

Research Article

# Catalytic Hydrogenation of Levulinic Acid in Water into $\gamma$ -Valerolactone over Bulk Structure of Inexpensive Intermetallic Ni-Sn Alloy Catalysts

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Received: 26th February 2015; Revised: 16th April 2015; Accepted: 22nd April 2015

## Abstract

A bulk structure of inexpensive intermetallic nickel-tin (Ni-Sn) alloys catalysts demonstrated highly selective in the hydrogenation of levulinic acid in water into  $\gamma$ -valerolactone. The intermetallic Ni-Sn catalysts were synthesized via a very simple thermochemical method from non-organometallic precursor at low temperature followed by hydrogen treatment at 673 K for 90 min. The molar ratio of nickel salt and tin salt was varied to obtain the corresponding Ni/Sn ratio of 4.0, 3.0, 2.0, 1.5, and 0.75. The formation of Ni-Sn alloy species was mainly depended on the composition and temperature of H<sub>2</sub> treatment. Intermetallics Ni-Sn that contain Ni<sub>3</sub>Sn, Ni<sub>3</sub>Sn<sub>2</sub>, and Ni<sub>3</sub>Sn<sub>4</sub> alloy phases are known to be effective heterogeneous catalysts for levulinic acid hydrogenation giving very excellent  $\gamma$ -valerolactone yield of >99% at 433 K, initial H<sub>2</sub> pressure of 4.0 MPa within 6 h. The effective hydrogenation was obtained in H<sub>2</sub>O without the formation of by-product. Intermetallic Ni-Sn(1.5) that contains Ni<sub>3</sub>Sn<sub>2</sub> alloy species demonstrated very stable and reusable catalyst without any significant loss of its selectivity. © 2015 BCREC UNDIP. All rights reserved.

**Keywords:** intermetallic nickel tin; Ni<sub>3</sub>Sn; Ni<sub>3</sub>Sn<sub>2</sub>; Ni<sub>3</sub>Sn<sub>4</sub>; levulinic acid;  $\gamma$ -valerolactone; hydrogenation

**How to Cite:** Rodiansono, R., Astuti, M.D., Ghofur, A., Sembiring, K.C. (2015). Catalytic Hydrogenation of Levulinic Acid in Water into  $\gamma$ -Valerolactone over Bulk Structure of Inexpensive Intermetallic Ni-Sn Alloy Catalysts. *Bulletin of Chemical Reaction Engineering & Catalysis*, 10 (2): 192-200. (doi:10.9767/bcrec.10.2.8284.192-200)

**Permalink/DOI:** <http://dx.doi.org/10.9767/bcrec.10.2.8284.192-200>

## 1. Introduction

$\gamma$ -valerolactone (GVL) has been identified as one of the most promising renewable molecules that can be converted into a variety of intermediate chemicals, from which a diverse range of

biofuels as well as commodities and fine chemicals [1-7]. GVL has been accepted to use a solvent for lacquers, insecticides and adhesives and some use in cutting oil, brake fluid and as a coupling agent in dye bath [2-4].

Previously, GVL is typically obtained from LA by catalytic hydrogenations in liquid phase in a batch reactor system. High temperature, high H<sub>2</sub> pressures, and noble metal-based catalysts were required to obtain high yield of GVL [4-9]. Christian *et al.* have reported LA hydro-

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generation at 493 K, 48 bar H<sub>2</sub> pressure over Raney Ni catalyst to give 94% yield of GVL, while over copper-chromite catalyst at 523 K and 202 bar H<sub>2</sub> pressure, resulted in a complex mixture of products composed of 11% GVL, 44% 1,4-PeD (1,4-pentanediol) and 22% water containing small amount of methyl tetrahydrofuran (MTHF) [8]. Schulte and Thomas reported the hydrogenation of LA by using platinum oxide catalyst in different organic solvents for 44 h, at 3 atm of H<sub>2</sub> to give 87% GVL yield [9]. Recent reported results showed that even though reaction conditions has been mild conditions however the employing noble metal catalysts are required to achieve high yield of GVL [10-12]. Bourne et al. used supercritical CO<sub>2</sub> for the hydrogenation of LA over 5% Ru/SiO<sub>2</sub> at 473 K and 100 bar hydrogen pressure with high yield of GVL [10]. The liquid phase hydrogenation of LA to GVL has been reported over 5% Ru/C in a batch reactor and obtained 99% selectivity to GVL at 92% conversion of LA at 403 K and 12 bar H<sub>2</sub> pressure in methanol solvent [11]. Most recently, Upare et al. reported the vapor phase hydrogenation of LA to VGL in continuous down flow over 5% Ru/C with almost 100% GVL selectivity [12]. Although several works have been reported as described above, the noble metal catalysts such as Rh, Ru, Pd, and Pt were mainly employed making it high cost and less favorable in point of view of industrial application. Therefore the search of a new facile, cost effective without the employing of noble metal catalyst has really been attracted so far.

We have reported a facile and efficient synthesis method of bimetallic Ni-Sn alloys both bulk and supported without organometallic tin precursor as starting materials via hydrothermal route from two types nickel metal precursor and its catalytic performances on [13,14] and selective hydrogenation of biomass-derived furfural into furfuryl alcohol with excellent activity and selectivity [15]. Firstly, from nickel chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O) and tin chloride dihydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O) to produce bulk and supported Ni-Sn alloy catalysts [13] and secondly, from Raney nickel supported on aluminium hydroxide (R-Ni/AlOH) and tin chloride dihydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O) to obtain Ni-Sn alloy supported on aluminium hydroxide (Ni-Sn/AlOH) [14,15] and applied for the chemoselective hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds into unsaturated alcohol and selective hydrogenation of biomass-derived furfural into furfuryl alcohol with excellent activity and selectivity.

In this present report, we continue to investigate the catalytic behaviour of bulk structure

of intermetallic Ni-Sn alloy in selective hydrogenation of biomass-derived levulinic acid (LA) in water. Bulk structure intermetallic Ni-Sn catalysts were synthesised according to our previous procedure that has been reported elsewhere [13]. Five types of intermetallic Ni-Sn with different Ni/Sn molar ratio were synthesised and the effect of reaction parameters such as temperature, initial H<sub>2</sub> pressure, time profile, solvent used, and reusability test are investigated. A commercially available of 5% Pd/C was also used as a catalyst for hydrogenation of LA to GVL as a comparison.

## 2. Materials and Methods

### 2.1. Chemicals

All chemicals were used as received and purchased from WAKO Pure Chemical unless otherwise stated nickel(II) chloride hexahydrate, 98%; tin(II) chloride dihydrate, 99.9%; aluminum hydroxide, and ethanol, 99.5%.

### 2.2. Synthesis Ni-Sn Alloys

A general procedure of the synthesis of Ni-Sn alloy with Sn/Ni ratio of 0.67 is described as follows according to our procedure that had been reported elsewhere [13]. A typically NiCl<sub>2</sub>·6H<sub>2</sub>O (7.2 mmol) was dissolved in deionised water (denoted as solution A), and SnCl<sub>2</sub>·2H<sub>2</sub>O (4.8 mmol) was dissolved in ethanol/2-methoxy ethanol (2:1) (denoted as solution B) at room temperature. Solutions A and B were mixed at room temperature; the temperature was subsequently raised to 323 K and the mixture was stirred for 12 h. The pH of the mixture was adjusted to 12 through the dropwise addition of an aqueous solution of NaOH (3.1 M). The mixture was then placed into a sealed-Teflon autoclave for the hydrothermal reaction at 423 K for 24 h. The resulting black precipitate was filtered, washed with distilled water, and then dried under vacuum overnight. Prior to the catalytic reaction, the obtained black powder was treated under hydrogen at 673K for 90 min.

### 2.3. Catalyst Characterization

Powder X-ray diffraction (XRD) measurements were recorded on a Mac Science M18XHF instrument using monochromatic CuK $\alpha$  radiation ( $\lambda = 0.15418$  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<sup>-1</sup> ( $a1 = 0.154057$  nm,  $a2 = 0.154433$  nm). 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 ( $S_{\text{BET}}$ ) and pore volume ( $V_{\text{p}}$ ) were measured using  $\text{N}_2$  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 [16]. SEM images of the synthesized catalysts were taken on a JEOL JSM-610SEM after the samples were coated using a JEOL JTC-1600 autofine coater.

The  $\text{H}_2$  uptake was determined through irreversible  $\text{H}_2$  chemisorption. After the catalyst was heated at 393 K under vacuum for 30 min, it was treated at 673 K under  $\text{H}_2$  for 30 min. The catalysts were subsequently cooled to room temperature under vacuum for 30 min. The  $\text{H}_2$  measurement was conducted at 273 K, and  $\text{H}_2$  uptake was calculated according to the method described in the literature [17, 18].

#### 2.4. General Procedure for the Transformation of LA

Catalyst (0.05 g), LA (2.0 mmol),  $\text{H}_2\text{O}$  (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  $\text{H}_2$  was introduced into the reactor with an initial  $\text{H}_2$  pressure of 4.0 MPa at room temperature, the temperature of the reactor was raised to 433 K. After 6 h, the conversion of LA and the yield of GVL were determined via GC analysis. For reusability test, the used Ni-Sn(1.5) 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  $\text{H}_2\text{O}$  was performed on a Shimadzu GC-8A equipped with a flame ionization detector and with Silicone OV-101 packing. A Shimadzu 14A with a flame ionization detector equipped with an InertCap® capillary column was used for product analyses for the hydrogenation of LA in alcohol or EtOH/ $\text{H}_2\text{O}$  solvents. Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-17B equipped with a thermal conductivity detector and with an RT- $\beta$ DEXsm capillary column.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a JNM-AL400 spectrometer at 400 MHz and 101 MHz, respectively; samples were dissolved in chloroform- $d_1$

or  $\text{D}_2\text{O}$  with TMS as an internal standard. Products were confirmed by the comparison of their GC retention time, mass,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra with those of authentic samples

### 3. Results and Discussion

#### 3.1. BET Surface Area and Ni Active Surface Area

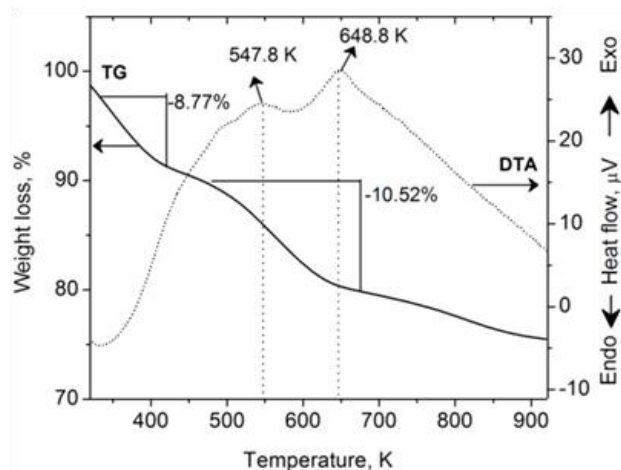
Bulk composition, identified Ni-Sn alloy phases, specific surface area  $S_{\text{BET}}$ , and crystallite sizes of the synthesized Ni-Sn alloy catalysts are summarized in Table 1. The bulk composition was determined by ICP-AES and the results are closely to the nominal value of the precursors. Five types of intermetallic Ni-Sn systems were successfully synthesized with Ni/Sn ratio of 4.0, 3.0, 2.0, 1.5, and 0.75.  $\text{H}_2$  maximum uptake for Ni/Sn ratio of 3.0, 1.5, and 0.75 was  $12 \mu\text{mol}\cdot\text{g}^{-1}$ ,  $9 \mu\text{mol}\cdot\text{g}^{-1}$ , and  $5 \mu\text{mol}\cdot\text{g}^{-1}$ , respectively. The increase of tin amount in Ni-Sn system enhanced  $S_{\text{BET}}$  significantly, but reduced the  $\text{H}_2$  uptake reflecting the decrease of the Ni surface activity due to the presence of Sn or the formation of Ni-Sn alloy. We found that nickel active surface area ( $\text{SNi}$ ) was  $2.9 \text{ m}^2\cdot\text{g}^{-1}_{\text{cat}}$ ,  $2.0 \text{ m}^2\cdot\text{g}^{-1}_{\text{cat}}$ , and  $0.3 \text{ m}^2\cdot\text{g}^{-1}_{\text{cat}}$ , respectively. It should be noted that our results are comparable to the previous study reported by Komatsu *et al.* [19] and Takenaka [21]. The average Ni-Sn crystallite sizes was derived from Scherrer's equation to the selected diffraction peaks of Ni-Sn alloy face. In the case of Ni/Sn ratio of 4.0 and 3.0  $\text{Ni}_3\text{Sn}(201)$  crystallite sizes was 12 nm and 14 nm, respectively. For Ni/Sn ratio of 2.0 and 1.5,  $\text{Ni}_3\text{Sn}_2(101)$  crystallite sizes was 28 nm and 27 nm, respectively, and  $\text{Ni}_3\text{Sn}_4(112)$  of Ni/Sn ratio of 0.75 was 23 nm.

TG-DTA measurements were carried out for the bulk Ni-Sn(1.5) sample that obtained after hydrothermal at 423 K for 24 h and the results are shown in Figure 1. TG curves showed two successive weight loss of 8.77% at 333-420 K and 10.52% at 473-675 K which can be attributed to the evaporation of  $\text{H}_2\text{O}$  and solvent and transformation of remained  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  and  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  into NiO and SnO, respectively [20, 21]. DTA curves confirmed that two exothermic peaks were observed at 548.7 K and 648.8 K which occurred simultaneously with the weight loss as shown in TG curves. Furthermore, the less of weight loss during pre-heated at 473-673 K indicated that Ni-Sn alloy formed during a hydrothermal treatment at 423 K for 24 h (Figure 1).

Low-magnification scanning electron micrographs of Ni-Sn(1.5) after  $\text{H}_2$  treatment at 673

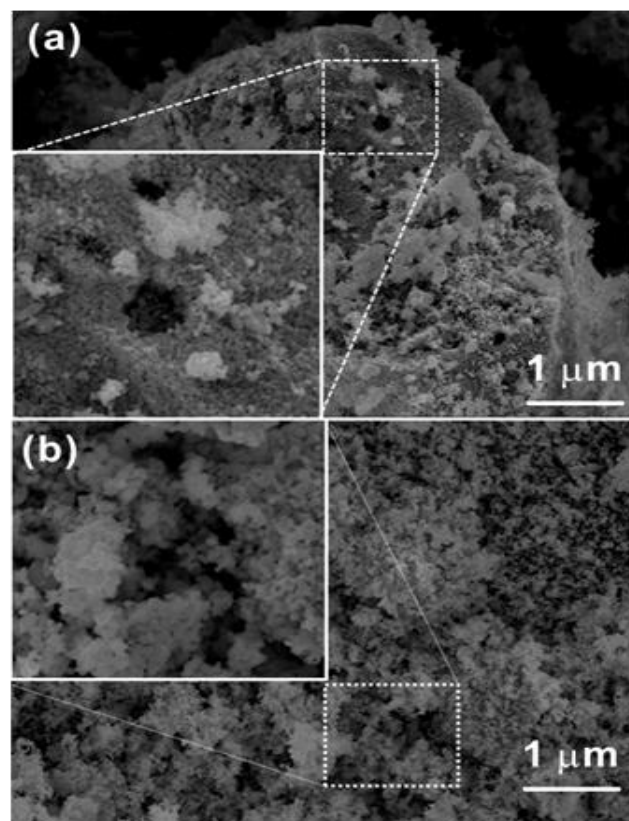
K for 1.5 h showed typical granular characteristics of Ni-Sn alloy phases (Figure 2(a)). High-magnification micrographs of the Ni-Sn(1.5) fresh catalyst (Figure 2a-inset) show a predominant porous region and a less-extensive solid phase distributed on top of the recovered Ni-Sn(1.5) catalyst appears to have a predominant porous region and a diffuse phase covering parts of the porous region (Figure 2b-inset).

The XRD patterns of the synthesized Ni-Sn alloys with Ni/Sn ratio of 4.0, 3.0, 2.0, 1.5, and 0.75 after H<sub>2</sub> treatment at 673 K for 1 h are shown in Figure 3. Single phase of intermetallic Ni-Sn was formed for each Ni/Sn ratio. No diffraction peaks of metallic nickel or tin were



**Figure 1.** TG-DTA profiles for the obtained Ni-Sn(1.5) from hydrothermal treatment at 423 K for 24 h

observed in Figure 3a-e. In the case of Ni/Sn ratio of 2.0 and 1.5, a single phase of Ni<sub>3</sub>Sn<sub>2</sub> alloy was formed (Figure 3a-b), while for Ni/Sn ratio of 4.0 and 3.0 gave a single phase Ni<sub>3</sub>Sn alloy (Figure 3c-d) and single phase of Ni<sub>3</sub>Sn<sub>4</sub> alloy was obtained for Ni/Sn ratio of 0.75 (Figure 3e).



**Figure 2.** SEM images of Ni-Sn(1.5) (a) fresh and (b) recovered after the reaction.

**Table 1.** Bulk composition, identified Ni-Sn alloy phases,  $S_{BET}$ , and crystallite sizes of the synthesised intermetallic Ni-Sn catalysts

Entry	Bulk composition <sup>a</sup>	Main alloy phase <sup>b</sup>	$S_{BET}^c/m^2.g^{-1}$	H <sub>2</sub> uptake <sup>d</sup> / μmolg <sup>-1</sup>	Crystallite sizes <sup>e</sup> /nm
1	Ni-Sn (4.0) (Ni <sub>79.9</sub> Sn <sub>20.1</sub> )	Ni <sub>3</sub> Sn	5.2	Nd	12 <sup>f</sup>
2	Ni-Sn(3.0) (Ni <sub>74.9</sub> Sn <sub>25.1</sub> )	Ni <sub>3</sub> Sn	5.1	12.0 (2.9)	14 <sup>f</sup>
3	Ni-Sn(2.0) (Ni <sub>66.2</sub> Sn <sub>33.8</sub> )	Ni <sub>3</sub> Sn <sub>2</sub>	19.7	Nd	28 <sup>g</sup>
4	Ni-Sn(1.5) (Ni <sub>59.9</sub> Sn <sub>40.1</sub> )	Ni <sub>3</sub> Sn <sub>2</sub>	12.1	9.0 (2.0)	27 <sup>g</sup>
5	Ni-Sn(0.75) (Ni <sub>42.7</sub> Sn <sub>57.3</sub> )	Ni <sub>3</sub> Sn <sub>4</sub>	57.0	5.0 (0.3)	23 <sup>h</sup>

<sup>a</sup>Determined by ICP-AES. <sup>b</sup>Based on the crystallographic data ICDD-JCPDS. <sup>c</sup>Determined by N<sub>2</sub> adsorption at 77 K. <sup>d</sup>Total H<sub>2</sub> uptake at 273 K (noted after corrected for physical and chemical adsorption); the value in the parenthesis is nickel active surface area ( $S_{Ni}$ ); nd = not determined. <sup>e</sup>Ni-Sn alloy crystallite size derived from the Scherrer's equation. <sup>f</sup>Ni<sub>3</sub>Sn(201). <sup>g</sup>Ni<sub>3</sub>Sn<sub>2</sub>(101). <sup>h</sup>Ni<sub>3</sub>Sn<sub>4</sub>(112).

It should be noted that our method was able to synthesize a single phase Ni-Sn alloy at 673 K which was much lower than the arc-melting or CVD methods [19, 22].

### 3.2. Selective Hydrogenation of LA to GVL

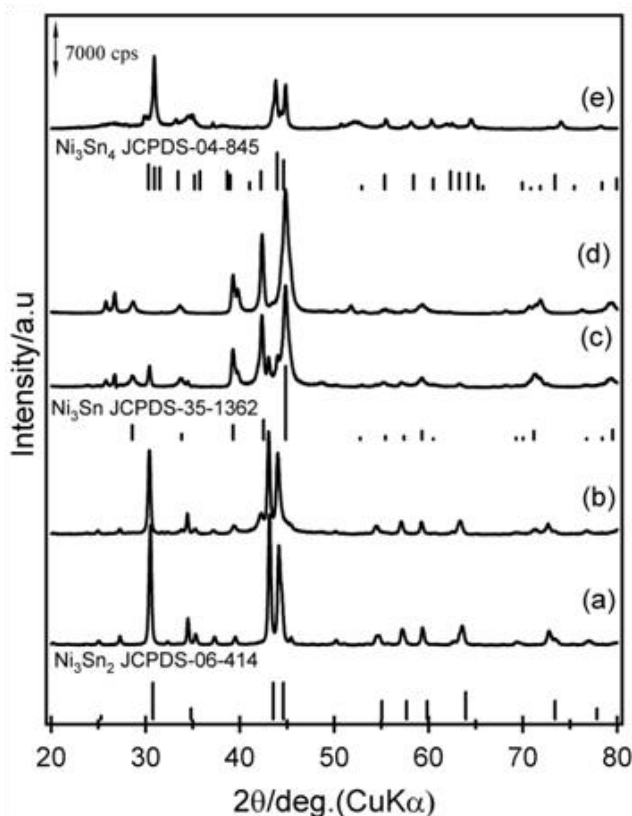
The catalytic activity of the synthesised Ni-Sn alloys was evaluated in the selective hydrogenation of LA to GVL in water according to the reaction of Scheme 1. The results of the selective hydrogenation of LA to GVL over various Ni-Sn alloy catalysts are summarized in Table 2.

An excellent selectivity of single phase Ni-Sn alloy catalysts was obtained in the aqueous phase hydrogenation of LA to GVL at 433 K, initial H<sub>2</sub> pressure of 4.0 MPa for 6 h. Single phase of Ni<sub>3</sub>Sn (Ni/Sn ratio of 4.0 and 3.0, entries 1, 2), Ni<sub>3</sub>Sn<sub>2</sub> (Ni/Sn ratio of 2.0 and 1.5, entries 3, 4), and Ni<sub>3</sub>Sn<sub>4</sub> (Ni/Sn ratio of 0.75, entry 5) were superior catalyst compared to R-Ni/AlOH and commercially available of Pd/C at the same conditions. In the case of Ni<sub>3</sub>Sn<sub>2</sub> with Ni/Sn ratio of 1.4 that obtained from hydrothermal of the mixture of R-Ni/AlOH and

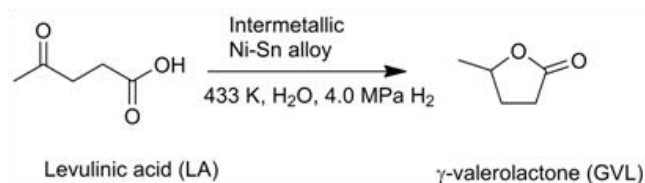
**Table 2.** Results of the selective hydrogenation of LA to GVL by means of various intermetallic Ni-Sn catalysts

Entry	Catalyst <sup>a</sup>	Conv. <sup>b</sup> /%	Yield <sup>c</sup> /%
1	Ni-Sn(4.0)	>99	>99
2	Ni-Sn(3.0)	>99	>99
3	Ni-Sn(2.0)	96	96
4	Ni-Sn(1.5)	>99	>99
5	Ni-Sn(0.75)	79	79
6	Ni-Sn(1.4)/AlOH <sup>d</sup>	97	97
7	R-Ni/AlOH <sup>e</sup>	99	99
8	Pd/C <sup>f</sup>	75	75

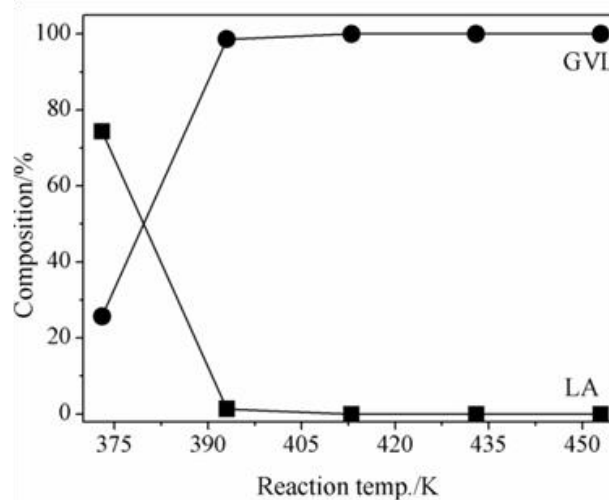
**Reaction conditions:** catalyst, 0.042 g; LA, 1.2 mmol; H<sub>2</sub>O, 3.5 ml; initial H<sub>2</sub> pressure, 4.0 MPa; temp. 433 K; reaction time, 6 h. <sup>a</sup>Determined by ICP-AES. <sup>b</sup>Determined by GC using an internal standard technique. <sup>c</sup>R-Ni/AlOH and SnCl<sub>2</sub>·2H<sub>2</sub>O were used as starting materials, the value in the parenthesis is Ni/Sn molar ratio [14]. <sup>d</sup>R-Ni/AlOH was prepared by alkali leaching of Raney Ni-Al alloy using a dilute aqueous solution of NaOH according to Petro *et al.* [23]. <sup>e</sup>Commercially available of Pd/C (5 wt%) and used as received



**Figure 3.** XRD patterns of the synthesized Ni-Sn alloys with different Ni/Sn ratio of (a) 1.5, (b) 2.0, (c) 3.0, (d) 4.0, and (e) 0.75 after H<sub>2</sub> treatment at 673 K for 1 h



**Scheme 1.** Reaction pathways of LA hydrogenation by intermetallic Ni-Sn alloy catalysts



**Figure 4.** Effect of reaction temperature on the product composition over Ni-Sn (1.5) alloy catalyst. Initial H<sub>2</sub> pressure of 4.0 MPa and reaction time of 6 h.

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  [14], the conversion of LA was 97% with GVL yield of 97% (entry 6). Aluminium hydroxide-supported Raney nickel (R-Ni/AlOH) also exhibited a substantial high selectivity towards GVL formation with the respect of 99% (entry 7). However, the commercially available of Pd/C catalyst gave 75% of LA with 75% GVL yield (entry 8).

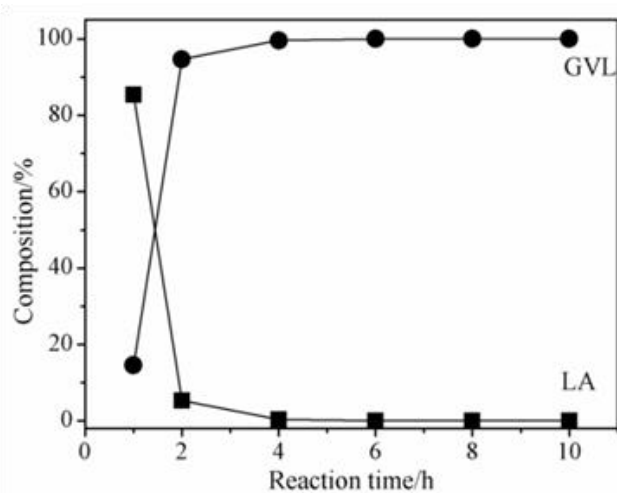
In order to understand the insight into the specific catalytic reaction of the bulk structure of intermetallic Ni-Sn alloy system, the aqueous phase hydrogenation of LA to GVL at different reaction conditions was also investigated. The effect of reaction temperature, initial  $\text{H}_2$  pressure, time profile, and effect of solvent were evaluated for Ni-Sn alloy with Ni/Sn ratio of 1.5.

### 3.2.1. Effect of Reaction Temperature

The effect of reaction temperature on the product composition in the selective hydrogenation of LA to GVL by means of Ni-Sn(1.5) alloy catalyst is shown in Figure 4. Reaction temperature was varied in the range of 373 K to 435 K at the initial  $\text{H}_2$  pressure of 4.0 MPa for 6 h. As increase of reaction temperature from 373 K to 403 K, the conversion of LA remarkably increased from 27% to 99%. LA was converted to GVL completely at 413 K after 6 h. We noted here that no by-products were formed even reaction temperature was raised up to 453 K.

### 3.2.2. Time Profile

We also examined the time profile in the selective hydrogenation of LA to GVL at 453 K,



**Figure 5.** Time profile of the selective hydrogenation of LA to GVL over Ni-Sn(1.5) alloy catalyst at reaction temperature of 433 K and initial  $\text{H}_2$  pressure of 4.0 MPa

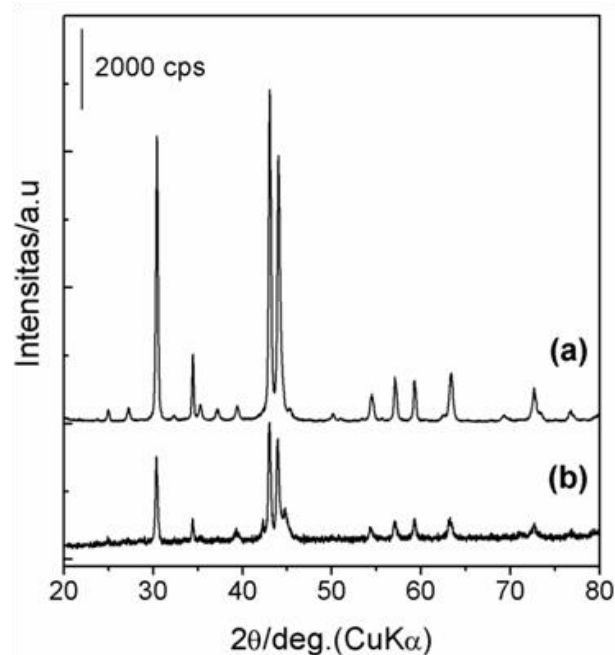
initial  $\text{H}_2$  pressure of 4 MPa for 1-10 h and the composition of the reaction product are shown in Figure 5. The LA conversion within 1 h was 15% and remarkably increased to 95% LA after 2 h at the same reaction condition. LA was converted completely after 6 h with yield and selectivity of >99%. No by-product was observed within the reaction time of 1 h to 10 h.

### 3.2.3. Effect of Initial $\text{H}_2$ Pressure

The effect initial  $\text{H}_2$  pressure on the product composition in the selective hydrogenation of LA to GVL by means of Ni-Sn(1.5) alloy catalyst is shown in Table 3. Initial  $\text{H}_2$  pressure was varied in the range of 1.0-5.0 MPa. At the initial  $\text{H}_2$  pressure of 1 MPa, only 8% of LA was converted (entry 1). The LA conversion remarkably increased almost 10 times from 7.8% to 79% when initial  $\text{H}_2$  pressure increased from 1 MPa to 2.0 MPa (entry 2). At the initial  $\text{H}_2$  pressure of 4.0 MPa, an excellent yield of GVL (>99%) at the completed reaction was achieved (entry 4). Further increase of the initial  $\text{H}_2$  pressure up to 5.0 MPa, the LA conversion slightly decreased to 88% at the same reaction condition (entry 5).

### 3.2.4. Solvent Effect

The effect of solvent used in the selective hydrogenation of LA to GVL by means of Ni-Sn



**Figure 6.** XRD patterns of (a) the recovered Ni-Sn(1.5) and (b) after  $\text{H}_2$  treatment at 673 K for 1 h.

(1.5) alloy catalyst was carried out and the product composition are summarized in Table 4. In ethanol system, 97% of LA was converted and gave 86% of GVL and 14% of by-products (entry 1). LA conversion and GVL selectivity increased significantly to 99% and 97%, respectively when the mixture of ethanol/H<sub>2</sub>O with volume ratio of 1.5/2.0 was used as a solvent (entry 2). It should be noted that LA conversion and GVL selectivity were >99% when H<sub>2</sub>O was used as a solvent (entry 3).

### 3.2.5. Reusability Test

A reusability test was performed on the Ni-Sn(1.5) catalyst, and the results are summarised in Table 5. The used Ni-Sn(1.5) catalyst was easily separated by either simple centrifugation or filtration after the reaction. The activity of the catalyst decreased while the high selectivity was maintained for at least four con-

secutive runs. Treatment of the used Ni-Sn(1.5) catalyst (after five runs) with H<sub>2</sub> at 673 K for 1 h restored the catalyst's original activity and selectivity.

XRD analysis of the recovered Ni-Sn(1.5) catalyst after the third run of the reaction confirmed that the Ni-Sn alloy structure was maintained. No change Ni-Sn alloy species was observed as shown in Figure 6. The amount of Ni and Sn that leached into the reaction solution was 1.58% and 5.3% after four runs, respectively.

### 4. Conclusions

Five types bulk structure of intermetallic Ni-Sn with different Ni/Sn molar ratio were synthesised via a thermochemical method. Intermetallics Ni-Sn that contain Ni<sub>3</sub>Sn, Ni<sub>3</sub>Sn<sub>2</sub>, and Ni<sub>3</sub>Sn<sub>4</sub> alloy phases are known to be effective heterogeneous catalysts for levulinic acid (LA)

**Table 3.** Effect of initial H<sub>2</sub> pressure on the product composition over Ni-Sn(1.5) alloy catalyst. Reaction temperature of 433 K and reaction time of 6 h

Entry	Initial H <sub>2</sub> pressure/MPa	Conv. <sup>a</sup> /%	Selectivity <sup>b</sup> /%	
			GVL	Others <sup>c</sup>
1	1.0	7.8	100	0
2	2.0	79.0	100	0
3	3.0	97.0	100	0
4	4.0	>99	100	0
5	5.0	88.0	100	0

Reaction conditions: catalyst, 0.042 g; LA, 1.2 mmol; solvent, 3.5 ml; initial H<sub>2</sub> pressure, 4.0 MPa; temp. 433 K; reaction time, 6 h. <sup>a</sup>Determined by GC using an internal standard technique. <sup>b</sup>Determined by GC using an internal standard technique. <sup>c</sup>GC area ratio; 1,4-pentanediol (1,4-PeD) and 2-methyltetrahydrofuran (2-MTHF) were detected by GC-MS

**Table 4.** Results of the effect of solvent used in the selective hydrogenation of LA over Ni-Sn(1.5) alloy catalyst.

Entry	Solvent	Conv. <sup>a</sup> /%	Selectivity <sup>b</sup> /%	
			GVL	Others <sup>c</sup>
1	Ethanol	97	86	14
2	Ethanol/H <sub>2</sub> O	99	97	3
3	H <sub>2</sub> O	>99	100	0

Reaction conditions: catalyst, 0.042 g; LA, 1.2 mmol; solvent, 3.5 ml; initial H<sub>2</sub> pressure, 4.0 MPa; temp. 433 K; reaction time, 6 h. <sup>a</sup>Determined by GC using an internal standard technique. <sup>b</sup>Determined by GC using an internal standard technique. <sup>c</sup>GC area ratio, 1,4-pentanediol (1,4-PeD) and 2-methyltetrahydrofuran (2-MTHF) were detected by GC-MS

**Table 5.** Results of reusability test of Ni-Sn(1.5) alloy catalyst in in hydrogenation of LA into GVL

Run	1	2	3	4	5 <sup>a</sup>
Conversion <sup>b</sup> /%	>99	89	78	61	>99
Yield <sup>b</sup> /%	>99	89	78	61	>99

Reaction conditions: catalyst, 0.042 g; LA, 1.2 mmol; solvent, 3.5 ml; initial H<sub>2</sub> pressure, 4.0 MPa; temp. 433 K; reaction time, 6 h. <sup>a</sup>The used catalyst was treated by H<sub>2</sub> at 673 K for 1 h before reaction. <sup>b</sup>Determined by GC using an internal standard technique

hydrogenation giving  $\gamma$ -valerolactone (GVL) yield of >99% at 433 K, initial H<sub>2</sub> pressure of 4.0 MPa within 6 h. The effective hydrogenation was obtained in H<sub>2</sub>O without the formation of by-product. Intermetallic Ni-Sn(1.5) that contains Ni<sub>3</sub>Sn<sub>2</sub> alloy species demonstrated high stability and good reusability without any significant loss of its selectivity.

### Acknowledgments

This work was financially by Kemenristek through Insentif SINas 2014 under contract number of DIPA-042-01.1.427922/2014. We thank to Prof. Shogo Shimazu for kind help in measurement of ICP-AES and XRD analyses, and to Dr. Eng. Indri B. Adilina for <sup>1</sup>H and <sup>13</sup>C NMR analyses.

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