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## Supplementary Information

# Continuous Production of 1,2-Pentanediol from Furfuryl Alcohol over Highly Stable Bimetallic Ni–Sn Alloy Catalysts

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**Synthesis of Co-Sn and Cu-Sn supported ZnO catalysts**

The Co-Sn and Cu-Sn supported ZnO catalysts, containing a total metal concentration of 10%, were synthesized by the sequential co-precipitation-deposition method. The catalysts Co-Sn(10%)/ZnO and Cu-Sn(10%)/ZnO were prepared by dissolving prescribed amounts of $Zn(NO_3)_2 \cdot 6H_2O$ (99.9%), $SnCl_4 \cdot 5H_2O$ (99.9%), and $Cu(NO_3)_2 \cdot xH_2O$ (99.9%) or $Co(NO_3)_2 \cdot 6H_2O$ (99.9%) separately in 400 mL of distilled water for 1 h. Subsequently, the mixtures underwent the co-precipitation and agitation process under the same conditions as those used for the 3Ni-3Sn/ZnO catalyst.

**Product analysis details**

The liquid samples underwent examination utilizing a gas chromatography (Donam GC, DS6200) equipped with a flame ionization detector (FID) and capillary column (HP-INNOWAX). Considering the clear separation of peaks (**Fig. S10**), n-octane was employed as an internal standard. The response factor for each product in equal concentrated was calculated from multiple injections with a known amount of internal standard. Finally, the conversion and product yield were calculated from the GC areas of initial feed and product with a known amount of n-octane using the formulas,

$$\text{Conversion of FAL (mol\%)} = \frac{Initial\ moles\ of\ FAL - unreacted\ moles\ of\ FAL}{Initial\ moles\ of\ FAL\ in\ feed} \times 100\ (\%)$$

$$\text{Product yield (mol\%)} = \frac{Moles\ of\ desired\ product}{Initial\ moles\ of\ FAL\ in\ feed} \times\ 100\ (\%)$$

The carbon balances of each product were calculated based on reaction mass balance and GC data.

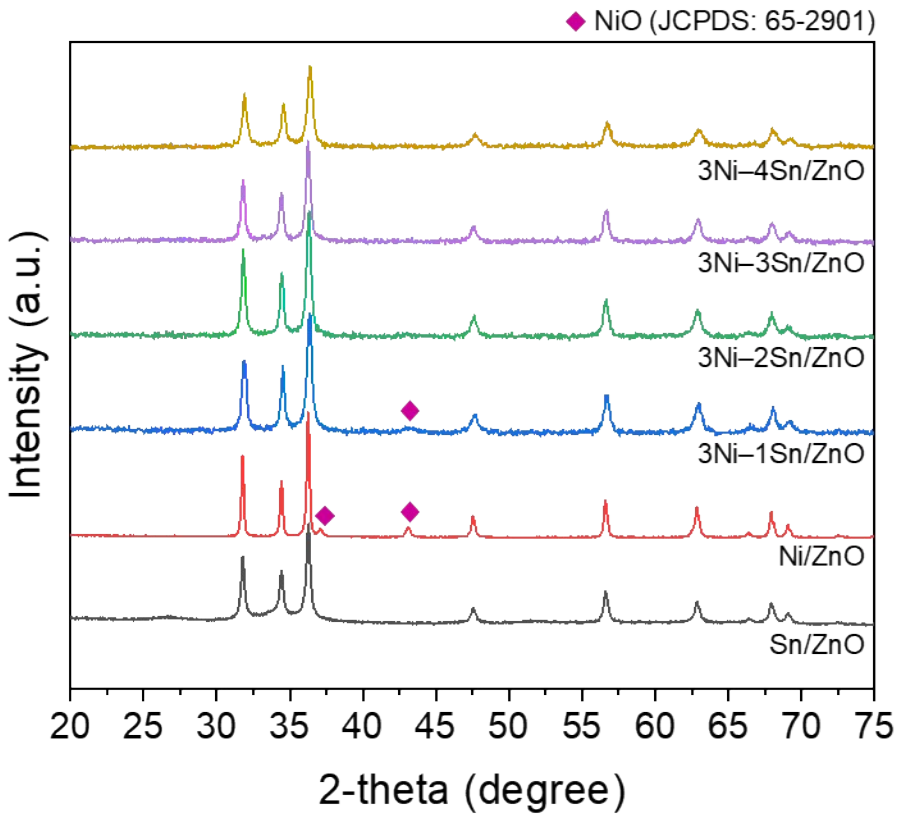


**Fig. S1** XRD patterns of calcined Sn/ZnO, Ni/ZnO, 3Ni–1Sn/ZnO, 3Ni–2Sn/ZnO, 3Ni–3Sn/ZnO, and 3Ni–4Sn/ZnO.

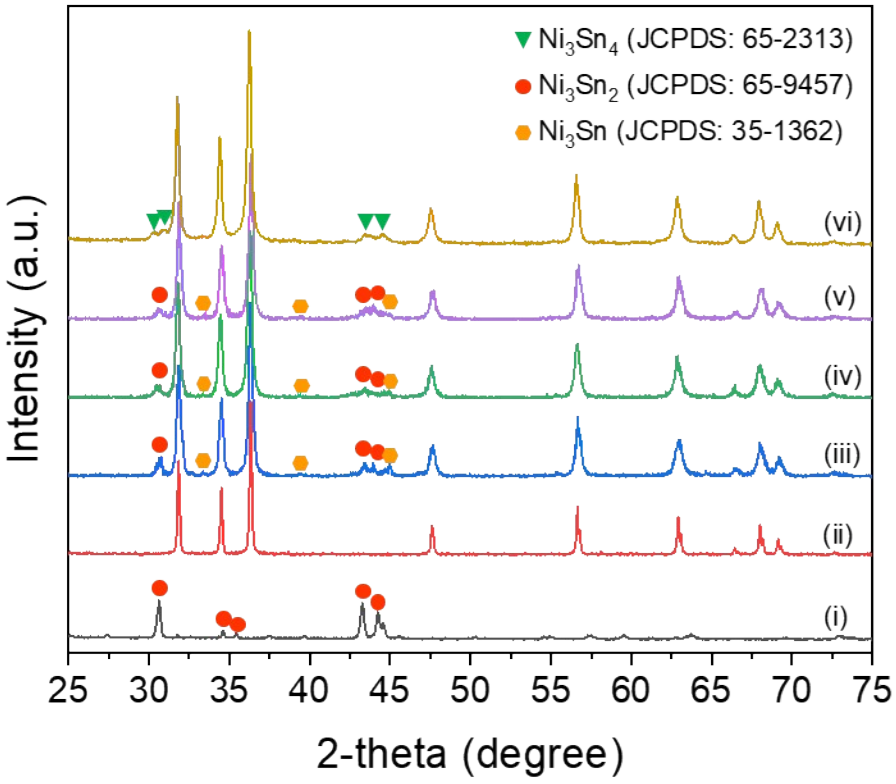


**Fig. S2** XRD patterns of reduced (i) unsupported Ni–Sn, (ii) ZnO support, (iii) 3Ni–1Sn/ZnO, (iv) 3Ni–2Sn/ZnO, (v) 3Ni–3Sn/ZnO, and (vi) 3Ni–4Sn/ZnO catalysts.

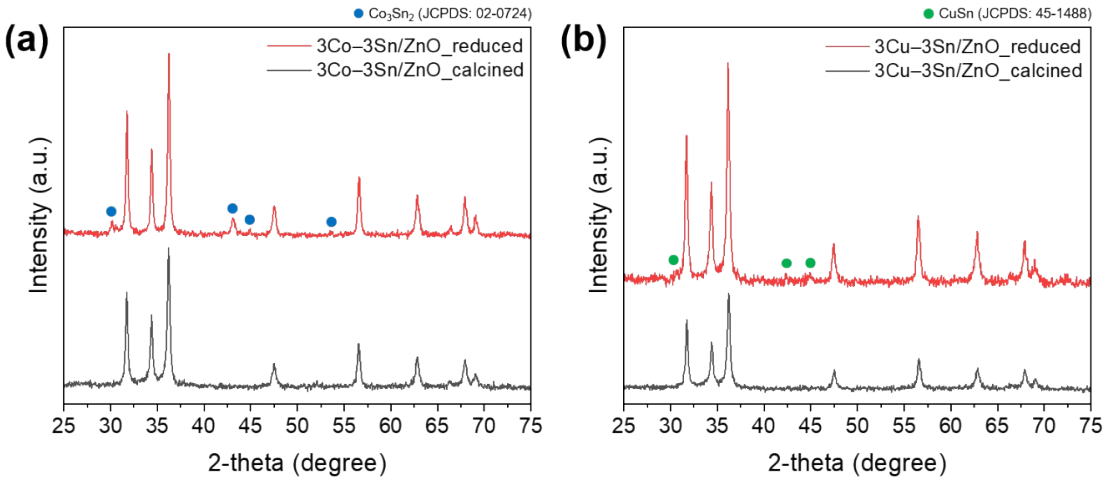


**Fig. S3** XRD patterns of calcined and reduced (a) Co–Sn/ZnO and (b) Cu–Sn/ZnO catalysts.

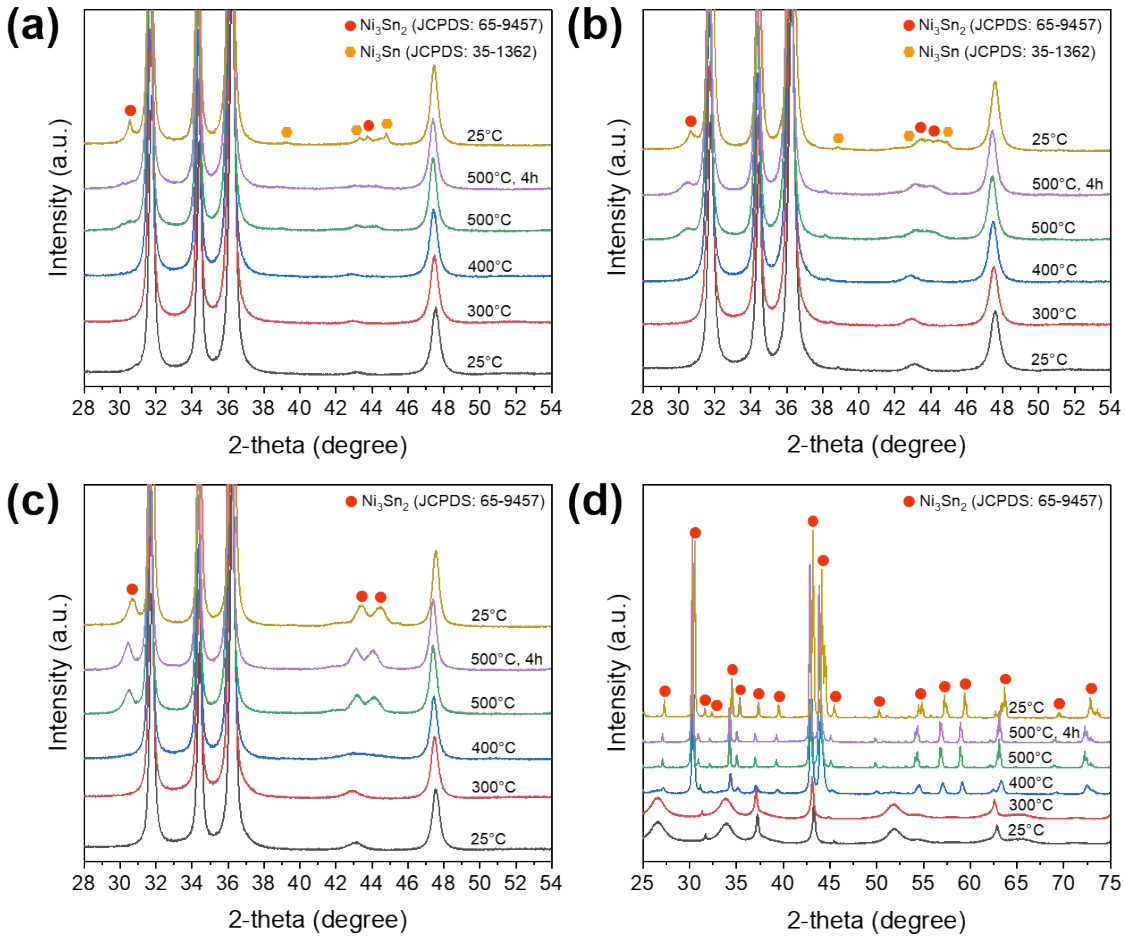


**Fig. S4** In-situ XRD patterns of calcined (a) 3Ni–3Sn(4%)/ZnO, (b) 3Ni–3Sn(6%)/ZnO, (c) 3Ni–2Sn/ZnO, and (d) unsupported 3Ni–2Sn catalysts under 10% $H_2$/Ar flow.

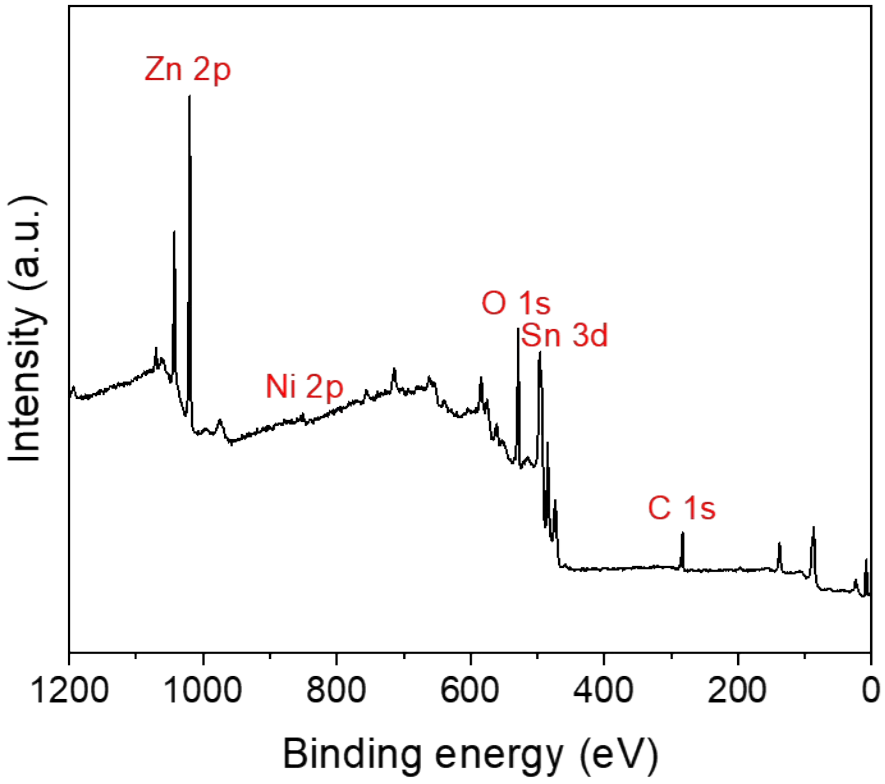


**Fig. S5** XPS survey spectra for the reduced 3Ni–3Sn/ZnO catalyst.

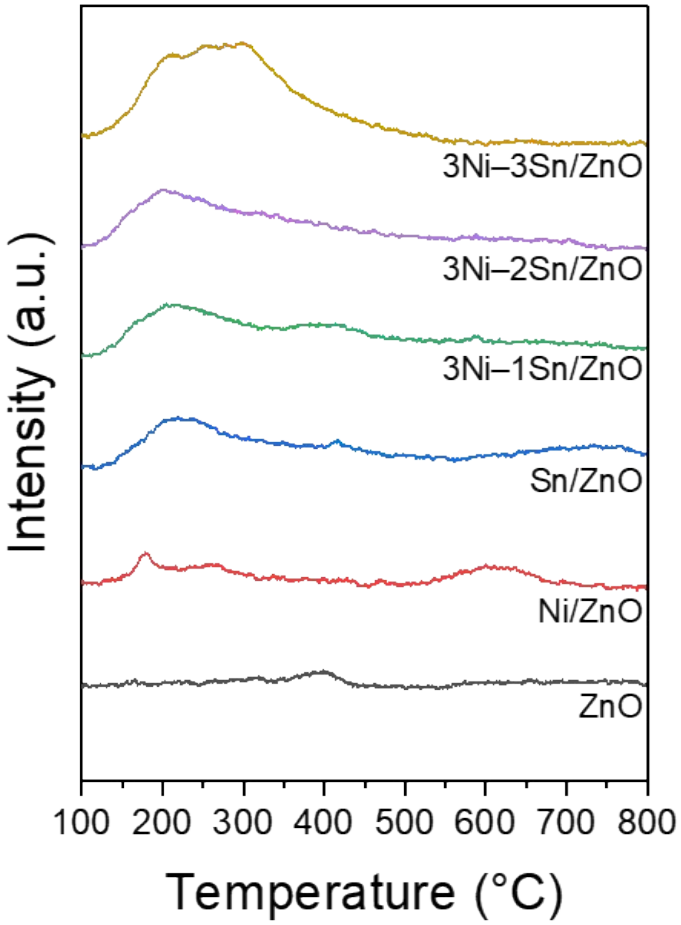


**Fig. S6** $NH_3$-TPD results of the synthesized catalysts.

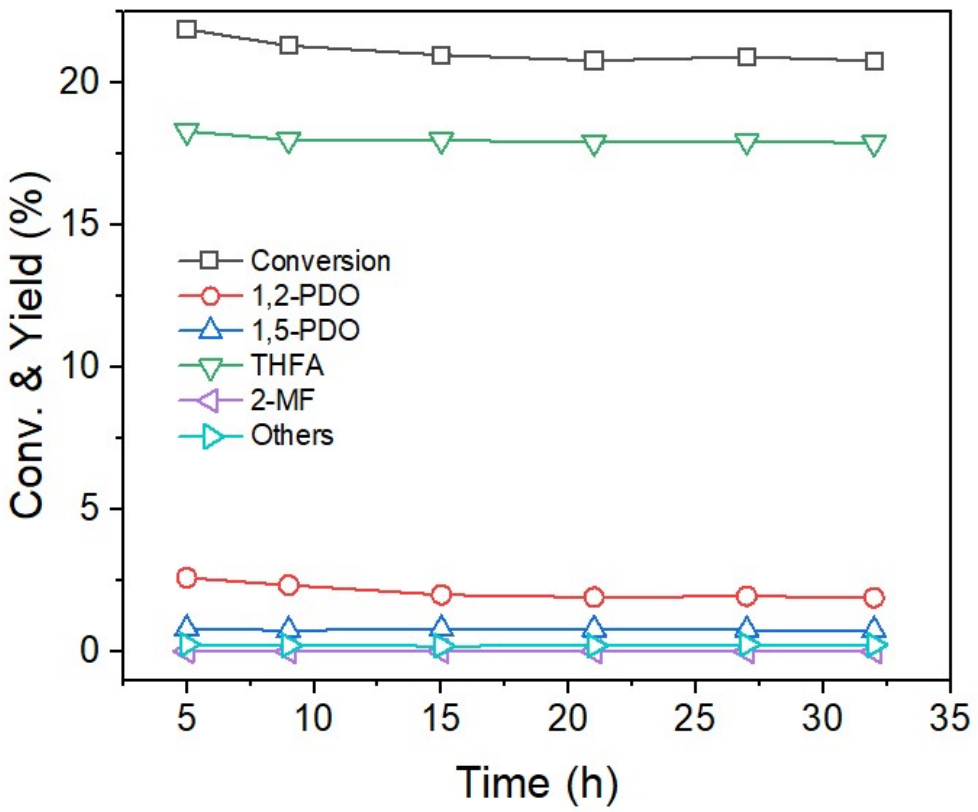


**Fig. S7** Time-on-stream data for the furfuryl alcohol (FAL) hydrogenolysis over 3Ni–3Sn/ZnO catalyst at low conversion level. Reaction conditions: 10% FAL in IPA, 1.0 g catalyst, 250 °C, WHSV= 5.0, $H_2$ 40 bar, $H_2$ flow 61 cc/min, TOS <30 h.

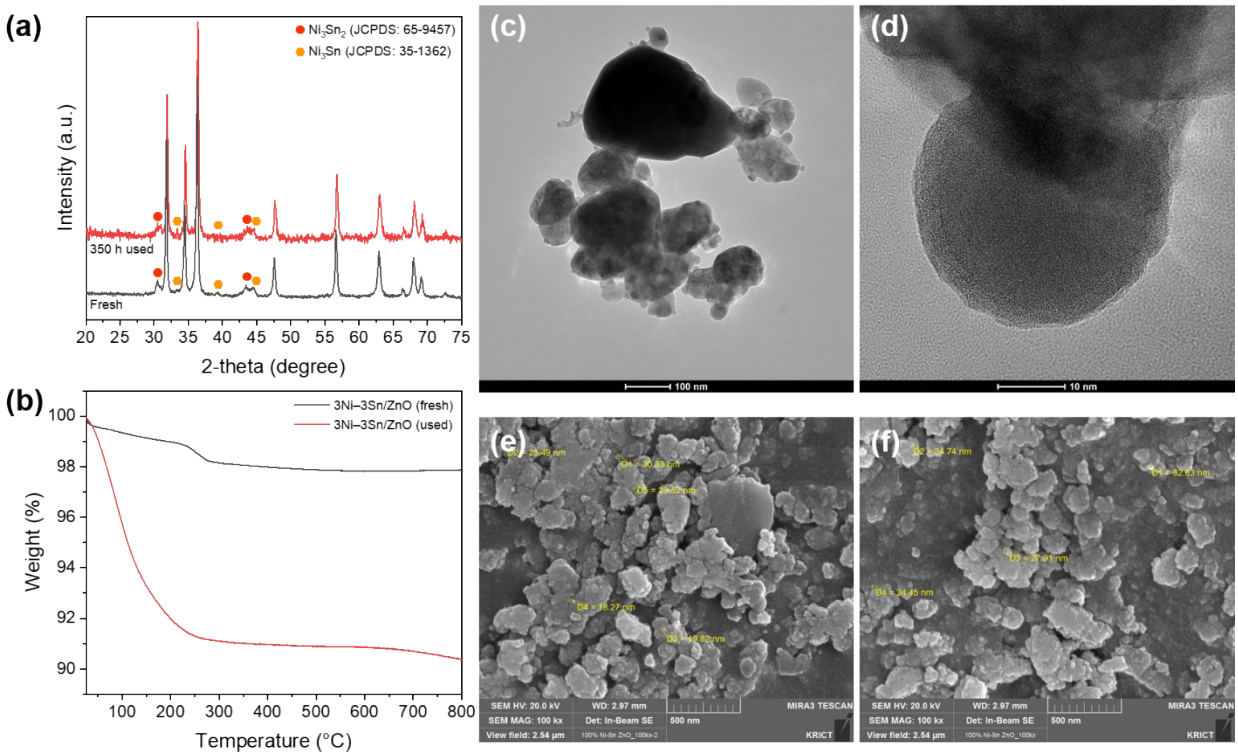


**Fig. S8** (a) XRD and (b) TGA patterns of the fresh and used catalysts after 450 h reaction. (c), (d) TEM images of the used 3Ni–3Sn/ZnO catalyst. SEM images of (e) fresh and (f) used 3Ni–3Sn/ZnO catalysts.

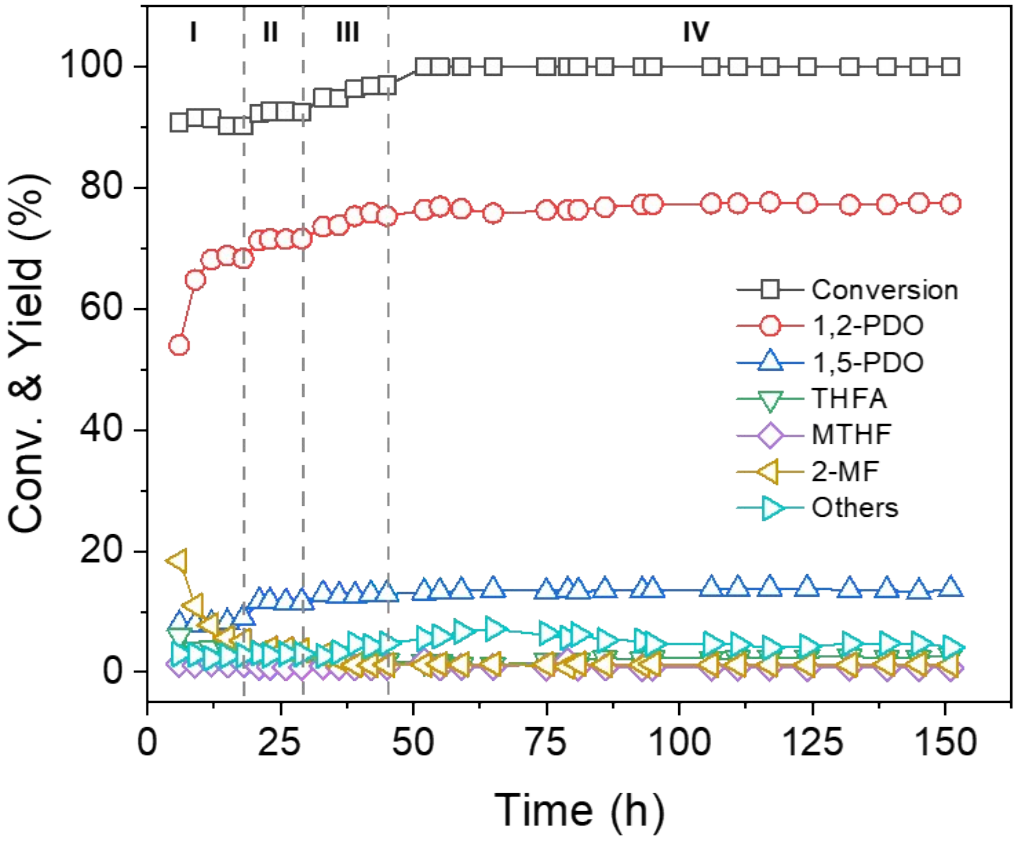


**Fig. S9** Time-on-stream data for the furfuryl alcohol (FAL) hydrogenolysis over 3Ni-3Sn(10%)/ZnO catalyst in an 1-inch scale-up reactor. Reaction conditions: 10% FAL in IPA, WHSV = 0.71, $H_2$ 40 bar, $H_2$ flow 600 cc/min, TOS <150 h. Temperature optimizations for the preheating zone/reaction zone: (I) 210°C/290°C, (II) 240°C/290°C, (III) 260°C/290°C, and (IV) 270°C/290°C.

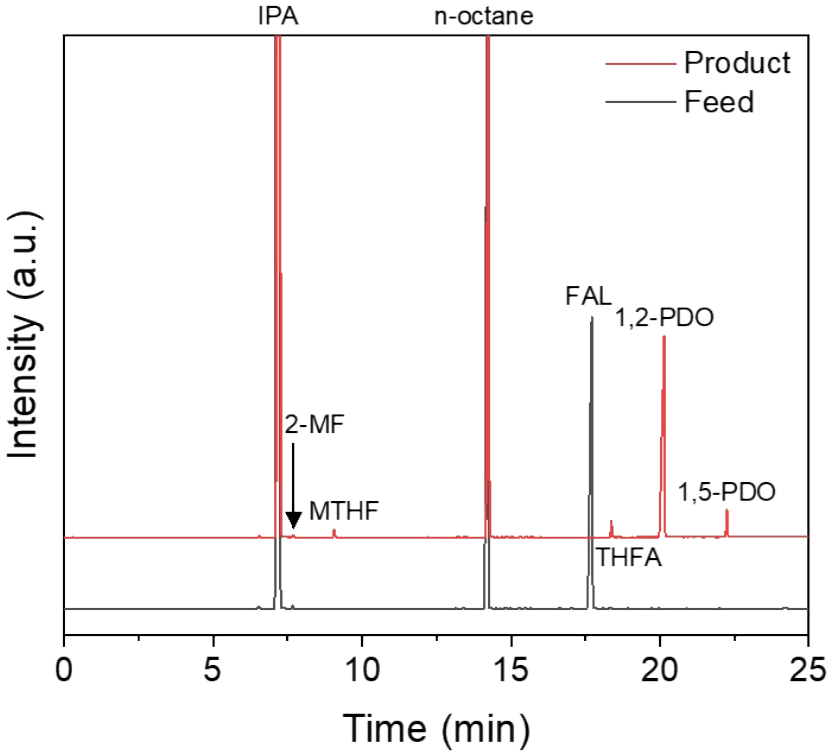


**Fig. S10** GC chromatographs of the 10% furfuryl alcohol (FAL) feed solution (black) and the reaction product (red) with n-octane as an internal standard at 100% conversion.

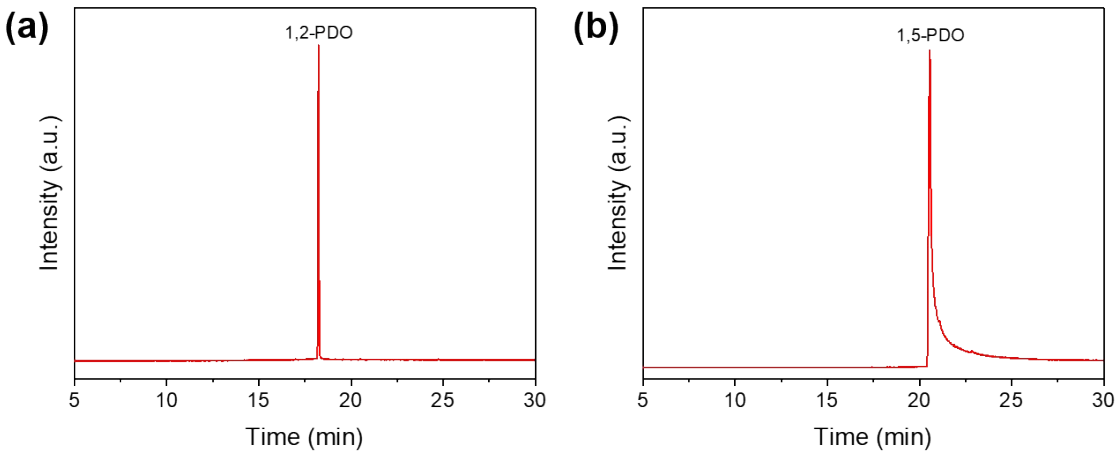


**Fig. S11** GC results of isolated (a) 1,2-PDO and (b) 1,5-PDO by distillation process.

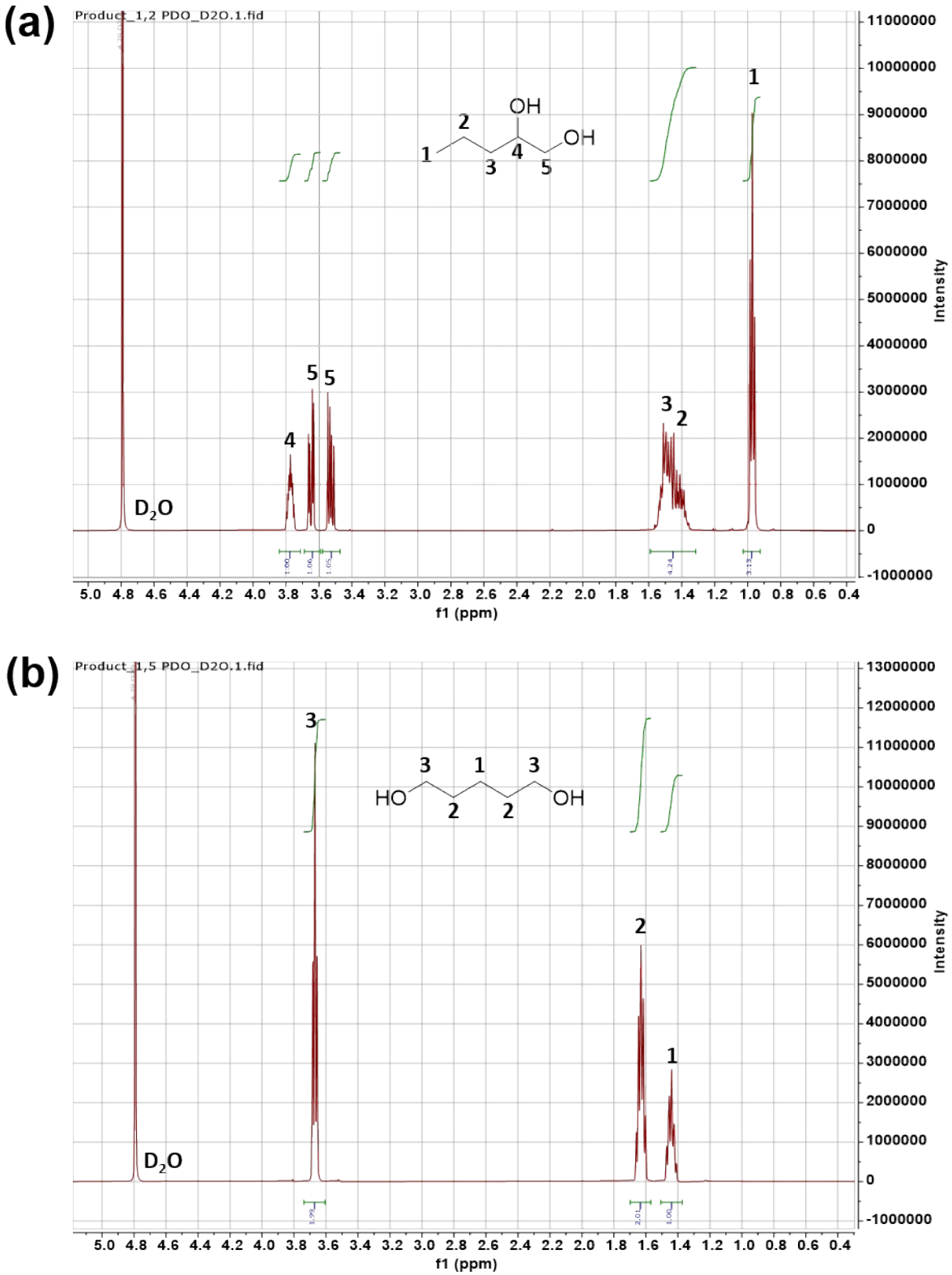


**Fig. S12** $^{1}$H-NMR spectra of isolated (a) 1,2-PDO and (b) 1,5-PDO by distillation process.

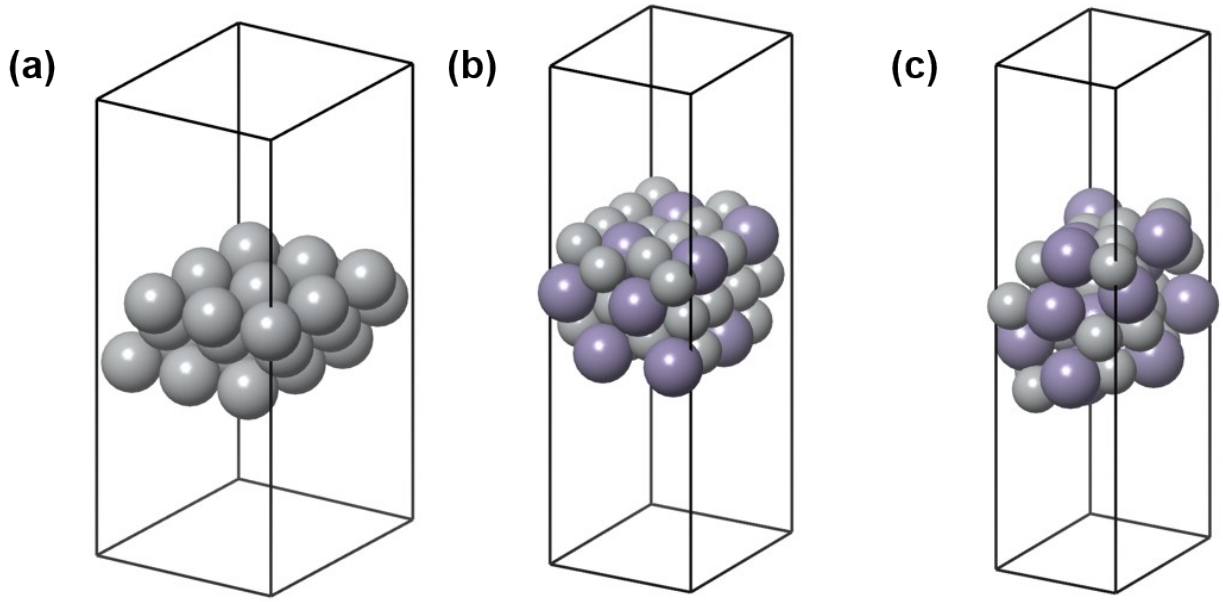


**Fig. S13** Diagonal view of (a) Ni (111), (b) $Ni_3Sn$ (100), and (c) $Ni_3Sn_2$ (101) surface slabs used for DFT study.

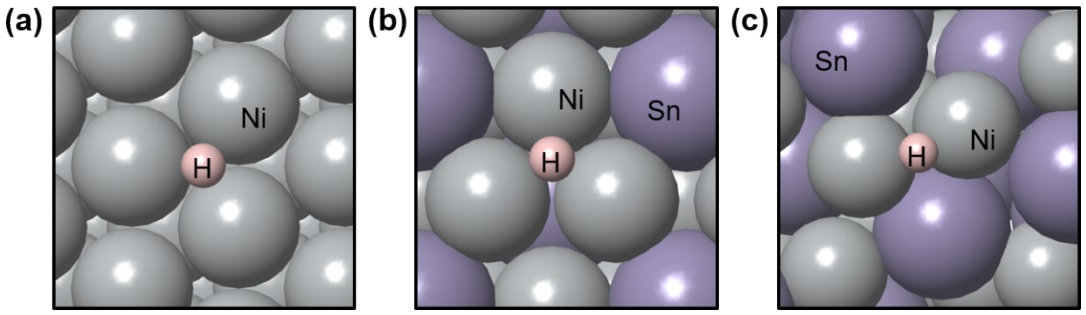


**Fig. S14** Top view of H adsorption configuration on (a) Ni (111), (b) $Ni_3Sn$ (100), and (c) $Ni_3Sn_2$ (101) surfaces.

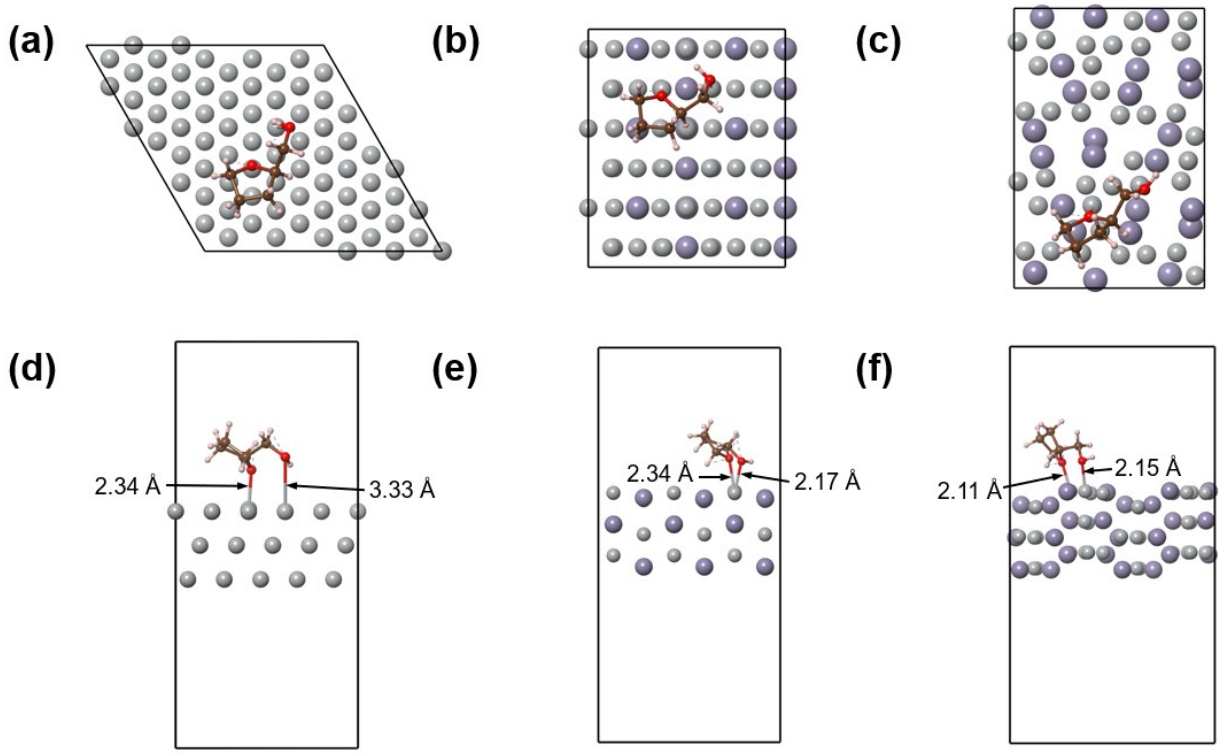


**Fig. S15** Top and side views of optimized configurations of THFA adsorption on (a) Ni (111), (b) $Ni_3Sn$ (100), and $Ni_3Sn_2$ (101) surfaces. The bond lengths between THFA and surfaces are included.

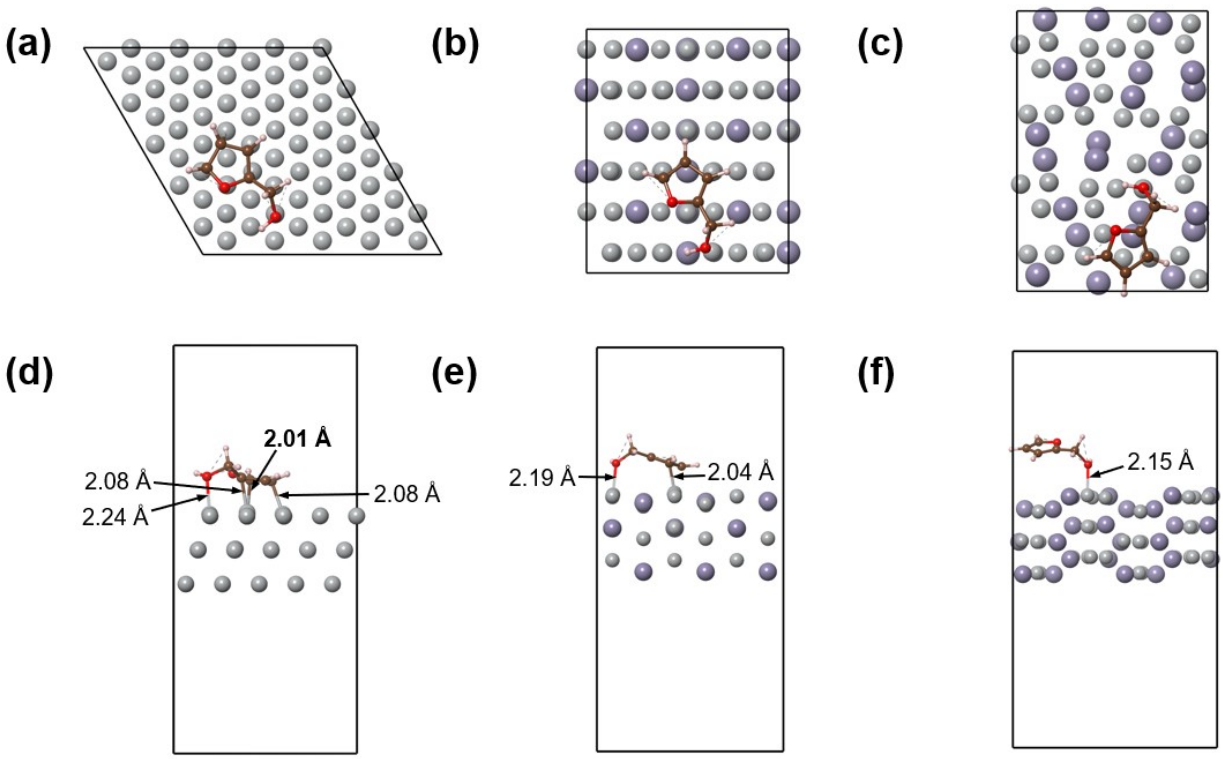


**Fig. S16** Top and side views of optimized configuration of FAL adsorption on (a) Ni (111), (b) $Ni_3Sn$ (100), and (c) $Ni_3Sn_2$ (101) surfaces. The bond lengths between FAL and surfaces are included.

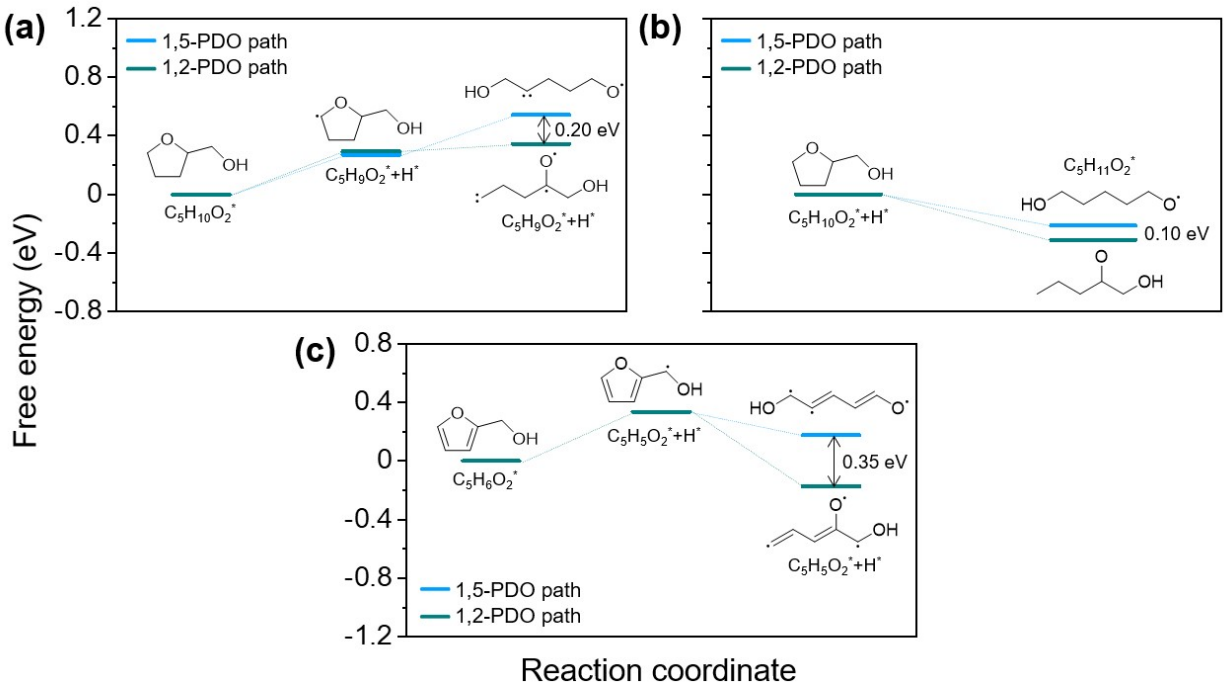


**Fig. S17** Relative energy diagrams for (a) THFA dehydrogenation-scission mechanism, (b) THFA hydrogenolysis mechanism, and (c) FAL dehydrogenation-scission mechanism on Ni (111) surface. T = 250 °C and P = 6 MPa.

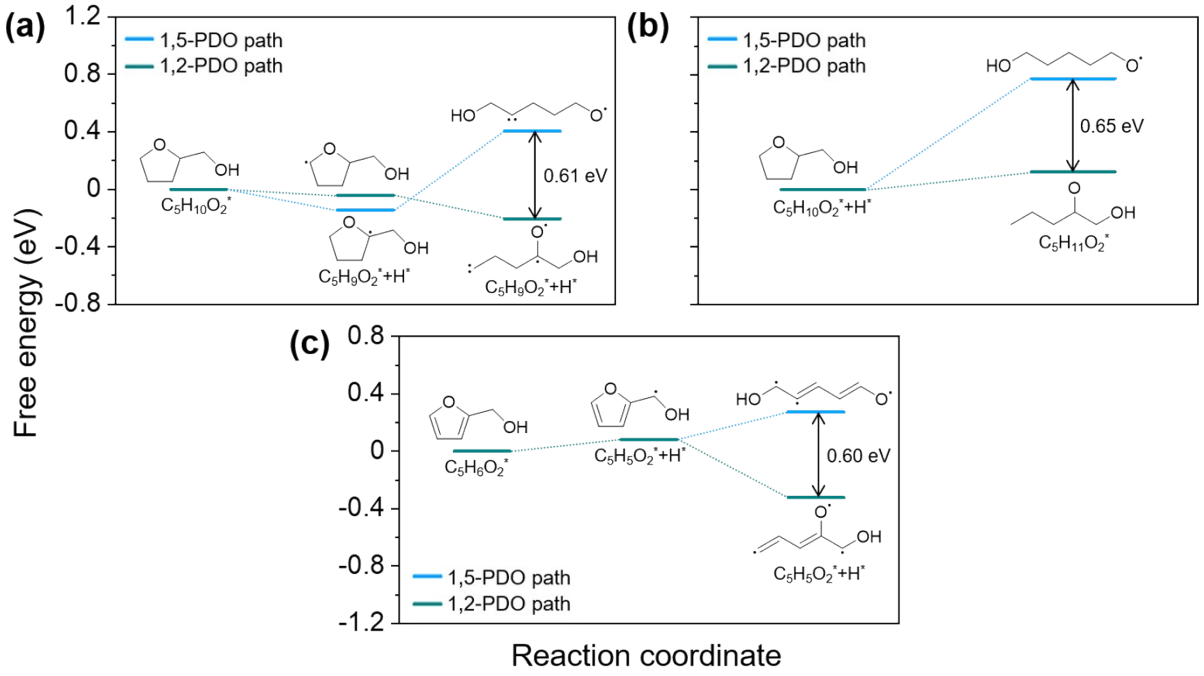


**Fig. S18** Relative energy diagrams for (a) THFA dehydrogenation-scission mechanism, (b) THFA hydrogenolysis mechanism, and (c) FAL dehydrogenation-scission mechanism on $Ni_3Sn$ (100) surface. T = 250 °C and P = 6 MPa.

**Table S1**. Amounts of precursors used in the catalyst synthesis.

| Catalyst | $Ni(NO_3)_2·6H_2O$ (g) | $SnCl_4·5H_2O$ (g) | $Zn(NO_3)_2·6H_2O$ (g) |
|---|---|---|---|
| Ni/ZnO | 4.95 | - | 33.23 |
| Sn/ZnO | - | 3.50 | 33.23 |
| 3Ni-1Sn/ZnO | 2.95 | 1.18 | 33.23 |
| 3Ni-2Sn/ZnO | 2.10 | 1.69 | 33.23 |
| 3Ni-3Sn/ZnO | 1.63 | 1.97 | 33.23 |
| 3Ni-4Sn/ZnO | 1.34 | 2.15 | 33.23 |
| 3Ni-3Sn(6%)/ZnO | 0.98 | 1.36 | 33.23 |
| 3Ni-3Sn(4%)/ZnO | 0.66 | 0.79 | 33.23 |
| | **$Ni(NO_3)_2·6H_2O$ (g)** | **$SnCl_4·5H_2O$ (g)** | **$Al(NO_3)_3·9H_2O$ (g)** |
| 3Ni-3Sn/$Al_2O_3$ | 1.63 | 1.97 | 33.11 |
| | **$Ni(NO_3)_2·6H_2O$ (g)** | **$SnCl_4·5H_2O$ (g)** | **$Ce(NO_3)_3·6H_2O$ (g)** |
| 3Ni-3Sn/$CeO_2$ | 1.63 | 1.97 | 22.70 |
| | **$Ni(NO_3)_2·6H_2O$ (g)** | **$SnCl_4·5H_2O$ (g)** | **30% colloidal silica** |
| 3Ni-3Sn/$SiO_2$ | 1.63 | 1.97 | 30.00 |
| | **$Co(NO_3)_2·6H_2O$ (g)** | **$SnCl_4·5H_2O$ (g)** | **$Zn(NO_3)_2·6H_2O$ (g)** |
| 3Co-3Sn/ZnO | 1.64 | 1.97 | 33.23 |
| | **$Cu(NO_3)_2·xH_2O$ (g)** | **$SnCl_4·5H_2O$ (g)** | **$Zn(NO_3)_2·6H_2O$ (g)** |
| 3Cu-3Sn/ZnO | 0.97 | 1.97 | 33.23 |

**Table S2**. The amount of $H_2$ consumed estimated from $H_2$-TPR analysis and the surface atomic concentration, and Sn/Ni ratio of the catalysts from XPS analysis.

| Catalyst | $H_2$ consumed (mmol/g) | Ni (at%/wt%) | Sn (at%/wt%) | Zn (at%/wt%) | $Ni^{2+}$/Ni total | $Sn^{2+/4+}$/Sn total | Sn/Ni (surface) |
|---|---|---|---|---|---|---|---|
| Ni/ZnO | 1.75 | 7.0/13.1 | - | 28.1/58.4 | - | - | - |
| Sn/ZnO | 1.23 | - | 12.7/36.2 | 27.5/43.0 | - | - | - |
| 3Ni-1Sn/ZnO | 1.77 | 4.4/5.6 | 13.8/36.0 | 27.6/39.5 | 65.6 | 82.3 | 3.1 |
| 3Ni-2Sn/ZnO | 1.61 | 3.7/4.9 | 13.7/36.7 | 25.5/37.7 | 62.2 | 73.0 | 3.7 |
| 3Ni-3Sn/ZnO | 1.73 | 2.7/3.5 | 14.0/37.0 | 27.1/39.5 | 57.0 | 67.9 | 5.2 |

**Table S3.** Catalytic results of furfuryl alcohol (FAL) hydrogenolysis over 4% and 6% (3Ni–3Sn)/ZnO catalysts.

| Catalyst | Temp (°C) | $H_2$ (bar) | Conv. (%) | Product yield (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 1,2-PDO | 1,5-PDO | THFA | MTHF | 2-MF | Others |
| 4% (3Ni–3Sn)/ZnO | 250 | 40 | 100 | 66.4 | 17.4 | 9.4 | 0.6 | 1.3 | 2.9 |
| 6% (3Ni–3Sn)/ZnO | 250 | 40 | 100 | 72.4 | 16.8 | 4.6 | 0.9 | 1.4 | 3.8 |

Reaction conditions: 10% FAL in IPA, 1.0 g of catalyst, WHSV = 1.0, $H_2$ 40 bar, $H_2$ flow 60 cc/min, and TOS < 50 h.

**Table S4.** Effect of pressure in furfuryl alcohol (FAL) hydrogenolysis over 3Ni–3Sn/ZnO catalyst.

| Entry | $H_2$ (bar) | Conv. (%) | Product yield (%) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 1,2-PDO | 1,5-PDO | THFA | MTHF | 2-MF | Others |
| 1 | 5 | 100 | 14.6 | 1.6 | 2.1 | 34.2 | 41.2 | 6.3 |
| 2 | 10 | 100 | 43.3 | 3.5 | 1.4 | 22.9 | 23.3 | 5.6 |
| 3 | 20 | 100 | 74.3 | 6.4 | 5.3 | 4.5 | 5.1 | 4.4 |
| 4 | 30 | 100 | 83.5 | 6.2 | 5.3 | 1.6 | 1.3 | 2.1 |
| 5 | 40 | 100 | 90.1 | 7.3 | 0.5 | 0.3 | 0.2 | 1.6 |

Reaction conditions: 10% FAL in IPA, 1.0 g of catalyst, 250 °C, WHSV = 1.0, $H_2$ pressure = 5–40 bar, $H_2$ flow = 60 cc/min, and TOS 20~50 h.

**Table S5.** Catalytic result of tetrahydrofurfuryl alcohol (THFA) hydrogenolysis over 3Ni–3Sn/ZnO catalyst.

| Catalyst | Temp (°C) | $H_2$ (bar) | Conv. (%) | Product yield (%) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 1,2-PDO | 1,5-PDO | MTHF | 2-MF | Others |
| 3Ni–3Sn/ZnO | 250 | 40 | 100 | 89.4 | 7.4 | 1.7 | 0.6 | 2.9 |

Reaction conditions: 10% THFA in IPA, 0.1 g of catalyst, WHSV = 1.0, $H_2$ 40 bar, $H_2$ flow 60 cc/min, and TOS < 50 h.

**Table S6.** Binding energies of THFA, FAL, and H over Ni (111), $Ni_3Sn$ (100), and $Ni_3Sn_2$ (101) surfaces. T = 250 °C and P = 6 MPa.

| Surface | Binding energy of THFA (eV) | Binding energy of FAL (eV) | Binding energy of H (eV) |
|---|---|---|---|
| Ni (111) | 2.10 | 2.23 | -0.26 |
| $Ni_3Sn$ (100) | 1.86 | 1.90 | -0.62 |
| $Ni_3Sn_2$ (101) | 1.81 | 2.23 | -0.14 |