

Electronic Supplementary Information for

Efficient hydrogenation of levulinic acid in water using supported Ni-Sn alloy on aluminium hydroxide catalysts

Rodiansono,^{a*} Maria Dewi Astuti^a, Takayoshi Hara,^b Nobuyuki Ichikuni^b and Shogo Shimazu^{*b}

^aDepartment of Chemistry, Lambung Mangkurat University, Jl. A. Yani Km 36 Banjarbaru, Indonesia 70714. Telp./fax: +62-511-477 3112; E-mail address: rodiansono@unlam.ac.id (Rodiansono).

^bGraduate School of Engineering, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan, Tel./fax: +81 43 290 3379. E-mail address: shimazu@faculty.chiba-u.jp (S. Shimazu).

Ni-Sn alloy catalysts supported on aluminium hydroxide (denoted as Ni-Sn(x)/AlOH, x = Ni/Sn ratio) were prepared via the hydrothermal treatment of the mixture of R-Ni/AlOH) and SnCl₂·2H₂O solution with different Ni/Sn ratios. The physicochemical properties of Ni-Sn/AlOH are summarised in Table S1. Based on the ICP-AES analyses, the loading amount of Sn was 0.45, 0.75, 1.04, 2.14, and 3.96 mmol g⁻¹ which were reflected in the Ni/Sn ratio of 7.9, 3.7, 3.0, 1.4, and 1.0, respectively. The Ni/Al ratio confirmed the presence of aluminium hydroxide that resulted from the alkali leaching of the Raney Ni-Al alloy precursor in the form of gibbsite and bayerite as indicated by the XRD patterns.^{S1}

Table S1 Chemical compositions, H₂-, CO-, and N₂-adsorption data (S_{BET}), and mean nickel particle size for R-Ni/AlOH and Ni-Sn/AlOH

Entry	Catalyst	Sn ^a (mmol g ⁻¹)	Ni/Δ ^a (molar ratio)	H ₂ uptake ^{b/} μmol g ⁻¹	CO uptake ^{c/} μmol g ⁻¹	S_{BET} ^{d/} m ² g ⁻¹	D^e /nm
1	R-Ni/AlOH	0	0.91	104	81	151	9.0
2	Ni-Sn(7.9)/AlOH	0.45	1.04	94	85	77	6.2
3	Ni-Sn(3.7)/AlOH	0.75	1.10	104	82	82	5.6
4	Ni-Sn(3.0)/AlOH	1.04	1.05	110	91	90	5.3
5	Ni-Sn(3.0)/AlOH ^f	1.02	1.05	76	nd ^g	72	nd ^g
6	Ni-Sn(1.4)/AlOH	2.14	0.86	102	92	76	4.1
7	Ni-Sn(1.4)/AlOH ^f	2.12	0.86	32	nd ^g	27	nd ^g
8	Ni-Sn(1.0)/AlOH	3.96	0.68	96	91	72	3.8

^a Determined by ICP-AES. ^b Based upon total H₂ uptake at 273 K (noted after corrected for physical and chemical adsorption). ^c Based upon total CO uptake at 273 K (noted after corrected for physical and chemical adsorption). ^d Determined by N₂ adsorption at 77 K. ^e Average Ni particle sizes, calculated according to the method described in the literature.^{S2} ^f After H₂ treatment at 273 K for 1 h. ^g Not determined.

The H₂ and CO uptakes, BET surface area (S_{BET}), and the average Ni particle sizes of R-Ni/AlOH and Ni-Sn/AlOH catalysts are summarised in Table S1. With increasing the loading amount of Sn, H₂ and CO uptakes and BET surface area varied whereas the average Ni particle sizes decreased (Table 1, entries 1-6).

Thermo gravimetric-differential thermal analysis (TG-DTA) profiles for Ni-Sn(1.4)/AlOH fresh are shown in Fig. S1. TG curve shows that small amount of H₂O and residue organic compound, i.e. ethanol was evaporated at 365-470 K. A significant loss of weight was observed at 521-551 K (approximately 14.6%) which corresponds to the transformation of gibbsite and bayerite into γ -alumina.^{S2-S4} Furthermore, DTA curve shows a good agreement to the TG curve that an endotherm peak at 540 K which corresponds to the dehydration of bayerite or gibbsite to γ -alumina.^{S3} In addition, neither weight loss nor an exothermal peak of the transformation of SnCl₂·H₂O into SnO₂ was observed at 600 K.^{S5} These results suggest that SnCl₂·2H₂O precursor may reacted completely with metallic Ni to form Ni-Sn alloy.

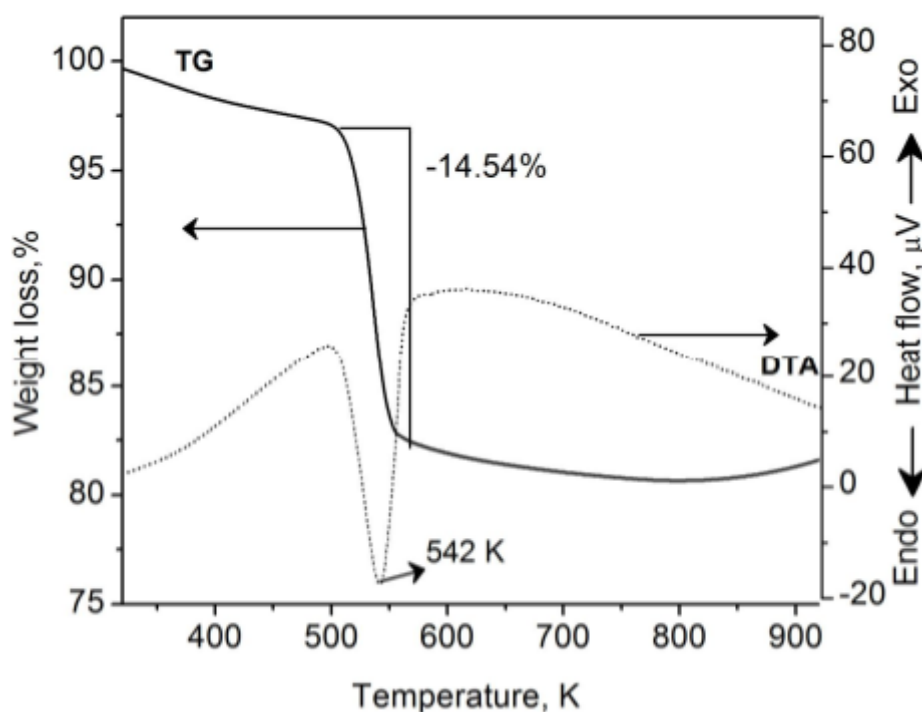


Fig. S1 Thermogram profiles of the *as prepared* Ni-Sn(1.4)/AlOH catalyst.

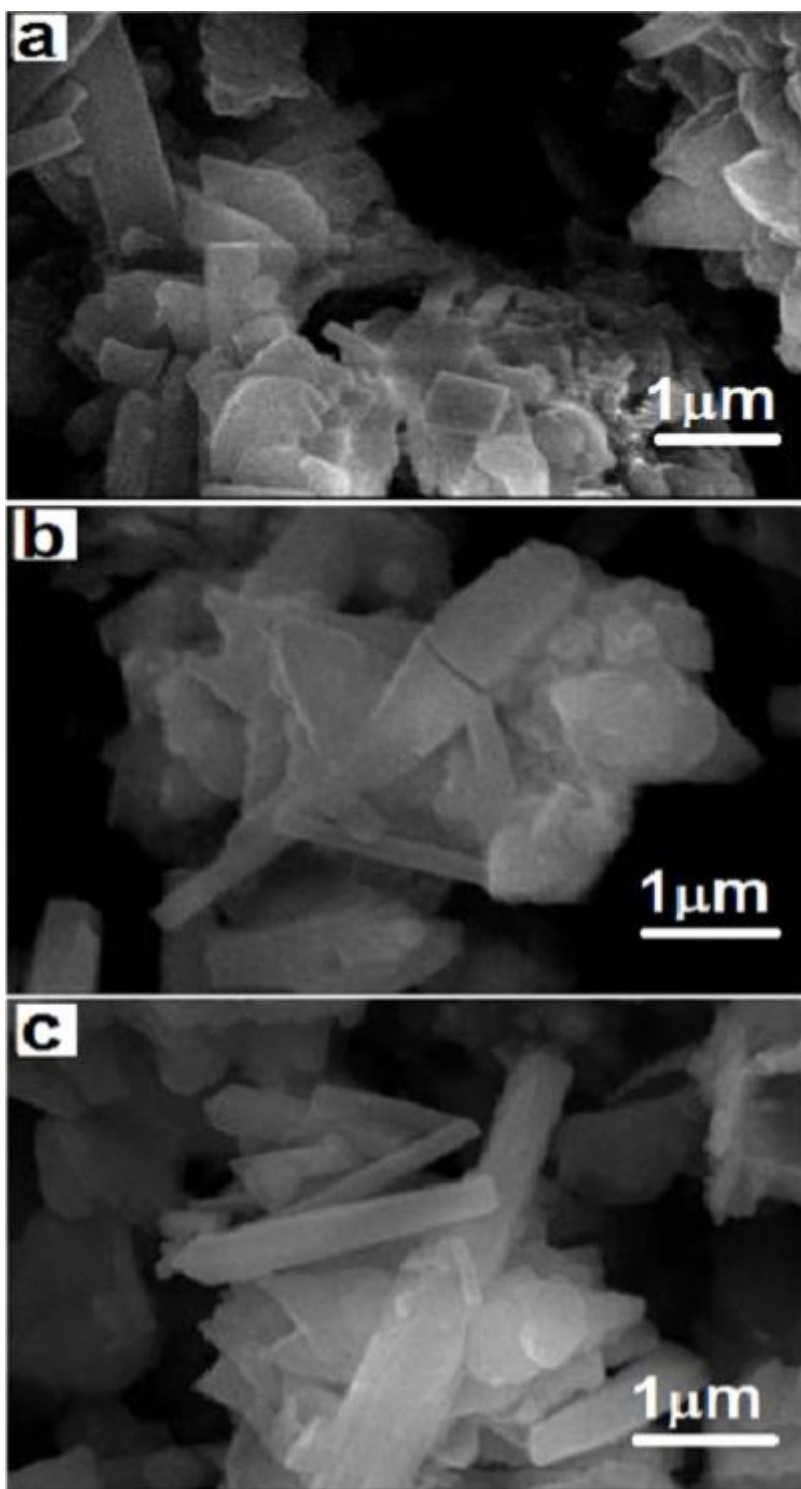


Fig. S2 SEM images of Ni-Sn(1.4)/AlOH catalysts. (a) fresh and H₂-treated at (b) 673 K and (c) 773 K for 1 h.

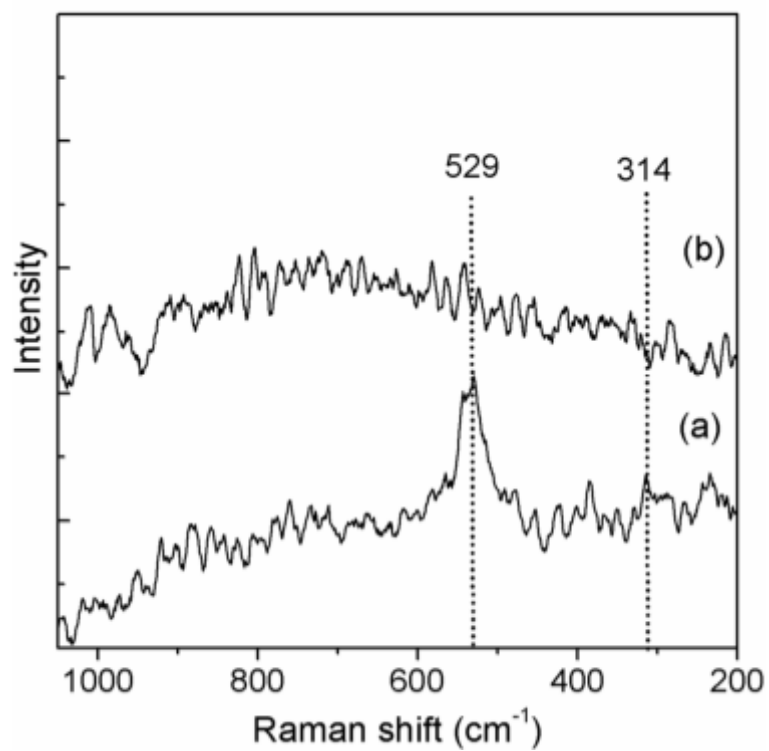


Fig. S3 Raman spectra of (a) the as-prepared Ni-Sn(1.4)/AlOH and (b) H_2 -treated at 673 K for 1.5 h.

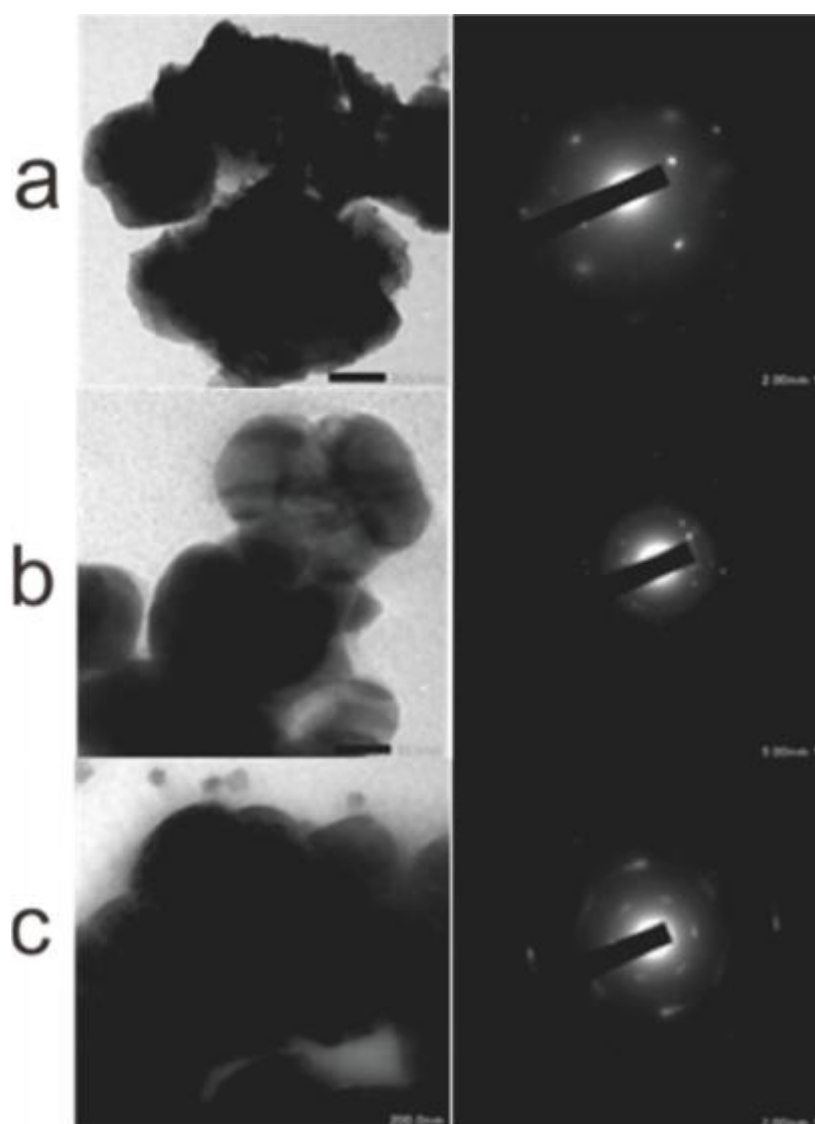


Fig. S4 TEM images and SAED for Ni-Sn(1.4)AlOH catalyst. (a) *as-prepared*, (b) after H₂ treatment at 673 K, and (c) recovered catalyst after the third reaction run.

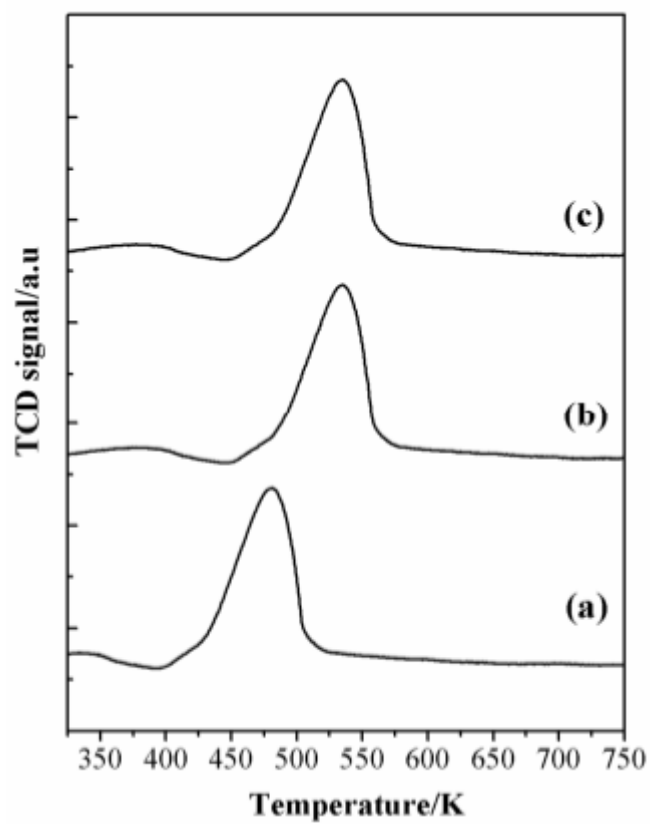


Fig. S5 Temperature programmed reduction of (a) the *as-prepared* and H₂-treated Ni-Sn(1.4)/AlOH catalyst at (b) 673 K and (c) 773 K.

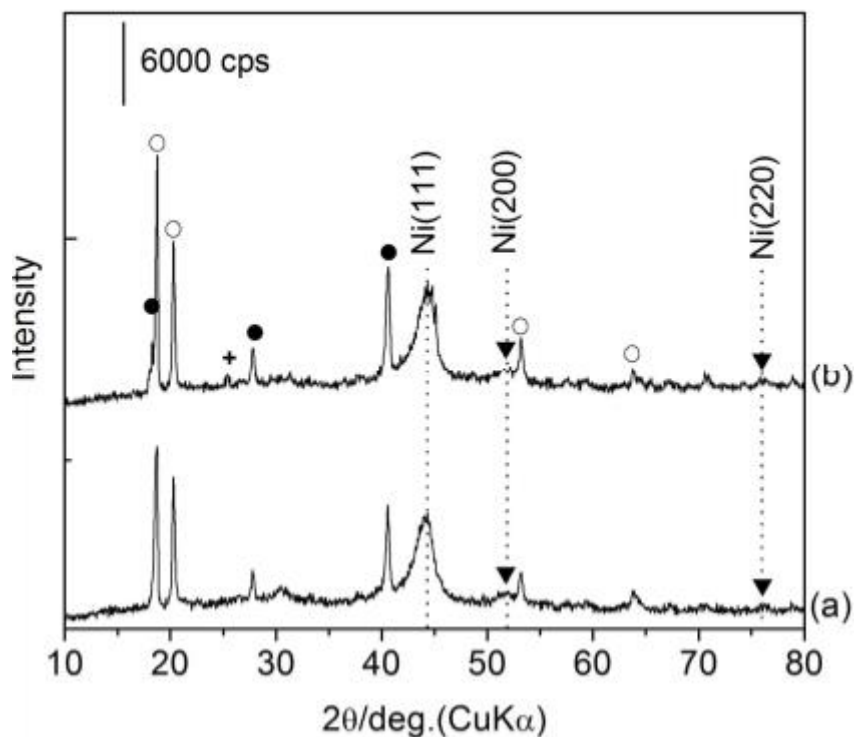


Fig. S6 XRD patterns of the recovered (a) Ni-Sn(1.4)/AlOH and (b) Ni-Sn(1.0)/AlOH catalysts. (□) bayerite; (□) gibbsite; (□) Sn; (●) Ni(0).

Table S2 Results of LA transformation over various Ni-M/AlOH (M= In, Ag, Zr, V, and Nb) catalysts

Entry	Catalysts	Conversion ^a /%	Yield ^b /%		
			LE	GVL	HVA
1	Ni-In/AlOH	57	0	57	0
2	Ni-Ag/AlOH	56	0	56	0
3	Ni-Zr/AlOH	53	0	53	0
4	Ni-V/AlOH	13	0	13	0
5	Ni-Nb/AlOH	32	0	32	0

Reaction conditions: catalyst (0.05 g), LA (2 mmol), solvent (3 mL), H₂ (4.0 MPa), 393 K, 120 min. ^a Conversion of LA. ^b Determined by GC using an internal standard technique; LE = levulinic ester; GVL = γ -valerolactone; HVA = hydroxyvaleric acid.

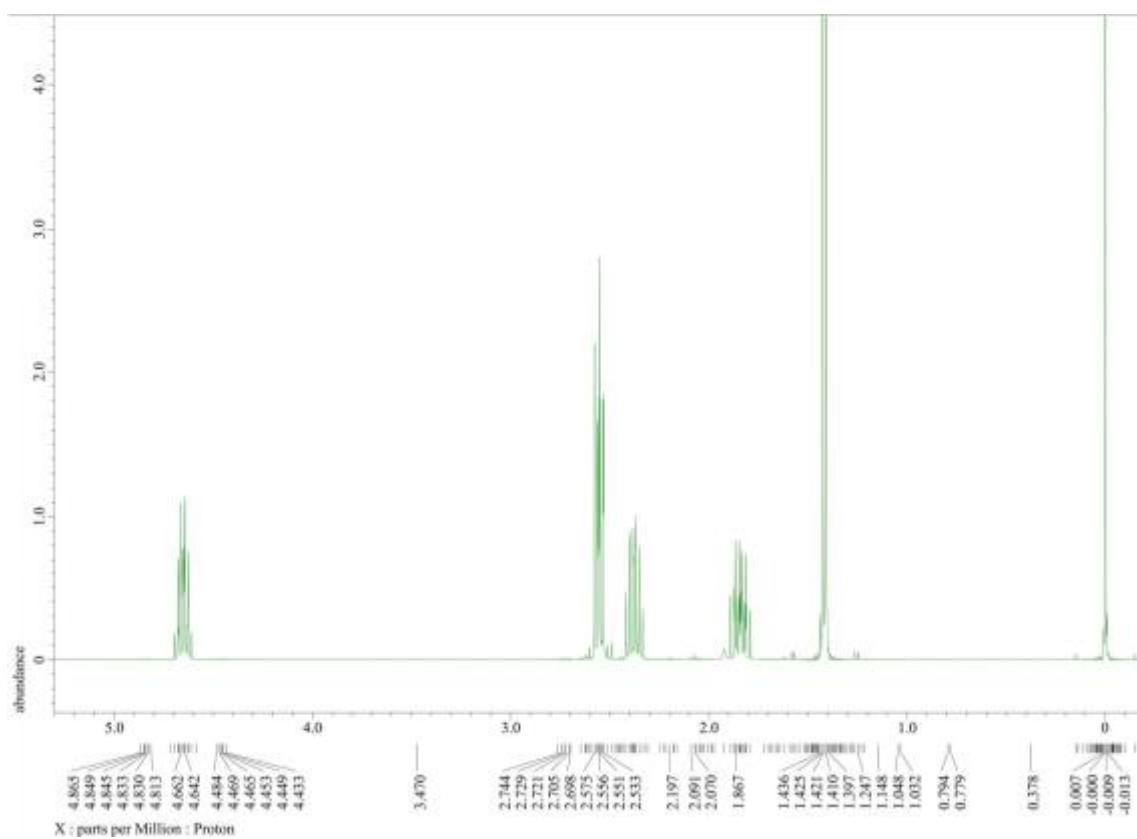


Fig. S7 ^1H NMR spectra of synthesised γ -valerolactone from hydrogenation of levulinic acid in water over Ni-Sn(1.4)/AlOH catalysts.

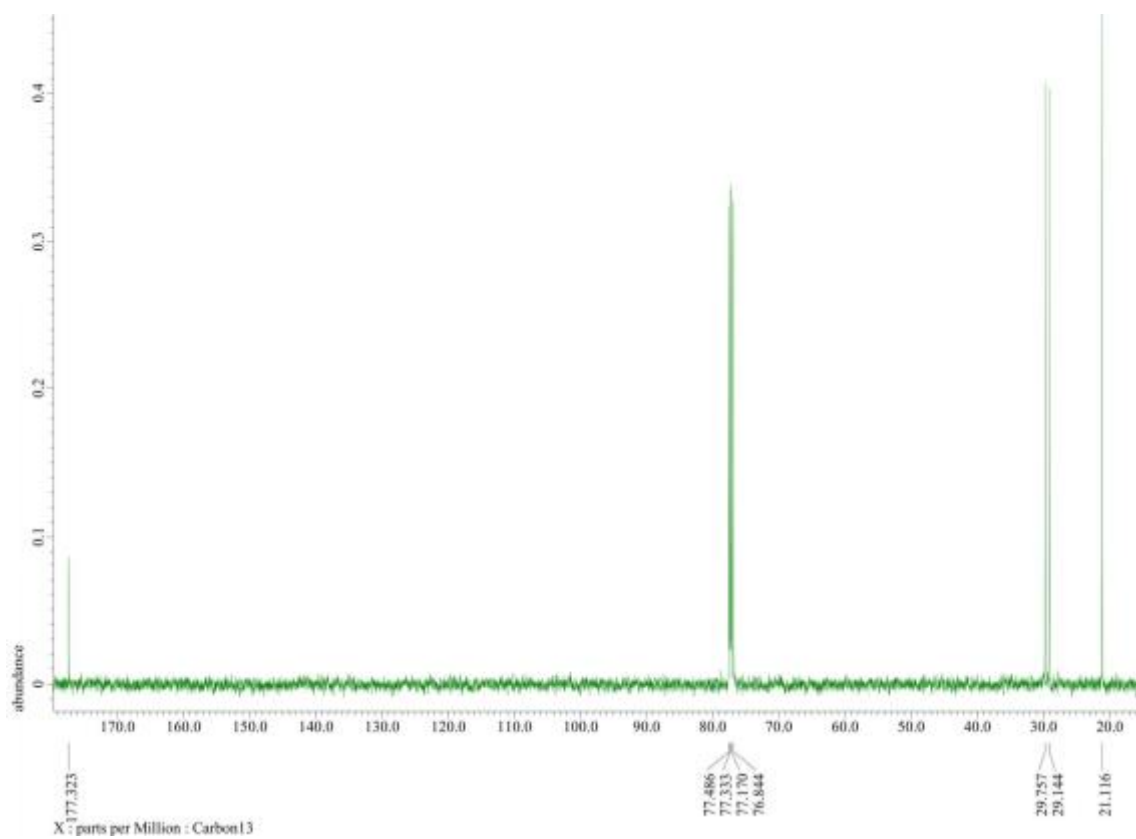


Fig. S8 ^{13}C NMR spectra of synthesised γ -valerolactone from hydrogenation of levulinic acid in water over Ni-Sn(1.4)/AlOH catalysts.

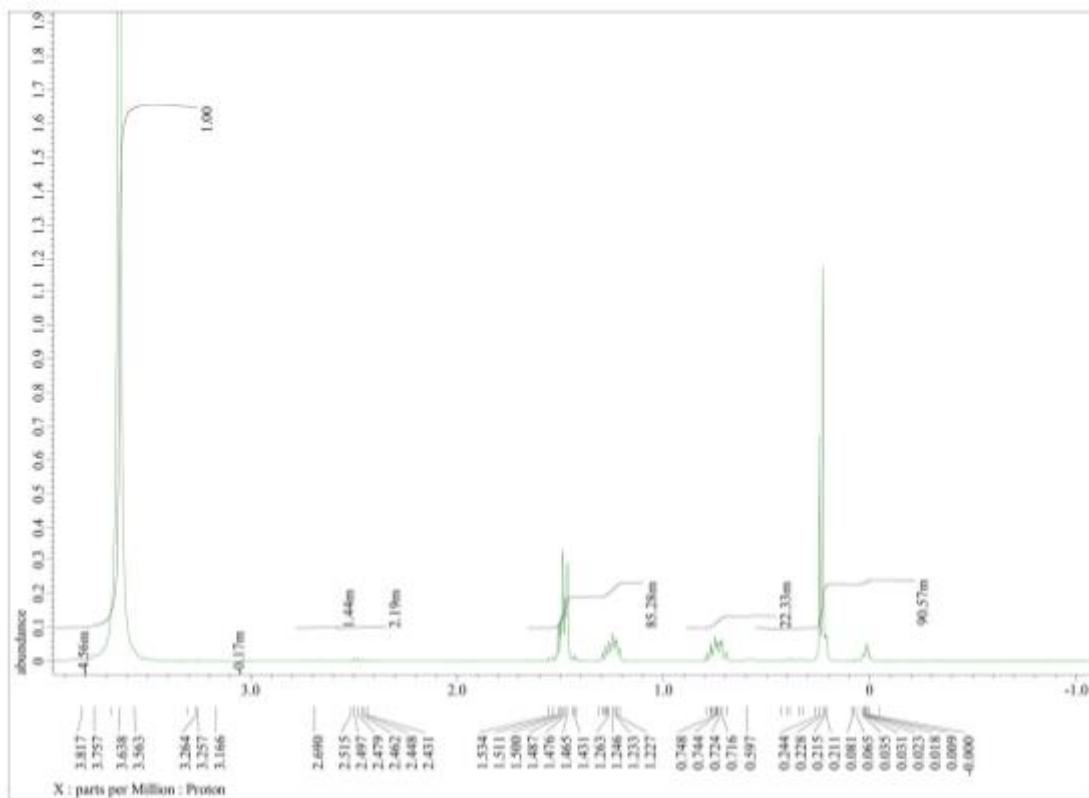


Fig. S9 ^1H NMR spectra of synthesised γ -valerolactone from hydrogenation of levulinic acid in D_2O over $\text{Ni-Sn}(1.4)/\text{AlOH}$ catalysts.^{S7}

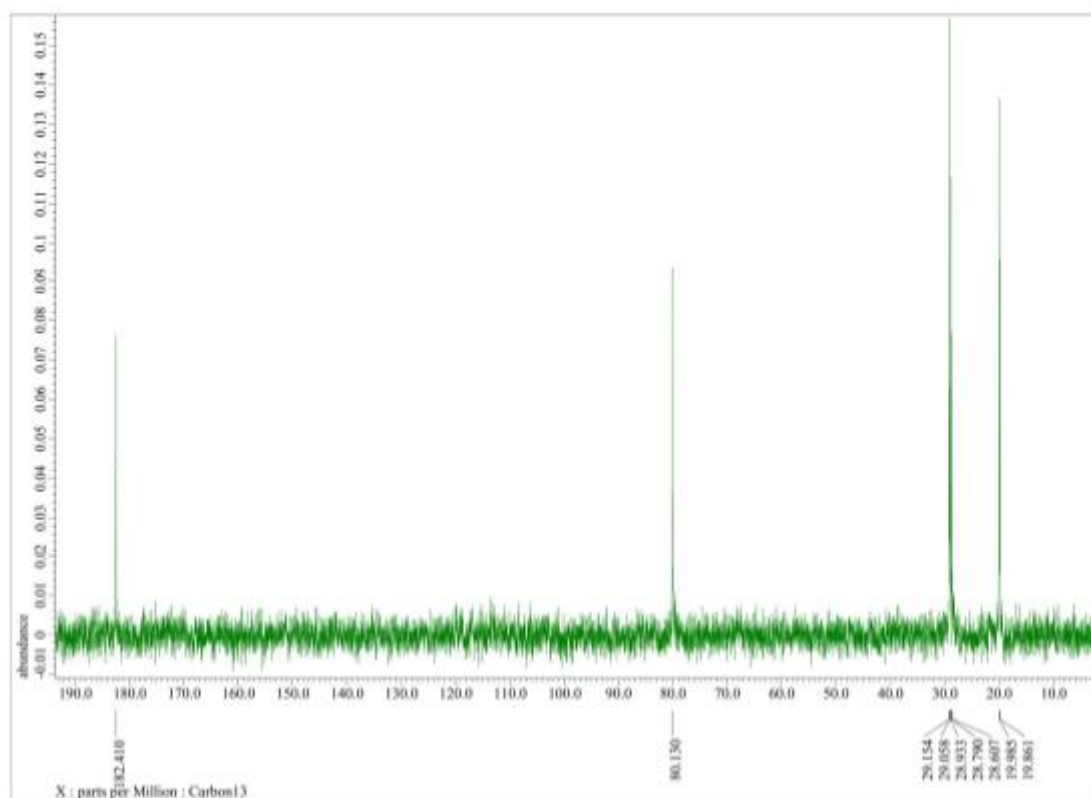


Fig. S10 ^{13}C NMR spectra of synthesised γ -valerolactone from hydrogenation of levulinic acid in D₂O over Ni-Sn(1.4)/AlOH catalysts.^{S7}

References

- S1 Rodiansono, T. Hara, N. Ichikuni, and S. Shimazu, *Chem Lett.*, 2012, 41, 769-771.
 S2 T. Tsuchida, T. Ishii, R. Furuichi, and H. Haga, *Thermochim. Acta* 1979, 34, 19-28.
 S3 T. Tsuchida and N. Ichikawa, *React. Solids*, 1989, 7, 207-217.
 S4 (a) C. H. Bartholomew, R. B. Pannel, and J. L. Butler, *J. Catal.* 1980, 65, 335-347. (b) C. H. Bartholomew and R. B. Pannel, *J. Catal.* 1980, 65, 390-401.
 S5 K. J. D. MacKenzie, J. Temuujin, and K. Okada, *Thermochim. Acta* 1999, 327, 103-108.
 S6 Q. F. Dong, C. Z. Wu, M. G. Jin, Z. C. Huang, M. S. Zheng, J. K. You, and Z. G. Lin, *Solid State Ionics* 2004, 167, 49-54.
 S7 J. Tan, J. Cui, T. Deng, X. Cui, G. Ding, Y. Zhu, and Y. Li, *ChemCatChem*, 2015, 7, 508-512.