BIDANG ENERGI 1

No.	Waktu	Kode	Judul	Peneliti Utama
RUANG HARUMAN			
	Hari / Tgl: Rabu, 1 Oktober 2014		BIDANG ENERGI	
1	10.00 – 10.30	RT-2014-0096	PENGEMBANGAN SEL SURYA DYE-SENSITIZED MENGGUNAKAN SUBSTRAT FLEKSIBEL UNTUK APLIKASI MOBILE CHARGING	Lia Muliani Pranoto, ST.MT
2	10.30 – 11.00	RT-2014-0422	Desain Prototipe Sel Surya Biohybrid: Kontrol Performansi Penangkapan Energi Cahaya dalam Skala Nano	Tatas Hardo Panintingjati Brotosudarmo
3	11.00 - 11.30	RT-2014-1211	Pengembangan sel surya berbasis dye dengan gel elektrolit hibrid dan proses fabrikasinya dengan teknik roll-printing sederhana	Dr. Rahmat Hidayat
4	11.30 - 12.00	RD-2014-1348	REKAYASA SEL SURYA DENGAN METODE DYE-SENSITIZED BERBASIS KOMPOSIT BACTERIAL CELLULOSE-POLYANILINE	Dini Cahyandari
	12.00 – 13.00	ISOMA		
5	13.00 – 13.30	RD-2014-0146	SINTESIS BIODIESEL DARI LIMBAH MINYAK NABATI TERKATALISIS (H2SO4/ZrO2) DAN (KOH/ ZrO2).	KARNA WIJAYA, DRS,M.ENG,PROF
6	13.30 – 14.00	RT-2014-0174	Produksi Biohidrogen Dari Bagas Tebu Melalui Kinerja Sinergis Enzim-Enzim Pendegradasi Lignoselulosa Diikuti Fermentasi Menggunakan Enterobacter aerogenes	Prof. Dr. Ir. Arief Widjaja, M.Eng
7	14.00 – 14.30	RD-2014-0206	Renewable Gasoline-blend g-Valerolactone (GVL) dari Senyawa Turunan Biomassa Asam Levulinat (LA) untuk Bahan Bakar Bauran Mesin Premium	Dr. Eng. RODIANSONO
8	14.30 – 15.00	RT-2014-0240	PENINGKATAN KINERJA PEMBANGKIT LISTRIK BIOGAS BERBASIS LIMBAH CAIR PABRIK KELAPA SAWIT DENGAN SCALE-UP BIOREAKTOR HIBRID ANAEROBIK DARI 2,5 M3 MENJADI 12,5 M3	Adrianto Ahmad, H., Prof., Dr., MT
	15.00 – 15.30	Rehat Cofee		
9	15.30 – 16.00	RT-2014-0622	Pengembangan Desain Stacking untuk meningkatkan kinerja Proton-exchange Fuel Celll Open Cathode sebagai aplikasi Backup Power	Agus Prasetyo Nuryadi, ST
10	16.00 – 16.30	RT-2014-1136	Pembuatan Membrane Electrode Assembly (MEA) Proton Exchange Membrane Fuel Cell (PEMFC) Kinerja Tinggi dengan Metode Elektrodeposisi dan Penyemprotan untuk Aplikasi Sumber Energi Base Transceiver Station (BTS)	Drs. Dedi Rohendi, M.T
11	16.30 – 17.00	RT-2014-0476	Sistem Penyimpan Hidrogen Dalam Bentuk Partikel Nano Ammonia Borane Untuk Aplikasi Hydrogen Fuel Cell	Ir. Imam Prasetyo,.M.Eng.,PhD

RISTEK

Sertifikat

Sertifikat ini diberikan kepada :

atas partisipasinya sebagai :

PEMAKALAH

Seminar Ilmiah Insentif Riset Sistem Inovasi Nasional

"Membangun Sinergi Riset Nasional untuk Kemandirian Teknologi"

Bandung, 1 - 2 Oktober 2014

Kementerian Riset dan Teknologi
Ketua Panitia

Ir. Ahmad Dading Gunadi, MA

BULK STRUCTURE OF INTERMETALLIC Ni-Sn CATALYSTS FOR HIGHLY SELECTIVE HYDROGENATION OF LEVULINIC ACID IN WATER INTO γ-VALEROLACTONE

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Abstract

Highly selective hydrogenation of biomass-based levulinic acid to γ-valerolactone efficiently catalyzed by single phase Ni-Sn alloy. Ni_3Sn, Ni_3Sn_2, and Ni_3Sn_4 are known to be effective heterogeneous catalysts giving excellence GVL yield of >99% at 433 K, initial H_2 pressure of 4 MPa within 6 h. The effective hydrogenation was obtained in H_2O solvent and no by-product was formed.

Keyword: Ni_3Sn, Ni_3Sn_2, Ni_3Sn_4, levulinic acid, γ-valerolactone

1. Introduction

γ-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 commodity and fine chemicals [1-12]. GVL has been also accepted to use as solvent for lacquers, insecticides and adhesives and some use in cutting oil, brake fluid and as a coupling agent in dye bath [2-4].

GVL is typically obtained from levulinic acid (LA) through catalytic hydrogenations in liquid phase in a batch reactor system. High temperature and high H_2 pressure were required to obtain substantial yield of GVL [14-23]. The yield of 94% GVL at 493 K and 48 bar H_2 pressure has been reported using Raney nickel catalyst in the liquid phase hydrogenation of LA [14]. They have also used copper chromite catalyst to hydrogenate LA at 523 K and 202 bar H_2 pressure, which 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). The hydrogenation of LA has been reported using platinum oxide catalyst in different organic solvents to give 87% GVL after 44 h at 3 bar hydrogen pressure [15]. The hydrogenation of LA in supercritical CO_2 has been studied in presence of Pd, Ru, Re and Pt supported on oxides catalysts and obtained good results with Ru/alumina at 473 K and 200 bar hydrogen pressure [2]. Bourne et al. used supercritical CO_2 for the hydrogenation of LA to GVL over 5%Ru/SiO_2 at 473 K and 100 bar hydrogen pressure [16]. Recently, 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 hydrogen pressure in methanol solvent [17]. 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 [22]. 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.

In this present report, we describe the selective hydrogenation of LA to GVL in by means of Ni-Sn alloy catalysts. We developed a non-precious metal catalyst such as Ni and Sn by alloying with controlled stoichiometric composition corresponding to Ni_3Sn, Ni_3Sn_2,

Ni$_3$Sn$_4$ alloy systems. Aqueous phase hydrogenation of LA was carried out in the batch reactor at range of 27 3-453 K, initial H$_2$ pressure of 1-5 MPa for 2-10 h. We found that Ni-Sn alloy catalysts demonstrated highly selective towards GVL product with the yield and the selectivity of 100%. A commercially available of 5%Pd/C was also used as a catalyst for hydrogenation of LA to GVL as comparison.

2. Experimental section

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%; sodium hydroxide, 99%; ethylene glycol, 95% and ethanol, 95%.

Synthesis Ni-Sn alloys

A general procedure of the synthesis of Ni-Sn alloy with Sn/Ni ratio of 0.67 is described as the follow. NiCl$_2$·6H$_2$O (7.2 mmol) was dissolved in deionized water (denoted as solution A) and SnCl$_2$·2H$_2$O (4.8 mmol) was dissolved in ethanol/2-methoxy ethanol (2:1) (denoted as solution B) at room temperature. Solution A and B were mixed at room temperature, then the temperature was raised to 323 K and stirred for 12 h. The pH of the mixture was adjusted to 12 by addition dropwise of an aqueous solution of NaOH. The mixture then placed in the sealed-Teflon autoclave for hydrothermal processes at 423 K for 24 h. The resulting black precipitate was filtered and washed with distilled water and acetone, and then dried in *vacuo* overnight. Prior to catalytic reaction test, the black solid of Ni-Sn alloys was treated by flowing hydrogen at 673K for 1 h. All catalysts were used in powdery form with granule size of <100 mesh.

Characterizations

Specific surface area (S$_{BET}$) and pore volume (V$_p$) were measured by N$_2$ physisorption at 77 K on the 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 specific surface area by means of the BET equation. The pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of about 0.995. The Barrett–Joyner–Halenda (BJH) approach was used to calculate pore volume and pore size distribution from desorption data [24].

Powder X-ray diffraction was taken on a Mac Science M18XHF instrument using monochromatic CuKα radiation (λ = 0.15418 nm). It was operated at 40 kV and 200 mA with a step width of 0.02^o and a scan speed of 4° min^{-1}. The bulk composition of the catalysts was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), using a SPS1700 HVR of SII instrument. The Ni active surface area (S$_{Ni}$) was determined by H$_2$ chemisorption. After the catalyst was heated at 393 K under vacuum for 30 min, it was heated at 673 K under H$_2$ for 30 min and under vacuo for 30 min, followed by evacuation to room temperature for 30 min. The adsorption of H$_2$ was conducted at 273 K. The S$_{Ni}$ was calculated from the volume of H$_2$ desorbed by assuming an H/Ni stoichiometry of 1 [25, 26].

3. Results and discussion

BET surface area and Ni active surface area

Bulk composition, N$_2$-, H$_2$-adsorption data of the synthesized Ni-Sn alloy catalysts are summarized in Table 1.

Table 1. Bulk composition, N$_2$-,H$_2$-adsorption of the synthesized Ni-Sn alloy catalysts

Entry	Alloy system	Bulk composition[a]	Sn/Ni[a] (molar ratio)	S$_{BET}$[b]/ m^{2}g^{-1}	H$_2$ uptake[c]/ μmol g^{-1}	S$_{Ni}$[c]/ m^{2}g^{-1}cat	Ni-Sn crystallite size[d]/nm
1	Ni$_3$Sn	Ni$_{74.9}$Sn$_{25.1}$	0.33	5	12	2.9	14[e]
2	Ni$_3$Sn$_2$	Ni$_{59.9}$Sn$_{40.1}$	0.67	12	9	2.0	27[f]
3	Ni$_3$Sn$_4$	Ni$_{42.7}$Sn$_{57.3}$	1.34	57	5	0.3	23[g]

[a] Determined by ICP-AES. [b] Determined by N$_2$ adsorption at 77 K. [c] Based upon total H$_2$ uptake at 273 K (noted after corrected for physical and chemical adsorption). [d] The value in the parenthesis is Ni crystallite size derived from the Scherrer`s equation. [e] Ni$_3$Sn(201). [f] Ni$_3$Sn$_2$(101). [g] Ni$_3$Sn$_4$(112).

The bulk composition was determined by ICP-AES and the results are closely to the nominal value of the precursors. Three types of Ni-Sn alloy systems were successfully synthesized with Sn/Ni ratio of 0.33, 0.67, and 1.34, respectively with BET surface area (S_{BET}) of 5 m^2 g^{-1}, 12 m^2 g^{-1}, and 57 m^2 g^{-1}, respectively. H_2 maximum uptake for Sn/Ni ratio of 0.34, 0,67, and 1.34 was 12 μmol g^{-1}, 9 μmol g^{-1}, and 5 μmol g^{-1}, respectively. The increase of tin amount in Ni-Sn system enhanced S_{BET} significantly, but reduced the nickel active surface area (S_{Ni}) 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 (S_{Ni}) was 2.9 m^2 g^{-1}_{cat}, 2.0 m^2 g^{-1}_{cat}, and 0.3 m^2 g^{-1}_{cat}, respectively. It should be noted that our results are comparable to the previously reported by Komatsu et al. [27]. The average Ni-Sn particle sizes was derived from Scherrer`s equation to selected diffraction peaks of Ni-Sn alloy face. In the case of Sn/Ni ratio of 0.33, $Ni_3Sn(201)$ particle sizes was 14 nm. For Sn/Ni ratio of 0.67, $Ni_3Sn_2(101)$ particle sizes was 27 nm, and $Ni_3Sn_4(112)$ of Sn/Ni ratio of 1.34 was 23 nm.
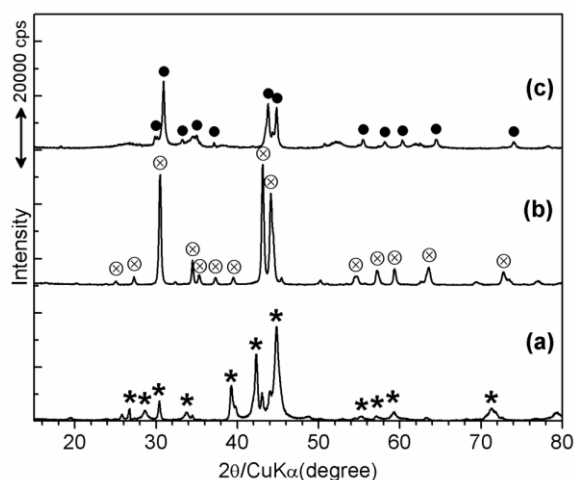
Figure 1 XRD patterns of the synthesized Ni-Sn alloys with different Sn/Ni ratio of 0.33 (a), 0.67 (b), and 1.34 (c) after H_2 treatment at 673 K for 1 h.

The XRD patterns of the synthesized Ni-Sn alloys with Sn/Ni ratio of 0.33, 0.67, and 1.34 after H_2 treatment at 673 K for 1 h are shown in **Figure 1**. Single phase of Ni-Sn alloy was formed for each Sn/Ni ratio. No diffraction peaks of metallic nickel or tin were observed in Figure 1a-b. In the case of Sn/Ni ratio of 0.33 a single phase of Ni_3Sn alloy was formed (Figure

1a), while for Sn/Ni ratio of 0.67 gave a single phase Ni_3Sn_2 alloy (Figure 1b) and single phase of Ni_3Sn_4 alloy was obtained for Sn/Ni ratio of 1.33 (Figure 1c). 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 [28].
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Selective hydrogenation of LA to GVL

The catalytic activity of the synthesized Ni-Sn alloys was evaluated in the selective hydrogenation of LA to GVL in aqueous solution 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.

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

Entry	Catalyst	Sn/Ni[a] (molar ratio)	Conv./%[b]	Yield/%[b]
1	Ni_3Sn	0.33	>99	>99
2	Ni_3Sn_4	1.34	>99	>99
3	Ni_3Sn_2	0.67	>99	>99
4	Ni_3Sn_2[c]	0.65	97	96
5	R-Ni/AlOH[d]	0	99	99
6	Pd/C[e]	0	75	75

Reaction conditions: catalyst, 0.042 g; LA, 1.2 mmol; H_2O, 3.5 mL; initial H_2 pressure, 4 MPa; temp. 433 K; reaction time, 6 h. [a] Determined by ICP-AES. [b] Determined by GC using an internal standard technique. [c] R-Ni/AlOH and $SnCl_2 \cdot 2H_2O$ were used as starting materials [29]. [d] 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. [30]. [e] Commercially available of Pd/C (5%) and used as received.

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_2 pressure of 4 MPa for 6 h. Single phase of Ni_3Sn, Ni_3Sn_4, and Ni_3Sn_2 were superior catalyst compared to R-Ni/AlOH and commercially available of Pd/C at the same conditions (entries 1, 2, and 3). In the case of Ni_3Sn_2 with ratio of 0.65 that obtained from hydrothermal of the mixture of R-Ni/AlOH and $SnCl_2 \cdot 2H_2O$ [29], the conversion of LA was 97% with GVL yield of 96% (entry 4). Aluminium hydroxide-supported Raney nickel

(R-Ni/AlOH) also exhibited a substantial high selectivity towards GVL formation with the respect of 99% (entry 5). However, the commercially available of Pd/C catalyst gave 75% of LA with yield of GVL yield of 75% (entry 6).

In order to understand the insight into the specific catalytic reaction of the single phase of Ni-Sn alloy system, the aqueous phase hydrogenation of LA to GVL at different reaction conditions was investigated. The effect of reaction temperature, initial H_2 pressure, time profile, and effect of solvent were evaluated for Ni-Sn alloy with Sn/Ni ratio of 0.67.

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_3Sn_2 alloy catalyst is shown in Figure 4. Reaction temperature was varied in the range of 373 K to 435 K at the initial H_2 pressure of 4 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 was performed at the temperature up to 453 K.
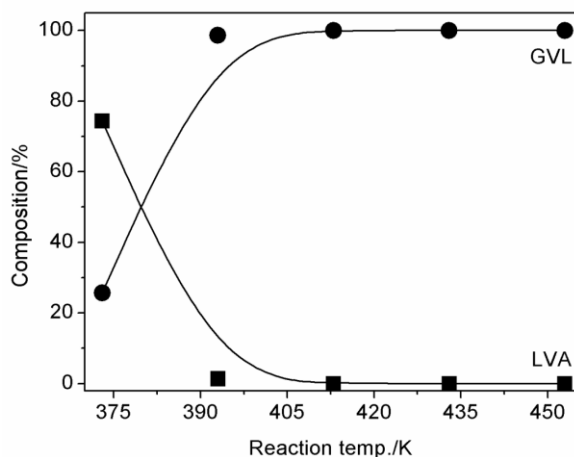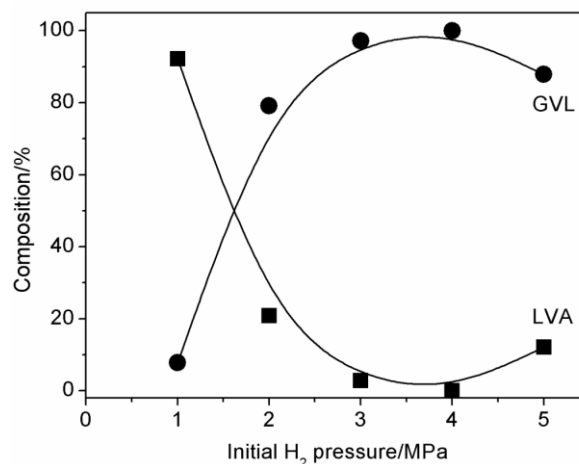

Figure 2. Effect of reaction temperature on the product composition over Ni_3Sn_2 alloy catalyst. Initial H_2 pressure of 4 MPa and reaction time of 6 h.
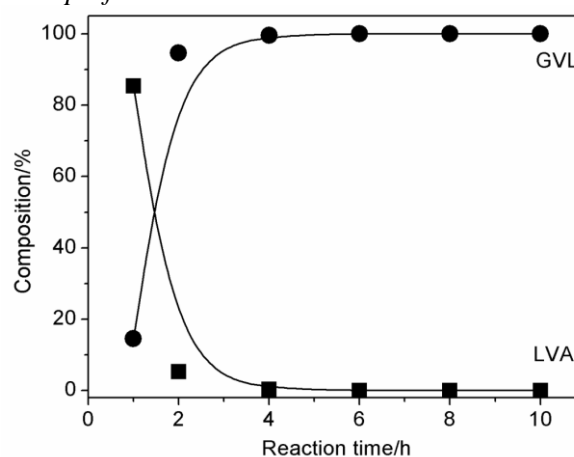
Effect initial H_2 pressure

The effect initial H_2 pressure on the product composition in the selective hydrogenation of LA to GVL by means of Ni_3Sn_2 alloy catalyst is

shown in Figure 5. Initial H_2 pressure was varied in the range of 1-5 MPa. At the initial H_2 pressure of 1 MPa, only 8% of LA was converted. The LA conversion remarkably increased almost 10 times from 8% to 79% when initial H_2 pressure increased from 1 MPa to 2 MPa. At the initial H_2 pressure of 4 MPa, an excellent yield of GVL (>99%) at the completed reaction was achieved. Further increase of the initial H_2 pressure up to 5 MPa, the LA conversion slightly decreased to 88% at the same reaction condition.

Figure 3. Effect of initial H_2 pressure on the product composition over Ni_3Sn_2 alloy catalyst. Reaction temperature of 433 K and reaction time of 6 h.

Time profile

Figure 4. Time profile of the selective hydrogenation of LA to GVL over Ni_3Sn_2 alloy catalyst at reaction temperature of 433 K and initial H_2 pressure of 4 MPa.

We also examined the time profile in the selective hydrogenation of LA to GVL at 453 K, initial H_2 pressure of 4 MPa for 1 -10 h and the composition of the reaction product are shown in Figure 4. 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.

Solvent effect

The effect of solvent used in the selective hydrogenation of LA to GVL by means of Ni_3Sn_2 alloy catalyst was carried out and the product composition are summarized in Table 3. 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_2O 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_2O was used as a solvent (entry 3).

Table 3. Results of the effect of solvent used in the selective hydrogenation of LA over Ni_3Sn_2 alloy catalyst

Entry	Solvent	Conv./%[b]	Selectivity/%[c]	
			GVL	Others[d]
1	Ethanol	97	86	14
2	Ethanol/H_2O	99	97	3
3	H_2O	>99	100	0

[a] Reaction conditions: catalyst, 0.042 g; LA, 1.2 mmol; solvent, 3.5 mL; initial H_2 pressure, 4 MPa; temp. 433 K; reaction time, 6 h. [b] Determined by GC using an internal standard technique. [c] GC area ratio [d] 1,4-pentanediol (1,4-PeD) and 2-methyl-tetrahydrofuran (2-MTHF) were detected by GC-MS.

4. Conclusions

Highly selective hydrogenation of biomass-based levulinic acid to γ-valerolactone efficiently catalyzed by single phase Ni-Sn alloy. Ni_3Sn, Ni_3Sn_2, and Ni_3Sn_4 are known to be effective heterogeneous catalysts giving excellence GVL yield of >99% at 433 K, initial H_2 pressure of 4 MPa within 6 h. The effective hydrogenation was obtained in H_2O solvent and no by-product was formed.

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