

CrossMark
click for updates

Cite this: DOI: 10.1039/c5cy01731a

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

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

Efficient hydrogenation of levulinic acid (LA) into γ -valerolactone (GVL) in water using highly dispersed Ni–Sn(x)/AlOH ($x = \text{Ni/Sn}$ ratio) was studied. Increasing the Sn amount in the Ni–Sn alloy up to 2.14 mmol g⁻¹ enhanced the yield of GVL, which slightly decreased when the Sn content was nearly 4 mmol g⁻¹ (feeding Ni/Sn = 1.0). A stoichiometric amount of GVL (>99%) was achieved by using Ni–Sn(x)/AlOH ($x = 3.0$ and 1.4) at 393 K for 120 min in H₂O. H₂-treated Ni–Sn(1.4)/AlOH consisting of Ni₃Sn₂ alloy species showed high selectivity towards GVL (>99% yield). The Ni–Sn(1.4)/AlOH catalyst was reusable for at least six consecutive runs without any significant loss of activity and selectivity.

Received 11th October 2015,
Accepted 24th November 2015

DOI: 10.1039/c5cy01731a

www.rsc.org/catalysis

Introduction

Recently, research on biomass feedstock valorisation has been aimed at the production of bio-based platform chemicals, fuels and various commodity products.¹ Bio-derived molecules provide an interesting challenge of selective hydrodeoxygenation through the use of appropriately designed catalyst systems that can reduce the number of processing steps as compared with fossil-derived hydrocarbons.² Among the oxygenated biomass-derived compounds, levulinic acid (LA) can be easily obtained *via* acidic hydrolysis of C-5 sugars in hemicellulose³ or catalytic conversion of furfuryl alcohol over heterogeneous acid catalysts.⁴ Downstream processing of LA and its ester gives several useful chemicals,⁵ *e.g.*, γ -valerolactone (GVL) can be obtained by the catalytic hydrogenation of LA or its ester.⁶ GVL may be used as a solvent⁷ or blended with conventional gasoline like ethanol.⁸ GVL can also be converted into a variety of chemicals such as 1,4-pentanediol,⁹ α -methylene γ -valerolactone,¹⁰ and pentenoic esters.¹¹ Furthermore, GVL can also be used as a precursor of gasoline or diesel fuels such as C8–C16 alkenes,¹² C9–C18 alkanes,¹³ C9 alkanes,¹⁴ valeric esters¹⁵ or butene isomers,¹⁶ aromatic hydrocarbons,¹⁷ and gasoline-like hydrocarbons.¹⁸

The synthesis of GVL through LA hydrogenation using heterogeneous catalysts of precious transition metals has been

extensively utilised to achieve a high yield of GVL.¹⁹ Poliakov *et al.*²⁰ used a Ru/SiO₂ catalyst under supercritical-CO₂ and H₂ up to 4.5 MPa at 473 K to give >99% GVL yield, while Galletti *et al.*²¹ combined a Ru/C catalyst and an acid co-catalyst under supercritical-CO₂ at relatively low temperature. Recently, Dumesic *et al.* reported the use of bimetallic Ru–Sn for LA hydrogenation to give GVL in *o*-isobutylphenol at a relatively high reaction temperature of 453 K. They claimed that the formation of intermetallics such as Ru₂Sn₃ and Ru₃Sn₇ retarded Sn leaching into the reaction solution.²² Although catalytic processes have been applied to the transformation of LA into GVL, precious metal catalysts were mainly utilised in these studies. Therefore, the preparation of economical heterogeneous catalysts to be substituted for these precious metals is essential for industrial application.

We have recently developed a synthetic procedure for inexpensive Ni–Sn alloy catalysts (in bulk and on various supports) and applied them for chemoselective hydrogenation of various unsaturated carbonyl compounds.^{23–25} In the present work, we have extended our study on the catalytic performances of Ni–Sn alloy catalysts supported on aluminium hydroxide (Ni–Sn(x)/AlOH, $x = \text{Ni/Sn}$ ratio) to the selective hydrogenation of biomass-derived LA into GVL as shown in Fig. 1. The effects of the Sn loading amount (Ni/Sn ratio), solvent, reaction temperature and initial H₂ pressure on the activity and selectivity to GVL, and the reusability of the catalysts were examined.

Results and discussion

Catalyst characterisation

The XRD patterns of Ni–Sn(x)/AlOH ($x = \text{Ni/Sn}$ molar ratio) exhibited broad peaks at $2\theta = 44.44^\circ$ due to the formation of Ni–Sn alloy phases such as Ni₃Sn and Ni₃Sn₂ reported

^a Department of Chemistry, Lambung Mangkurat University, Jl. A. Yani Km 36, Banjarbaru 70714, Indonesia. E-mail: rodiansono@unlam.ac.id; Fax: +62 511 477 3112; Tel: +62 511 477 3112

^b Graduate School of Engineering, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan. E-mail: shimazu@faculty.chiba-u.jp; Fax: +81 43 290 3379; Tel: +81 43 290 3379

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5cy01731a

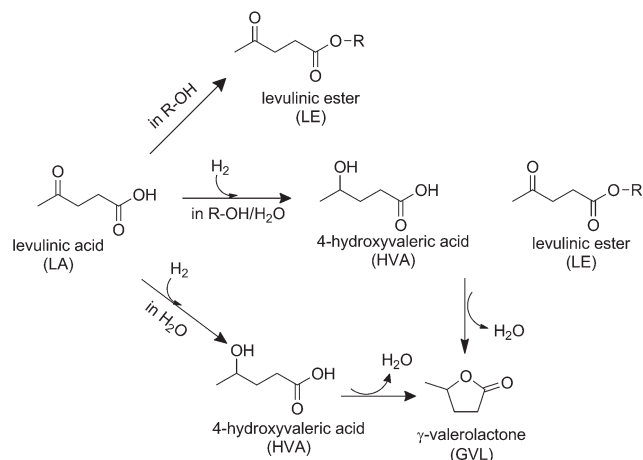


Fig. 1 Possible reaction pathways for catalytic transformation of LA into GVL over Ni-Sn alloy catalysts.

previously.^{24,25} The TG-DTA results for Ni-Sn(1.4)/AlOH confirmed that neither weight loss nor an exothermal peak of the transformation from SnCl₂·H₂O to SnO₂ was observed at 600 K. These results suggest that the SnCl₂·2H₂O precursor might have reacted completely with metallic Ni to form a Ni-Sn alloy (Fig. S1, ESI†). Based on the ICP-AES analysis, the loading amounts of Sn were 0.45, 0.75, 1.04, 2.14 and 3.96 mmol g⁻¹ which were reflected in the Ni/Sn ratios of 7.9, 3.7, 3.0, 1.4 and 1.0, respectively (Table S1, ESI†). 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.^{23,24} The physicochemical properties of the Ni-Sn(*x*)/AlOH catalysts *e.g.* H₂ uptake, BET surface area (*S*_{BET}), total pore volume (*V*_p) and average pore diameter (*d*_{pore}) are summarised in Table S1, ESI†. It can be observed that with increasing loading amount of Sn, the H₂ and CO uptakes and BET surface areas varied, whereas the average Ni particle sizes slightly decreased (Table S1, entries 1–6, ESI†).

The scanning electron microscopy (SEM) images of the as-prepared, H₂-treated and recovered Ni-Sn(1.4)/AlOH catalysts are shown in Fig. S2, ESI†. The SEM images of Ni-Sn(1.4)/AlOH before and after H₂ treatment revealed that the morphological differences between the fresh and hydrogen-treated catalysts are readily visible in Fig. S2, ESI†. The as-prepared Ni-Sn(1.4)/AlOH is constituted by Ni-rich angular particles and irregularly oriented Al-rich crystal-like particles. Besides the spongy morphology of Ni, the Al-rich region contains hexagonal prismatic rods and spiral crystals constructed from plates stacked perpendicular to the longitudinal axis, which are characteristic morphologies of gibbsite and bayerite, respectively.^{26,27} The characteristic morphologies of the Al-rich region were maintained and became more rigid after hydrogen treatment at 773 K (Fig. S2, ESI†). In the case of H₂-treated Ni-Sn(1.4)/AlOH, the XRD patterns showed that the formation of a Ni-Sn alloy phase as a Ni₃Sn₂ species and the transformation of bayerite and gibbsite into amorphous alumina were observed clearly. The low-frequency Raman

spectroscopy results for the as-prepared Ni-Sn(1.4)/AlOH showed a band at 529 cm⁻¹ which can be attributed to the γ(OH) vibrational mode and Al-O-Al deformation while the band at 314 cm⁻¹ was ascribed to Al-O-Al stretching vibrations of gibbsite or bayerite.²⁸ On the other hand, the bands of Al-O-Al deformation and Al-O-Al stretching vibrations disappeared after H₂ treatment at 673 K for 1.5 h due to the formation of amorphous alumina²⁹ that had also not been detected by XRD^{24,25} (see Fig. S3, ESI†).

The TEM images and SAED patterns of the 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) are shown in Fig. S4, ESI†. The TPR profiles of the freshly as-prepared and H₂-treated Ni-Sn(1.4)/AlOH catalysts revealed that the hydrogen consumption peak was the consequence of a reduction process of the metallic oxides of the catalyst during the preparation (see Fig. S5, ESI†).

Catalytic reactions

Effect of solvent. We studied the effect of solvents used in LA transformation over the Ni-Sn(1.4)/AlOH catalyst and the results are summarised in Table 1.

In the alcohol solvents such as methanol, ethanol, 2-propanol and 1-propanol, the LA conversions were 14%, 20%, 10% and 15%, giving levulinic esters without GVL formation (entries 1–4), respectively. Surprisingly, nearly 100% LA conversion and 100% GVL yield were achieved when H₂O was used as the solvent (entry 5).

The high conversion of LA and the high selectivity to GVL in the water solvent can be attributed to the presence of H-bonded water molecules or single chemisorbed water on metallic surfaces that can dramatically reduce the energy span of the reaction pathway, hence enhancing the catalytic activity.^{30a} Alternatively, the increase in the surface concentration of hydrogen atoms due to dissociated water and

Table 1 Results of LA hydrogenation in various solvents using Ni-Sn(1.4)/AlOH catalysts

Entry	Solvent	Conversion ^a /%	Yield ^b /%		
			LE	GVL	HVA
1	Methanol	14	14	0	0
2	Ethanol	20	13	0	7
3	2-Propanol	10	10	0	0
4	1-Propanol	15	15	0	0
5	H ₂ O	>99	0	>99	0
6 ^c	Methanol/H ₂ O	81	6	75	0
7 ^c	Ethanol/H ₂ O	>99	3	96	1
8 ^c	2-Propanol/H ₂ O	>99	0	>99	0
9	1,4-Dioxane	35	0	34	0
10	Acetonitrile	13	0	11	0
11	Tetrahydrofuran (THF)	21	0	19	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. ^c The volume ratio of alcohol/H₂O was 1.0/1.0.

strong interaction between water and the substrate through hydrogen bonding lowers the activation energy barrier and leads to high hydrogenation rates.^{30b-d} Tan *et al.* observed that the substituted proton (D) on the carbon C5 of GVL originally came from D₂O during LA hydrogenation in D₂O solvent.³¹ Moreover, we also intentionally carried out the reaction in D₂O solvent under the same reaction conditions (¹³C and ¹H NMR spectra are available in Fig. S8 and S9, ESI,† respectively) and the results are in good agreement with the previous reports. The influence of H₂O on the LA conversion and GVL yield was clearly observed when alcohol/H₂O (1:1 volume ratio) was used as the solvent. The conversion of LA and the yield of GVL remarkably increased to 81% and 75%, respectively, and the levulinic ester (methyl 4-oxopentanoate) yield diminished to 6% in methanol/H₂O (entry 6). In the ethanol/H₂O solvent, LA conversion was 100%, giving 96% GVL, 3% LE (ethyl 4-oxopentanoate) and 1% HVA (4-hydroxyvaleric acid) (entry 7), while in 2-propanol/H₂O, >99% GVL yield was obtained without propyl 4-oxopentanoate formation under the same reaction conditions (entry 8). We also evaluated several aprotic solvents such as 1,4-dioxane, acetonitrile and THF, and the results showed that LA conversion was only 35%, 13% and 21%, respectively (entries 9–11). We believe that the reaction mechanism of LA hydrogenation over Ni–Sn(*x*)/AlOH alloy catalysts proceeds *via* hydrogenation of C=O of the carbon C5 of LA to form HVA and without the formation of an ester. The formation of HVA would prevent esterification or hydrolysis while in the presence of high H₂ pressure or due to the main reaction being carried out in water or water/alcohol.^{30a} It can be clearly observed that the reaction did not occur effectively when alcohols or other aprotic solvents were used as the solvents or even if the reaction time was extended until 720 min at 393 K and 4.0 MPa H₂ (Fig. 4). Therefore, it can be concluded that the hydrogenation of LA into GVL over the Ni–Sn alloy catalyst proceeded efficiently in the

H₂O solvent system. For further investigation, the H₂O solvent will be used for the examination of various Ni–Sn(*x*)/AlOH catalysts and the effect of various reaction conditions such as initial H₂ pressure and temperature, along with their time profile and reusability studies.

Effect of Sn loading amount. The results of LA hydrogenation in H₂O using supported Ni–Sn/AlOH alloy catalysts are summarized in Table 2.

By using Ni–Sn(7.9)/AlOH and Ni–Sn(3.7)/AlOH catalysts, GVL yields of 97% and 98% were obtained, respectively (entries 1 and 2). Upon increasing the Sn loading amount from 0.45 mmol g⁻¹ to 1.04 mmol g⁻¹ (Ni/Sn = 3.0), a GVL yield of >99% was obtained (entry 3) and this high yield was maintained up to 2.14 mmol g⁻¹ of Sn loading amount (Ni/Sn = 1.4). In contrast, Ni–Sn(1.0)/AlOH (Sn = 3.96 mmol g⁻¹) gave 64% LA conversion with 100% selectivity to GVL (entry 5). After H₂ treatment at 673 K for 1 h, the Ni–Sn(3.0)/AlOH catalyst gave 87% yield of GVL (entry 6). In contrast, H₂-treated Ni–Sn(1.4)/AlOH catalysts at 673–873 K gave 100% GVL yield (entries 7–9). The formation of Ni–Sn alloy phases in Ni–Sn(1.4)/AlOH after H₂ treatment may play an important role for the effective Ni–Sn species that can be rationally speculated as Ni₃Sn₂, while in Ni–Sn(3.0)/AlOH, Ni₃Sn, Ni₃Sn₄ and β-Sn were formed which were readily detected by XRD.²⁴ We found that the reaction rate of LA hydrogenation over the as-prepared Ni–Sn(1.4)/AlOH was 0.26 mmol g_{cat}⁻¹ min⁻¹ (conversion 71%), while those over H₂-treated Ni–Sn(1.4)/AlOH and Ni–Sn(3.0)/AlOH are 0.28 mmol g_{cat}⁻¹ min⁻¹ (conversion 81%) and 0.18 mmol g_{cat}⁻¹ min⁻¹ (conversion 47%), respectively, after 60 min of reaction at 393 K and 4.0 MPa H₂. Moreover, R–Ni/AlOH showed a low LA conversion giving 31% GVL yield under the same reaction conditions (entry 10). On the other hand, Sn/AlOH,³² SnO, SnO₂ and SnCl₂·2H₂O were not active for LA transformation under the same conditions (entries 11–14). In addition, the

Table 2 Results of LA hydrogenation over various Ni–Sn(*x*)/AlOH alloy catalysts

Entry	Catalyst ^a	Ni ^b /mmol g ⁻¹	Al ^b /mmol g ⁻¹	Sn ^b /mmol g ⁻¹	Conversion ^c /%	Yield ^d /%
1	Ni–Sn(7.9)/AlOH	3.56	3.44	0.45	97	97
2	Ni–Sn(3.7)/AlOH	2.81	2.52	0.75	98	98
3	Ni–Sn(3.0)/AlOH	3.09	2.88	1.04	>99	>99
4	Ni–Sn(1.4)/AlOH	3.01	3.48	2.14	>99	>99
5	Ni–Sn(1.0)/AlOH	3.78	5.49	3.96	64	64
6	Ni–Sn(3.0)/AlOH ^e	3.09	2.88	1.04	87	87
7	Ni–Sn(1.4)/AlOH ^e	3.01	3.48	2.14	>99	>99
8	Ni–Sn(1.4)/AlOH ^f	3.01	3.48	2.14	>99	>99
9	Ni–Sn(1.4)/AlOH ^g	3.01	3.48	2.14	>99	>99
10	R–Ni/AlOH	3.46	3.80	0	31	31
11	Sn/AlOH			4.10 ^h	0	0
12	SnO				0	0
13	SnO ₂				0	0
14	SnCl ₂ ·2H ₂ O				0	0
15	None				0	0

^a Values in parentheses are Ni/Sn molar ratios. Reaction conditions: catalyst (0.05 g), LA (2 mmol), H₂O (3.0 mL), H₂ (4.0 MPa), 393 K, 120 min.

^b Loading amount of Ni, Al and Sn, determined by ICP-AES. ^c Conversion of LA, determined by GC using an internal standard. ^d Yield of GVL determined by GC using an internal standard technique. Reaction time for entries 6–9 was 180 min. ^e The catalysts were treated with H₂ at 673 K for 1.5 h. ^f After H₂ treatment at 773 K for 1.5 h. ^g After H₂ treatment at 873 K for 1.5 h. ^h Feeding amount of Sn, prepared by an impregnation method.

transformation of LA into GVL did not proceed without a catalyst (entry 15). We also intentionally evaluated the effect of second metals rather than tin, such as indium (In), silver (Ag), zirconium (Zr) and niobium (Nb), which showed low conversions of LA.³³

Effect of reaction temperature. The effect of reaction temperature on the yield of GVL in the transformation of LA over the Ni-Sn(1.4)/AlOH catalyst is shown in Fig. 2.

It can be observed that LA conversion gradually increased with increasing temperature from 353 K to 383 K and became flat between 393 K and 453 K without a change in the yield and selectivity to GVL (100%). On the other hand, further transformation of the GVL product was not observed even though the reaction time was extended up to 24 h at 393 K over the Ni-Sn(1.4)/AlOH catalyst. Therefore, it can be concluded that the selectivity to GVL did not depend on the reaction temperature.

Effect of initial H₂ pressure. The effect of initial H₂ pressure on the yield of GVL in the transformation of LA over the Ni-Sn(1.4)/AlOH catalyst is shown in Fig. 3. As the initial H₂ pressure increased, the GVL yield increased smoothly, reaching nearly 100% up to 3.5 MPa within 180 min. Therefore, the initial H₂ pressure of 3.5–4.0 MPa was used as the optimised condition for LA transformation over Ni-Sn alloy catalysts.

Time profiles. The time profiles of LA transformation over the Ni-Sn(1.4)/AlOH catalyst in different solvents used are shown in Fig. 4. In H₂O and ethanol/H₂O, high activity for LA transformation was observed and almost 100% LA conversion (>99% GVL yield) was achieved after 120 min and 180 min, respectively. Moreover, the high yield of GVL was retained (>99%) even though the reaction temperature was raised to 453 K (Fig. 2) or the reaction time was extended to 720 min (Fig. 4). In contrast, in ethanol, LA transformation into GVL increased slightly giving only 8% GVL yield even after 720 min with 57% LA conversion.

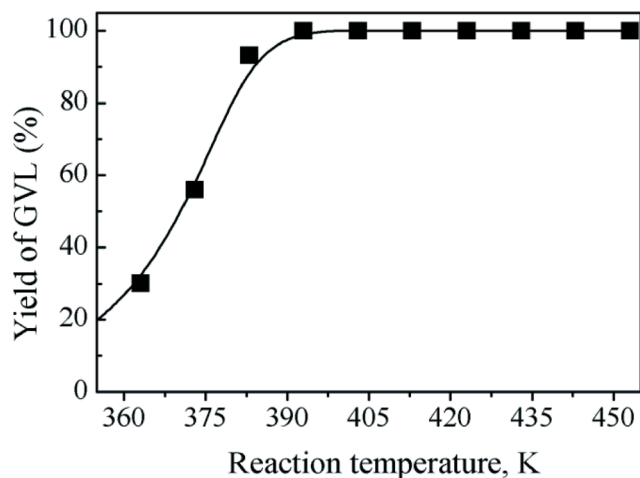


Fig. 2 Effect of reaction temperature on the GVL yield in the transformation of LA over the Ni-Sn(1.4)/AlOH catalyst. Reaction conditions: catalyst (0.05 g), LA (2 mmol), H₂O (3 mL), H₂ (4.0 MPa), 180 min.

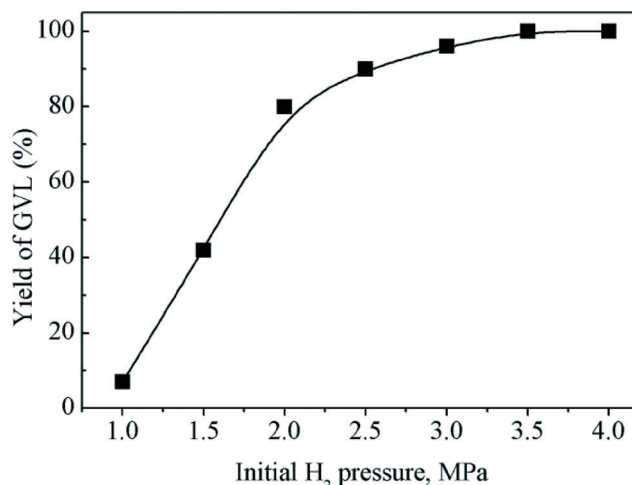


Fig. 3 Effect of initial H₂ pressure on the GVL yield in the transformation of LA over the Ni-Sn(1.4)/AlOH catalyst. Reaction conditions: catalyst (0.05 g), LA (2 mmol), H₂O (3 mL), 393 K, 120 min.

Reusability test. An important parameter of heterogeneous catalysts is stability during reactions. The reusability of the Ni-Sn(1.4)/AlOH catalyst in LA transformation into GVL was evaluated (Table 3).

The used Ni-Sn(1.4)/AlOH catalyst was easily separated by either simple centrifugation or filtration after the reaction. The recovered Ni-Sn(1.4)/AlOH catalyst was then dried under vacuum without any further treatments. The activity and selectivity were maintained for at least six consecutive runs. The amounts of metal leaching into the reaction solution were analysed by ICP-AES and were found to be 1.1 mol% (Ni), 5.0 mol% (Sn) and 6.5 mol% (Al) after the sixth run. In addition, the XRD patterns of the recovered Ni-Sn(1.4)/AlOH showed that the catalyst had no significant change from the fresh Ni-Sn(1.4)/AlOH even after six consecutive runs (Fig. S6, ESI[†]).

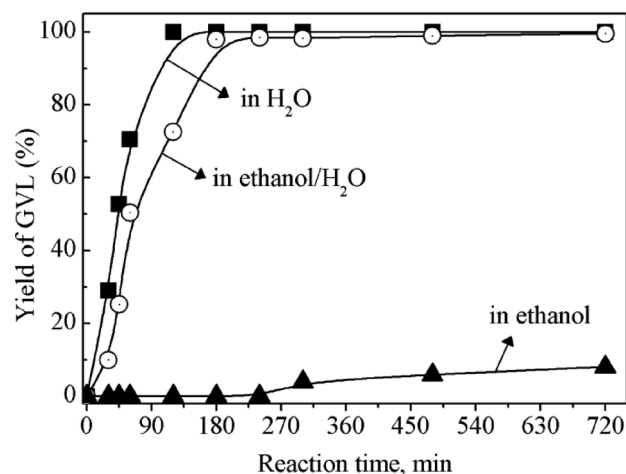


Fig. 4 Time profiles of LA transformation over the Ni-Sn(1.4)/AlOH catalyst in different solvents used. Reaction conditions: catalyst (0.05 g), LA (2 mmol), solvent (3 mL), H₂ (4.0 MPa), 393 K.

Table 3 Reusability test of the Ni-Sn(1.4)/AlOH catalyst in the transformation of LA into GVL

Run	1	2	3	4	5	6
Conversion (%)	>99	>99	>99	>99	>99	99
Yield ^a (%)	>99	>99	>99	>99	>99	99
Selectivity ^a (%)	100	100	100	100	100	100

Reaction conditions: catalyst (0.05 g), LA (2 mmol), H₂O (3 mL), H₂ (4.0 MPa), 393 K, 120 min. ^a Yield and selectivity to GVL, determined by GC using an internal standard technique.

Experimental

Materials

Raney Ni–Al alloy (50% wt Ni and 50% wt Al, Kanto Chemical Co., Inc.), NaOH (Wako) and SnCl₂·2H₂O (Wako) were purchased and used as-received. All organic chemical compounds were purified using standard procedures prior to use.

Catalyst preparation

Synthesis of R-Ni/AlOH. A typical procedure for the synthesis of Raney nickel supported on an aluminium hydroxide catalyst (denoted as R-Ni/AlOH) is described as follows:^{24,34} 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 the filtrate was neutralized, and then stored in water. The catalyst was dried under vacuum before the catalytic reaction.

Synthesis of Ni-Sn/AlOH. A typical procedure for the synthesis of a nickel–tin alloy supported on aluminium hydroxide (denoted as Ni-Sn(7.9)/AlOH, 7.9 is the Ni/Sn molar ratio) is described as follows:^{24,25} R-Ni/AlOH that was obtained from the above procedure was mixed with a solution that contained 0.45 mmol of SnCl₂·2H₂O at room temperature and stirred for 2 h. 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 and ethanol, and dried under vacuum overnight. In order to confirm the formation of the Ni-Sn alloy, H₂ treatment at 773 K for 1 h was carried out for the Ni-Sn(3.0)/AlOH and Ni-Sn(1.4)/AlOH samples. The XRD patterns of the H₂-treated catalysts had been reported previously.²⁴

Catalyst characterisation. Powder X-ray diffraction (XRD) measurements were conducted on a Mac Science M18XHF instrument using monochromatic Cu K α radiation (λ = 0.15418 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 (α 1 = 0.154057 nm, α 2 = 0.154433 nm). ICP measurements were performed on an SPS 1800H plasma spectrometer (Seiko Instruments Inc., Japan, Ni: 221.7162 nm and Sn: 189.898

nm). The BET surface area (S_{BET}) and pore volume (V_{p}) were measured using N₂ 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 measurements. 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.³⁵ The SEM images of the synthesised catalysts were taken on a JEOL JSM-610 SEM after the samples were coated using a JEOL JTC-1600 autofine coater. The TEM images were taken on a JEOL JEM1400. Raman spectra were taken on a JASCO NRS-2100 laser Raman spectrophotometer with an Ar beam lamp of 488 nm and 514.5 nm.

The H₂ uptake was determined through irreversible H₂ chemisorption. After the catalyst was heated at 393 K under vacuum for 30 min, it was heated at 673 K under H₂ for 30 min. The catalysts were subsequently cooled to room temperature under vacuum for 30 min. H₂ measurement was conducted at 273 K, and the H₂ uptake was calculated according to the method described in the literature.³⁶

Temperature-programmed reduction (TPR) was carried out on a Micromeritics AutoChem II chemisorption analyser according to a procedure previously reported.³⁷ The catalyst samples were outgassed at 423 K for 1 h and then cooled to 313 K under an Ar flow of 70 ml min⁻¹. TPR profiles were registered while heating the samples from 313 K to 1073 K at a heating rate of 283 K min⁻¹ under 50 ml min⁻¹ flow of a 10% H₂–Ar mixture.

General procedure for the transformation of LA. The catalyst (0.05 g), LA (2.0 mmol), H₂O (3 mL) as a solvent, and 1,8-octanediol (0.2 mmol) as an internal standard were placed into a glass reaction tube, fitted inside a stainless steel reactor. After H₂ was introduced into the reactor with an initial H₂ pressure of 4.0 MPa at room temperature, the temperature of the reactor was raised to 393 K. After 120 min, the conversion of LA and the yield of GVL were determined *via* GC analysis. For the reusability test, the used Ni-Sn(1.4)/AlOH catalyst was easily separated using either simple centrifugation or filtration in air, and then it was utilized repeatedly without any additional treatments.

Analysis of GVL for the hydrogenation of LA in H₂O was performed on a Shimadzu GC-8A equipped with a flame ionisation detector and Silicone OV-101 packing. A Shimadzu 14A with a flame ionisation detector equipped with an InertCap® 1 capillary column was used for product analyses for the hydrogenation of LA in alcohol or EtOH/H₂O solvents. Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-17B equipped with a thermal conductivity detector and an RT- β DEXsm capillary column. ¹H and ¹³C NMR spectra were obtained on a JNM-AL400 spectrometer at 400 MHz and 101 MHz, respectively; the samples were dissolved in chloroform-*d*₁ or D₂O with TMS as an internal standard. The products were identified by GC-MS, ¹H and ¹³C NMR spectra (Fig. S7 and S8, ESI†).

Conclusions

Efficient transformation of levulinic acid (LA) into γ -valerolactone (GVL) using Ni-Sn(x)/AlOH ($x = \text{Ni/Sn}$ ratio) was studied. Increasing the amount of Sn up to 2.14 mmol g⁻¹ enhanced the GVL yield which slightly decreased when Ni/Sn = 1.0. A high yield of GVL (>99%) was achieved over Ni-Sn(x)/AlOH ($x = 3.0$ and 1.4) at 393 K for 120 min. The Ni-Sn(1.4)/AlOH catalyst was reusable for at least six consecutive runs without any significant loss of activity and selectivity.

Acknowledgements

This work was partially financially supported by Kemenristek through Insentif Riset SINas FY 2014 under contract number DIPA-042-01.1.427922/2014 and JSPS Bilateral Joint Research Projects (2014–2017). Laser Raman measurements were financially supported by KLN and International Publication Project DGHE FY 2015 under contract number DIPA-023-04.1.673453/2015. We thank Dr. Indri B. Adilina for kind help in measurement of ¹H NMR and ¹³C NMR. We also acknowledge Professor Selahattin Yilmaz at Izmir Yuksek Institute of Technology (IYTE), Izmir, Turkey for kind help in TPR measurements.

Notes and references

- (a) M. J. Climent, A. Corma and S. Iborra, *Green Chem.*, 2014, **16**, 516–547; (b) M. Besson, P. Gallezot and C. Pine, *Chem. Rev.*, 2014, **114**, 1827–1870.
- (a) C. H. Zhou, X. Xia, C. X. Lin, D. S. Tonga and J. Beltramini, *Chem. Soc. Rev.*, 2011, **40**, 5588–5617; (b) P. Mäki-Arvela, T. Salmi, B. Holmbom, S. Willför and D. Y. Murzin, *Chem. Rev.*, 2011, **111**, 5638–5666; (c) P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538–1558; (d) C. Chatterjee, F. Pong and A. Sen, *Green Chem.*, 2015, **17**, 40–71.
- (a) W. Rackemann and W. O. S. Doherty, *Biofuels, Bioprod. Biorefin.*, 2011, **5**, 198–214; (b) S. T. Enzo Montoneri, D. Carnaroglio, M. Caporaso and G. Cravotto, *Green Chem.*, 2014, **16**, 73–76; (c) R. F. Perez and M. A. Fraga, *Green Chem.*, 2014, **16**, 3942–3950; (d) H. Rena, B. Girisuta, Y. Zhou and L. Liu, *Carbohydr. Polym.*, 2015, **117**, 569–576.
- (a) G. M. Gonzalez Maldonado, R. S. Assary, J. A. Dumesic and L. A. Curtiss, *Energy Environ. Sci.*, 2012, **5**, 6981–6989; (b) G. Wang, Z. Zhang and L. Song, *Green Chem.*, 2014, **16**, 1436–1443; (c) M. A. Mellmer, J. M. R. Gallo, D. M. Alonso and J. A. Dumesic, *ACS Catal.*, 2015, **5**, 3354–3359; (d) B. Lu, S. An, D. Song, F. Su, X. Yang and Y. Guo, *Green Chem.*, 2015, **17**, 1767–1778.
- B. V. Timokhin, V. A. Baransky and G. D. Eliseeva, *Russ. Chem. Rev.*, 1999, **68**, 73–84.
- (a) A. M. Hengne and C. V. Rode, *Green Chem.*, 2012, **14**, 1064–1072; (b) J. M. Tukacs, M. Novák, G. Dibó and L. T. Mika, *Catal. Sci. Technol.*, 2014, **4**, 2908–2912; (c) V. S. Jaya, M. Sudhakar, S. N. Kumar and A. Venugopal, *RSC Adv.*, 2015, **5**, 9044–9049; (d) K. Shimizu, S. Kanno and K. Kon, *Green Chem.*, 2014, **16**, 3899–3903; (e) E. F. Mai, M. A. Machado, T. E. Davies, J. A. Lopez-Sanchez and V. Teixeira da Silva, *Green Chem.*, 2014, **16**, 4092–4097; (f) Y. Yao, Z. Wang, S. Zhao, D. Wang, Z. Wu and M. Zhang, *Catal. Today*, 2014, **234**, 245–250; (g) B. Putrakumar, N. Nagaraju, V. P. Kumar and K. V. R. Chary, *Catal. Today*, 2015, **250**, 209–217; (h) X. Tang, L. Hu, Y. Sun, G. Zhao, W. Hao and L. Lin, *RSC Adv.*, 2013, **3**, 10277–10284; (i) A. M. Hengne, S. B. Kamble and C. V. Rode, *Green Chem.*, 2013, **15**, 2540–2547; (j) H. Zhou, J. Song, H. Fan, B. Zhang, Y. Yang, J. Hu, Q. Zhu and B. Han, *Green Chem.*, 2014, **16**, 3870–3875.
- (a) I. T. Horvath, *Green Chem.*, 2008, **10**, 1024–1028; (b) D. Fegyverneki, L. Orha, G. Lang and I. T. Horvath, *Tetrahedron Lett.*, 2010, **66**, 1078–1081; (c) A. Strádi, M. Molnár, M. Óvári, G. Dibó, F. U. Richter and L. T. Mika, *Green Chem.*, 2013, **15**, 1857–1862; (d) E. I. Gürbüz, J. M. R. Gallo, D. M. Alonso, S. G. Wettstein, W. Y. Lim and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2013, **52**, 1270–1274; (e) G. Strappaveccia, L. Luciani, E. Bartollini, A. Marrocchi, F. do Pizzo and L. Vaccaro, *Green Chem.*, 2015, **17**, 1071–1076.
- (a) I. T. Horvath, H. Mehdi, V. Fabos, L. Boda and L. T. Mika, *Green Chem.*, 2008, **10**, 238–242; (b) Á. Bereczky, K. Lukács, M. Farkas and S. Dóbbé, *Nat. Resour.*, 2014, **5**, 177–191.
- (a) W. Luo, M. Sankar, A. M. Beale, Q. He, C. J. Kiely, P. C. A. Bruijninx and B. M. Weckhuysen, *Nat. Commun.*, 2015, **6**, 6540; (b) H. Mehdi, V. Fabos, R. Tuba, A. Bodor, L. T. Mika and I. T. Horvath, *Top. Catal.*, 2008, **48**, 49–54; (c) M. Li, G. Li, N. Li, A. Wang, W. Dong, X. Wang and Y. Cong, *Chem. Commun.*, 2014, **50**, 1414–1416.
- L. E. Manzer, *Appl. Catal., A*, 2004, **272**, 249–256.
- (a) J. P. Lange, J. Z. Vestering and R. J. Haan, *Chem. Commun.*, 2007, 3488–3490; (b) K. Yan, T. Lafleur, X. Wu, J. Chai, G. Wu and X. Xie, *Chem. Commun.*, 2015, **51**, 6984–6987.
- J. C. Serrano-Ruiz, D. J. Braden, R. M. West and J. A. Dumesic, *Appl. Catal., B*, 2010, **100**, 184–189.
- J. C. Serrano-Ruiz, D. Wang and J. A. Dumesic, *Green Chem.*, 2010, **12**, 574–577.
- J. Q. Bond, D. M. Alonso, D. Wang, R. M. West and J. A. Dumesic, *Science*, 2010, **327**, 1110–1114.
- J. P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke and H. Gosselink, *Angew. Chem., Int. Ed.*, 2010, **49**, 4479–4483.
- (a) J. Q. Bond, D. Martin Alonso, R. M. West and J. A. Dumesic, *Langmuir*, 2010, **26**, 16291–16298; (b) J. Q. Bond, D. Wang, D. M. Alonso and J. A. Dumesic, *J. Catal.*, 2011, **2**, 290–299.
- Y. Zhao, Y. Fu and Q. X. Guo, *Bioresour. Technol.*, 2012, **114**, 740–744.
- M. Mascal, S. Dutta and I. Gandarias, *Angew. Chem., Int. Ed.*, 2014, **53**, 1854–1857.
- (a) C. O. Cervantes and J. J. García, *Inorg. Chim. Acta*, 2013, **397**, 124–128; (b) M. Sudhakar, M. L. Kantam, V. S. Jaya, R. Kishore, K. V. Ramanujachary and A. Venugop, *Catal. Commun.*, 2014, **50**, 101–104; (c) D. Xianlong, L. Yongmei, W. Jianqiang, C. Yong and F. Kangnian, *Cuihua Xuebao*, 2013, **34**, 993–1001; (d) L. Deng, J. Li, D. M. Lai, Y. Fu and Q. X. Guo, *Angew. Chem., Int. Ed.*, 2009, **48**,

- 6529–6532; (e) L. Deng, Y. Zhao, J. A. Li, Y. Fu, B. Liao and Q. X. Guo, *ChemSusChem*, 2010, 3, 1172–1175; (f) R. Handana, D. Chunai, C. B. Rasrendra, B. Girisuta and H. J. Heeres, *Green Chem.*, 2009, 11, 1247–1255; (g) Z. P. Yan, L. Lin and S. J. Liu, *Energy Fuels*, 2009, 23, 3853–3858; (h) X. L. Du, L. He, S. Zhao, Y. M. Liu, Y. Cao, H. Y. He and K. N. Fan, *Angew. Chem., Int. Ed.*, 2011, 50, 7815–7819.
- 20 R. A. Bourne, J. G. Steven, J. Kie and M. Poliakoff, *Chem. Commun.*, 2007, 4632–4634.
- 21 A. M. R. Galleti, C. Antonetti, V. De Luise and M. Martinelli, *Green Chem.*, 2012, 14, 688–694.
- 22 S. G. Wettstein, J. Q. Bond, D. M. Alonso, H. N. Phamb, A. K. Datye and J. A. Dumesic, *Appl. Catal., B*, 2012, 117–118, 321–329.
- 23 R. Rodiansono, S. Khairi, T. Hara, N. Ichikuni and S. Shimazu, *Catal. Sci. Technol.*, 2012, 2, 2139–2145.
- 24 R. Rodiansono, T. Hara, N. Ichikuni and S. Shimazu, *Chem. Lett.*, 2012, 41, 769–771.
- 25 R. Rodiansono, T. Hara, N. Ichikuni and S. Shimazu, *Bull. Chem. React. Eng. Catal.*, 2014, 9(1), 53–59.
- 26 (a) T. Tsuchida and N. Ichikawa, *React. Solids*, 1989, 7, 207–217; (b) S. D. Vaidya and N. V. Thakkar, *J. Phys. Chem.*, 2001, 62, 977–986; (c) Z. S. Wittmann, E. Kantor, K. Belafi, L. Peterfy and L. P. Farkas, *Talanta*, 1992, 39, 1583–1586.
- 27 (a) C. Sweegers, H. C. de Coninck, H. Meekes, W. J. P. van Enkevort, I. D. K. Hiralal and A. Rijkeboer, *J. Cryst. Growth*, 2001, 233, 567–582; (b) C. Sweegers, H. C. de Coninck, H. Meekes, W. J. P. van Enkevort, I. D. K. Hiralal and A. Rijkeboer, *Appl. Surf. Sci.*, 2002, 187, 218–234; (c) G. Lefèvre and M. Fedoroff, *Mater. Lett.*, 2002, 56, 978–983.
- 28 (a) H. D. Ruan, R. L. Frost and J. T. Klopogge, *J. Raman Spectrosc.*, 2001, 32(9), 745–750; (b) H. D. Ruan, R. L. Frost, J. T. Klopogge and L. Duong, *Spectrochim. Acta, Part A*, 2002, 58, 265–272.
- 29 S. Cava, S. M. Tebcherani, I. A. Souza, S. A. Pianaro, C. A. Paskocimas, E. Longo and J. A. Varela, *Mater. Chem. Phys.*, 2007, 103, 394–399.
- 30 (a) C. Michel, J. Zaffran, A. M. Ruppert, J. Matras-Michalsk, M. Jędrzejczyk, J. Grams and P. Sautet, *Chem. Commun.*, 2014, 50, 12450–12453; (b) C. Michel and P. Gallezot, *ACS Catal.*, 2015, 5, 4130–4132; (c) C. Michel, F. Auneau, F. Delbecq and P. Sautet, *ACS Catal.*, 2011, 1(10), 1430–1440; (d) D. Loffreda, C. Michel, F. Delbecq and P. Sautet, *J. Catal.*, 2013, 308, 374–385.
- 31 J. Tan, J. Cui, T. Deng, X. Cui, G. Ding, Y. Zhu and Y. Li, *ChemCatChem*, 2015, 7, 508–512.
- 32 Sn/AlOH was prepared by an impregnation method at room temperature (Sn feeding amount was 4.07 mmol g⁻¹) followed by H₂ treatment at 673 K for 1 h.
- 33 Ni-In/AlOH, Ni-Ag/AlOH and Ni-Zr/AlOH catalysts gave LA conversion of 57%, 56% and 53%, respectively (Table S2, entries 1–3, ESI†). Other second metals such as vanadium (V) and niobium (Nb) in Ni-V/AlOH and Ni-Nb/AlOH catalysts showed very low conversion of LA under the same reaction conditions (Table S2, entries 4 and 5, ESI†). These catalysts were prepared in a similar way to the Ni-Sn(x)/AlOH catalysts.
- 34 J. Petro, A. Bota, K. Laszlo, H. Beyer, E. Kalman and I. Dódony, *Appl. Catal., A*, 2000, 190, 73–86.
- 35 S. Lowell, J. E. Shields, M. A. Thomas and M. Thommes, *Characterization of porous solids and powders: surface area, pore size and density*, Kluwer Academic Publishers, Netherlands, 2004, ch. 8.
- 36 (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.
- 37 C. O. Depboylu, S. Yilmaz and S. Akkurt, *Int. J. Chem. React. Eng.*, 2011, 9, A27.