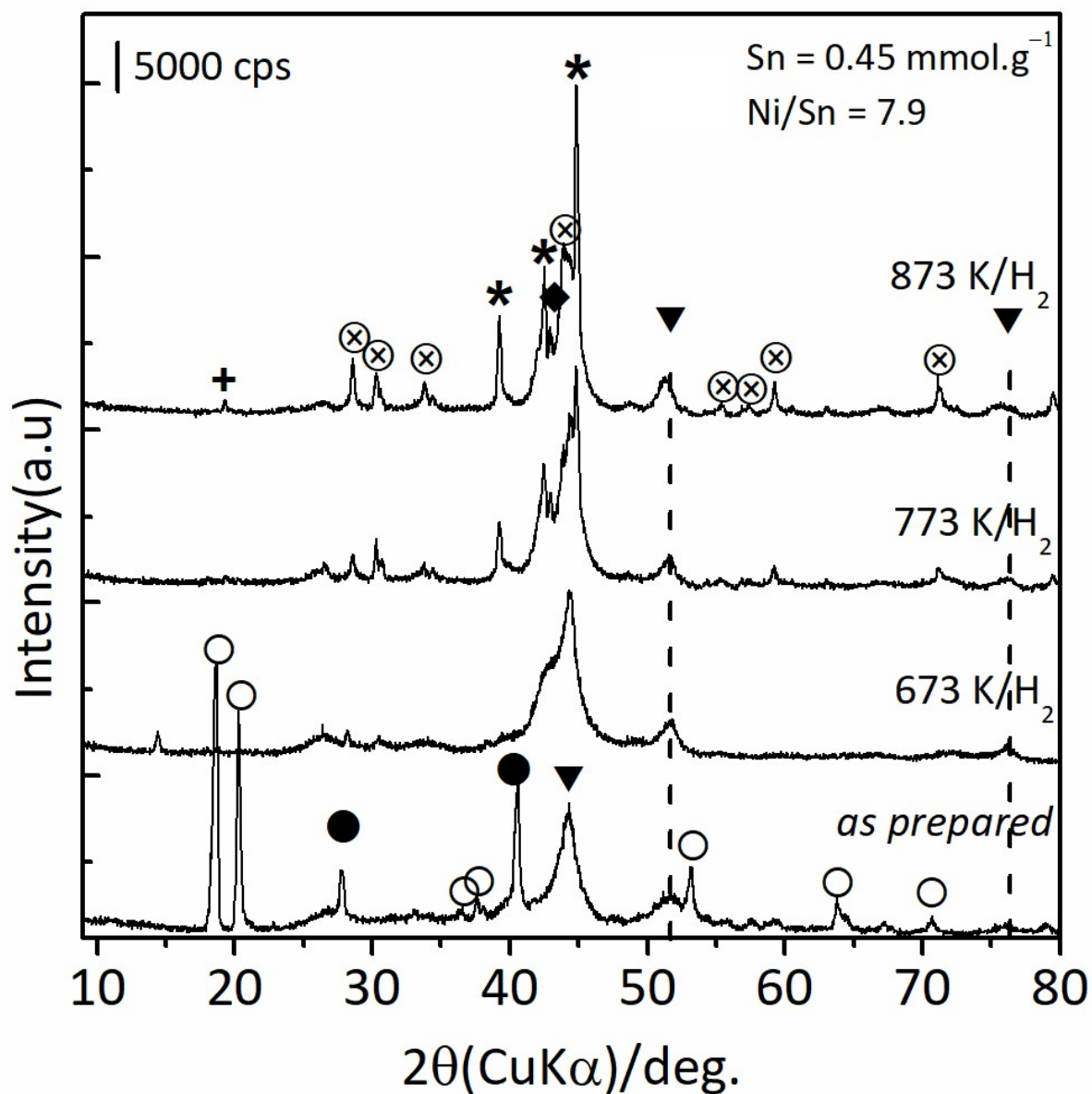


Fig. S4 XRD patterns of as-prepared Ni-Sn(7.9)/AlOH catalyst and after reduction with H_2 at 673-873 K for 1.5 h. (○) Gibbsite. (●) Bayerite. (➤) Ni_3Sn . (➤) Ni_3Sn_2 . (⊗) Ni(0). (+) $\beta\text{-Sn}$.^{13,14}

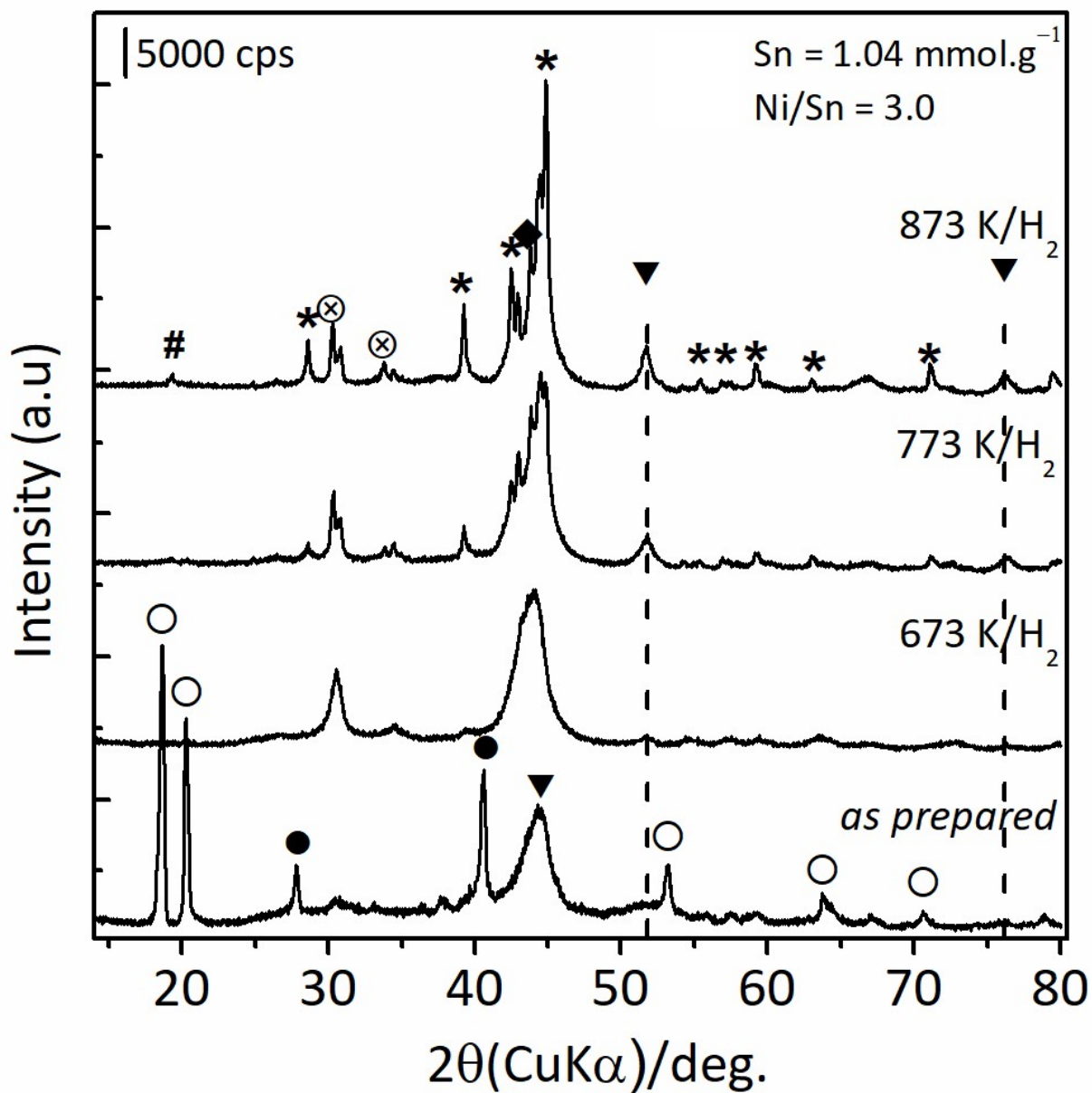


Fig. S5 XRD patterns of as-prepared Ni-Sn(3.0)/AlOH catalyst and after reduction with H₂ at 673-873 K for 1.5 h. (○) Gibbsite. (●) Bayerite. (➤) Ni₃Sn. (▼) Ni₃Sn₂. (⊗) Ni(O). (+) β-Sn.^{13,14}

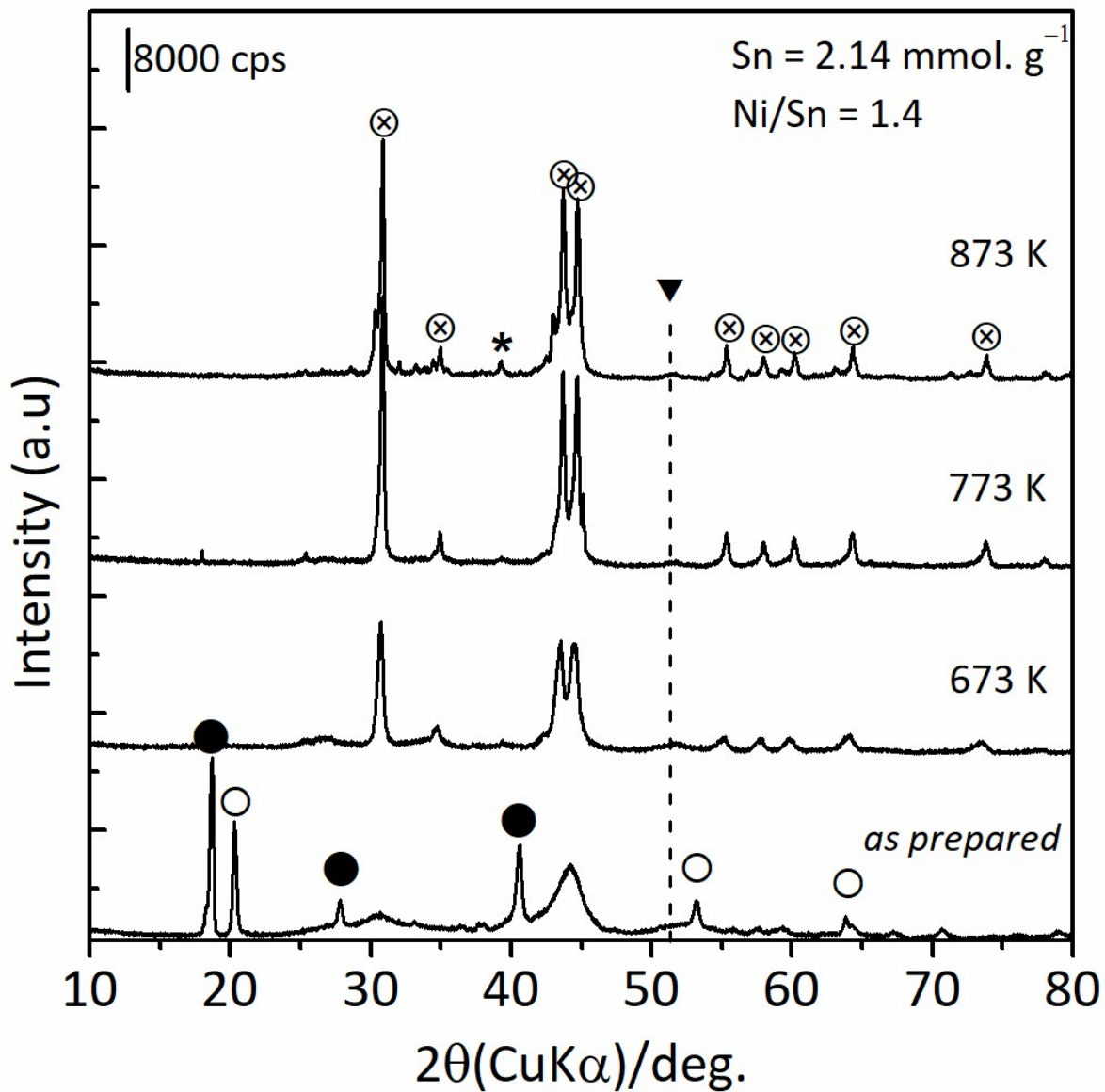


Fig. S6 XRD patterns of as-prepared Ni-Sn(1.4)/AlOH catalyst and after reduction with H₂ at 673-873 K for 1.5 h. (○) Gibbsite. (●) Bayerite. (➤) Ni₃Sn. (⊕) Ni₃Sn₂. (⊙) Ni(0). (+) β-Sn.^{13,14}

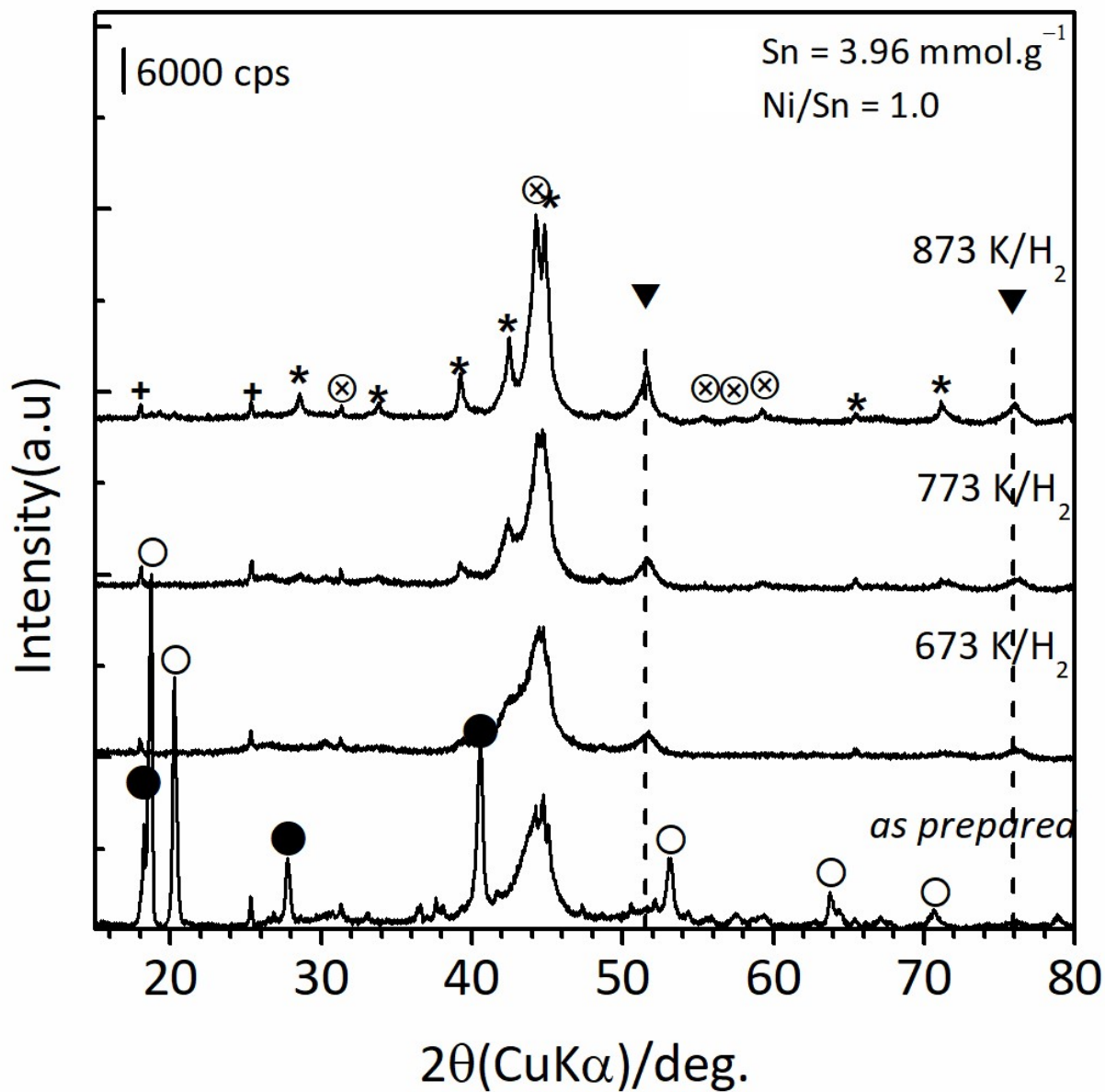


Fig. S7 XRD patterns of the as-prepared Ni-Sn(1.0)/AlOH catalyst and after reduction with H₂ at 673-873 K for 1.5 h. (○) Gibbsite. (●) Bayerite. (▼) Ni₃Sn. (⊗) Ni₃Sn₂. (⊙) Ni(O). (+) β-Sn^{13,14}

Table S4. Results of catalytic conversion of FFald to 1,4-PeD over RNi–Sn(x)/AA (x = Ni/Sn molar ratio; 7.9, 3.7, and 1.0) after reduction with H₂ at 673-873 K for 1.5 h

Entry	Catalyst ^a	Conv. ^b (%)	Yield (%) ^c							
			1,4-PeD	1,2-PeD	1,5-PeD	FFalc	THFalc	2H2MeTHF	2-MeTHF	Others ^d
1	RNi–Sn(7.9)/AA 673/H ₂	100	26	0	0	0	67	7	0	0
2	RNi–Sn(7.9)/AA 773/H ₂	100	29	0	0	0	64	7	0	0
3	RNi–Sn(7.9)/AA 873/H ₂	100	39	0	0	0	52	9	0	0
4	RNi–Sn(3.7)/AA 673/H ₂	100	51	3	0	0	9	35	1	1
5	RNi–Sn(3.7)/AA 773/H ₂	100	55	4	2	0	4	35	0	0
6	RNi–Sn(3.7)/AA 873/H ₂	100	32	9	2	0	14	42	0	1
7	RNi–Sn(1.0)/AA 673/H ₂	100	42	1	6	0	25	23	2	1
8	RNi–Sn(1.0)/AA 773/H ₂	100	46	0	0	0	25	25	2	2
9	RNi–Sn(1.0)/AA 873/H ₂	100	49	2	0	0	22	26	1	0

Reaction conditions: catalyst, 44 mg; substrate, 1.2 mmol; solvent, ethanol/H₂O, 3.5 ml (1.5: 2.0 volume ratio); initial H₂ pressure, 3.0 MPa; 433 K, 12 h. ^aValues in the parentheses are the Sn loading amounts. The compositions were determined by the ICP-AES analysis. ^bConversion of FFald was determined by GC analysis using an internal standard technique. ^cYield of the product was determined by GC and GC-MS analyses using an internal standard technique. ^dOthers include 2-methyltetrahydrofuran (2-MeTHF) and condensation product of FFalc, unless otherwise stated. **FFald** = furfuraldehyde. **PeD** = pentanediol. **FFalc** = furfuryl alcohol. **THFalc** = tetrahydrofurfuryl alcohol. **2H2MeTHF** = 2-hydroxy-2-methyl tetrahydrofuran. **2-MeTHF** = 2-methyl tetrahydrofuran.

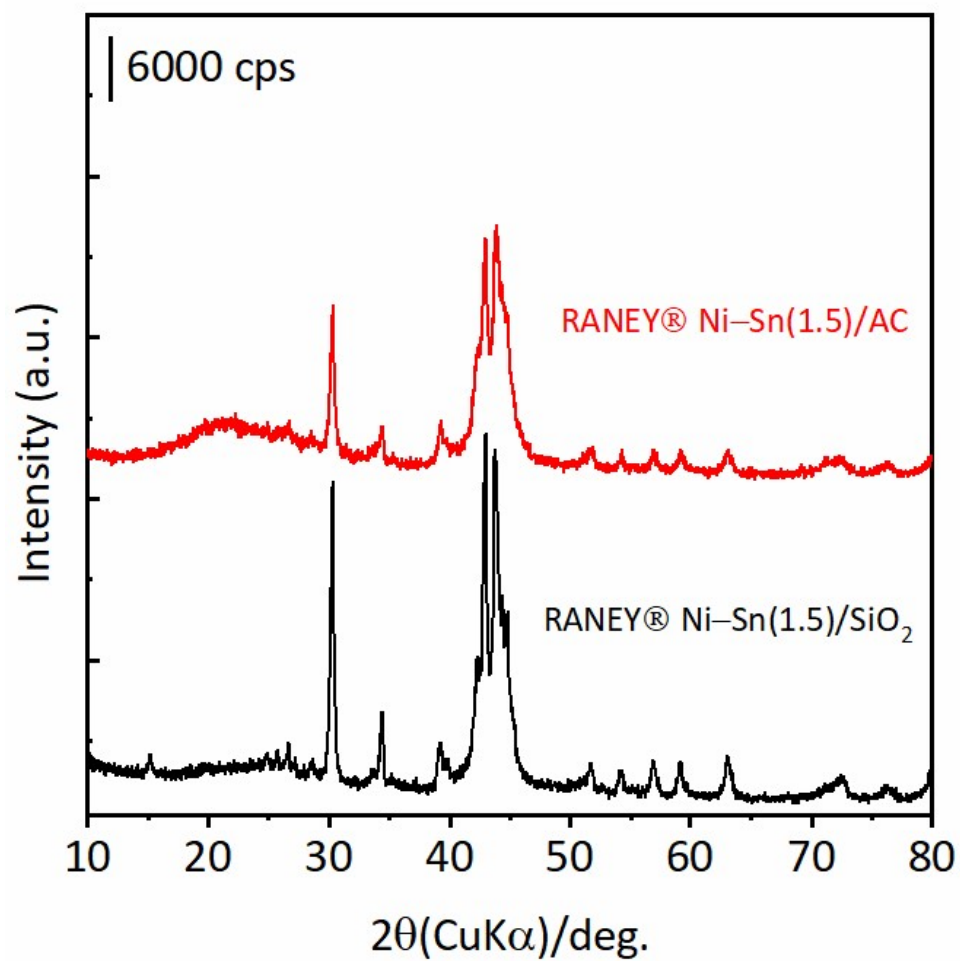


Fig. S8 XRD patterns of the RANEY® Ni-Sn(1.5)/C and RANEY® Ni-Sn(1.5)/SiO₂ catalysts after reduction with H₂ at 673 K for 1.5 h.

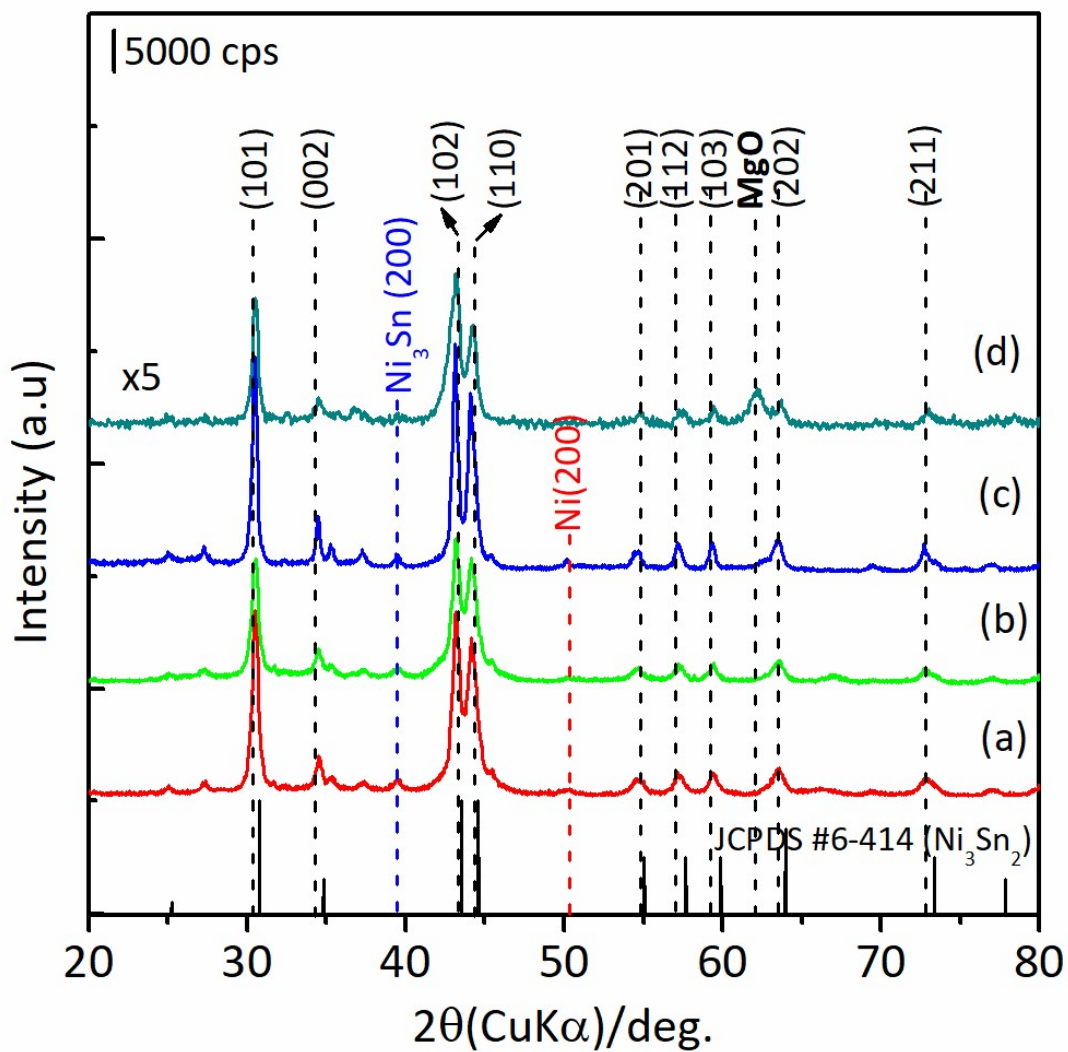


Fig. S9 The XRD patterns of various supported Ni-Sn(1.5) (Ni_3Sn_2) (a) c-AlOH , (b) $\gamma\text{-Al}_2\text{O}_3$, (c) active carbon (AC), and (d) MgO after reduction with H_2 at 673 K for 1.5 h. The plotted data were compared with JCPDS card of #06-414 (Ni_3Sn_2).

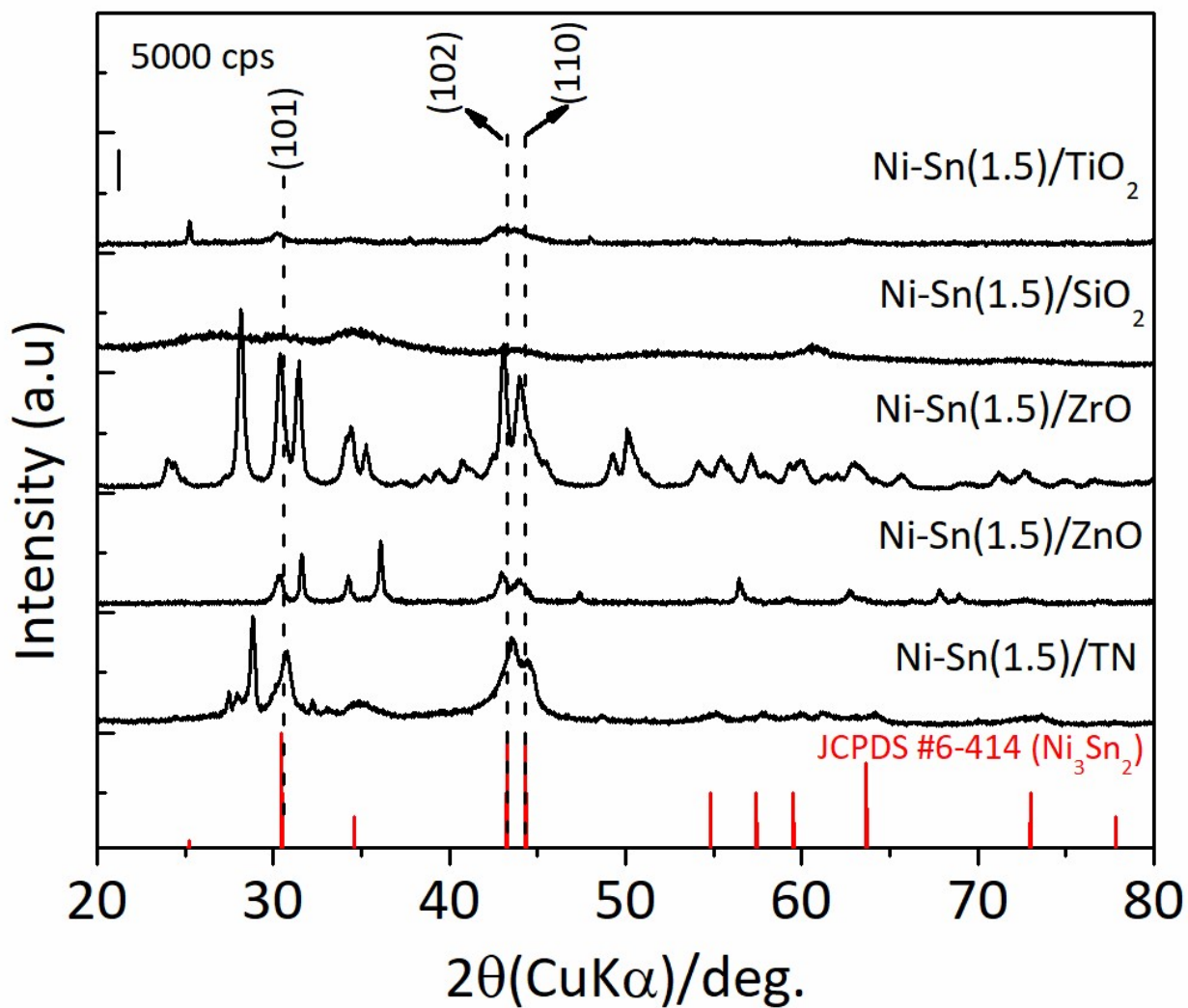


Fig. S10 XRD patterns of various supported Ni-Sn(1.5) (Ni_3Sn_2) catalysts after reduction with H_2 at 673 K for 1.5 h. The plotted data were compared with JCPDS card of #06-414 (Ni_3Sn_2).

Table S5 Results of the selective synthesis of 1,4-PeD from FFald using various supported Ni–Sn(1.5) (Ni₃Sn₂) alloy catalysts

Entry	Catalyst ^a	Conv. ^b (%)	Yield ^c (%)							
			1,4-PeD	1,2-PeD	1,5-PeD	FFalc	THFalc	2H2MeTHF	2-MeTHF	Others ^d
1	Ni–Sn(1.5)/SiO ₂	98	0	0	3	72	21	2	2	0
2	Ni–Sn(1.5)/ZrO ₂	>99	0	2	1	54	42	0	1	0
3	Ni–Sn(1.5)/TN	>99	0	0	0	0	90	0	3	7
4	Ni–Sn(1.5)/MCM-41	>99	0	0	0	0	91	0	5	4

Reaction conditions: catalyst, 44 mg; substrate, 1.2 mmol; solvent, ethanol/H₂O, 3.5 ml (1.5 : 2.0 volume ratio); initial H₂ pressure, 3.0 MPa, 433 K, 12 h. ^aValues in the parenthesis are Ni/Sn molar ratio, determined by using ICP-OES. ^bConversion of FFald was determined by GC analysis using an internal standard technique. ^cYield of product was determined by GC and GC-MS analyses using an internal standard technique. ^dUnknown product may be the condensation product of FFald or FFalc according to GC and GC-MS data. **PeD** = pentanediol. **FFalc** = furfuryl alcohol. **THFalc** = tetrahydrofurfuryl alcohol. **2H2MeTHF** = 2-hydroxy-2-methyl tetrahydrofuran. **2-MeTHF** = 2-methyl tetrahydrofuran.

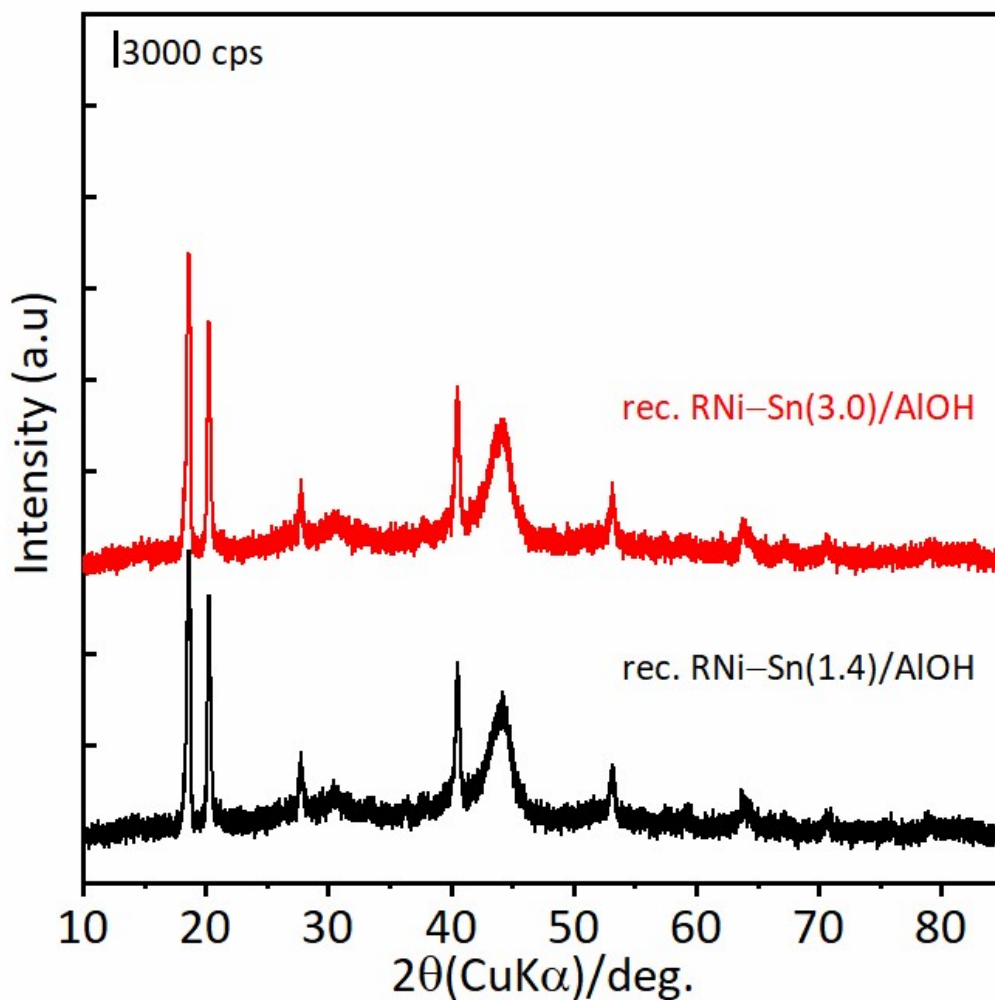


Fig. S11. XRD patterns of recovered RNi-Sn(3.0)/AlOH and RNi-Sn(1.4)/AlOH after the fifth run of reusability tests in the catalytic conversion of FFald to 1,4-PeD. The recovered catalysts were dried in vacuo at room temperature for overnight.

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