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ARTICLE

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

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Efficient hydrogenation of levulinic acid (LA) into γ-valerolactone (GVL) in water using a highly dispersed Ni-Sn(*x*)/AlOH (*x* = Ni/Sn ratio) was studied. Increasing Sn amount in 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*). Stoichiometric amount of GVL (>99%) was achieved by means of Ni-Sn(*x*)/AlOH (*x* = 3.0 and 1.4) at 393 K for 120 min in H_2O. H_2-treated Ni-Sn(*1.4*)/AlOH consisting of Ni_3Sn_2 alloy species showed high selectivity towards GVL (>99% yield). Ni-Sn(*1.4*)/AlOH catalyst was reusable for at least six consecutive runs without any significant loss of activity and selectivity.

Introduction

Recently, research on the biomass feedstock valorisation has been aimed at the production of biobased platform chemicals, fuels, and various commodity products.[1] Bio-derived molecules supply an interesting challenge of selective hydrodeoxygenation by using appropriately designed catalyst systems that can reduce the number of processing steps as compared with fossil derived hydrocarbons.[2] Among of oxygenated biomass-derived compounds, levulinic acid (LA) can be easily obtained via acidic hydrolysis of C-5 sugars in hemicellulose[3] 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 ester-LA.[6] GVL may be used as solvents[7] or blended with the 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 also can be used as a precursor of gasoline or diesel fuels such as C8–C16 alkenes,[12] C9–C18 alkanes,[13] C9 alkanes,[14] valeric esters,[15] or butene isomers,[16] aromatic hydrocarbon, [17] and gasoline-like hydrocarbon.[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] Poliakoff et al.[20] used Ru/SiO_2 catalyst under supercritical-CO_2 and H_2 up to 4.5 MPa at 473 K to give>99% GVL yield, while Galleti et al.[21] combined Ru/C catalyst and acid co-catalyst under supercritical-CO_2 at relatively low temperature. Recently, Dumesic et al. reported the use of bimetallic Ru-Sn for LA hydrogenation to give GVL in *o-iso*-butylphenol at relatively high reaction temperature of 453 K. They claimed that the formation of intermetallics such as Ru_2Sn_3 and Ru_3Sn_7 retarded Sn leaching into the reaction solution.[22] Although the catalytic processes have been applied for the transformation of LA into GVL, the precious metal catalysts were mainly utilised in the their studies. Therefore, the preparation of economical heterogeneous catalysts for substituting the precious metals has to be essential for industrial application.

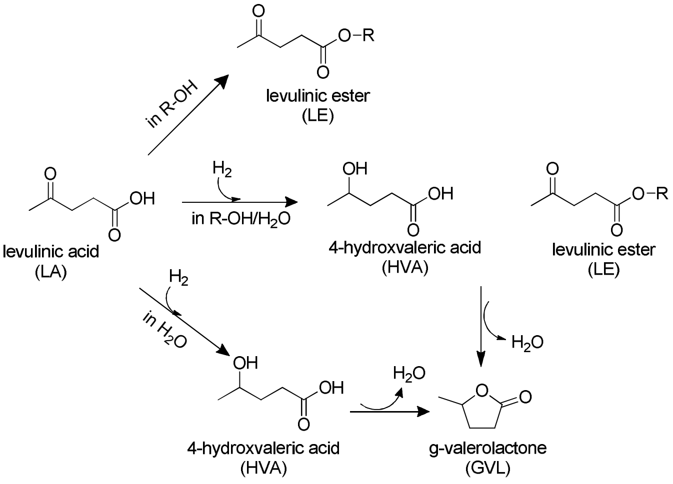

Fig. 1 Possible reaction pathways for catalytic transformation of LA into GVL over Ni-Sn alloy catalysts.

We have recently developed the 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 catalytic performances of

Ni-Sn alloy catalysts supported on aluminium hydroxide (Ni-Sn(*x*)/AlOH, *x* = Ni/Sn ratio) in 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, initial H_2 pressure, and reusability test on activity and selectivity to GVL were examined.

Results and discussion

Catalyst characterisations

The XRD patterns of Ni-Sn(*x*)/AlOH (*x* = Ni/Sn molar ratio) exhibited broadened peaks at 2θ = 44.44° due to the formation of Ni-Sn alloy phases such as Ni_3Sn and Ni_3Sn_2 reported previously.[24,25] The TG-DTA results of Ni-Sn(*1.4*)/AlOH confirmed that neither weight loss nor an exothermal peak of the transformation from $SnCl_2{\cdot}H_2O$ to SnO_2 was observed at 600 K. These results suggest that $SnCl_2{\cdot}2H_2O$ precursor might reacted completely with metallic Ni to form Ni-Sn alloy (Fig. S1, ESI†). Based on the ICP-AES analyses, the loading amount of Sn was 0.45, 0.75, 1.04, 2.14, and 3.96 mmolg^{-1} which were reflected in the Ni/Sn ratio 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 Ni-Sn(*x*)/AlOH catalysts e.g. H_2 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 the loading amount of Sn, H_2 and CO uptakes and BET surface area varied whereas the average Ni particle sizes slightly decreased (Table S1, entries 1-6 ESI†).

Scanning electron microscopy (SEM) images of as-prepared, H_2-treated, and recovered Ni-Sn(*1.4*)/AlOH catalysts are shown in Fig. S2, ESI†. SEM images for Ni-Sn(*1.4*)/AlOH before and after H_2 treatment revealed that the morphological differences between fresh and after hydrogenation treatment are readily visible in the 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 by plates stacking perpendicular to the longitudinal axis, which are characteristic morphologies of gibbsite and bayerite, respectively.[26,27] The characteristic morphologies of Al-rich region were maintained and become more rigid after hydrogen treatment at 773 K (Fig. S2 ESI†). _In the case of H_2-treated Ni-Sn(*1.4*)/AlOH, XRD patterns showed that the formation of Ni-Sn alloy phase as Ni_3Sn_2 species and the transformation of bayerite and gibbsite into amorphous alumina was observed clearly. The results of the low frequency Raman spectrum of the as-prepared Ni-Sn(*1.4*)/AlOH showed 529 cm^{-1} band which can be attributed to γ(OH) vibrational mode and Al-O-Al deformation while the 314 cm^{-1} band with is 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 H_2 treatment at 673 K for 1.5 h due to the formation of amorphous alumina[29] that also already had been not detected by XRD.[24,25] (See Fig. S3 ESI†).

TEM images and SAED for Ni-Sn(*1.4*)AlOH catalyst. (a) as-prepared, (b) after H_2 treatment at 673 K, and (c) recovered catalyst after the third reaction run are shown in Fig. S4 ESI†. TPR profiles of fresh as prepared and H_2-treated Ni-Sn(*1.4*)/AlOH 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 Ni-Sn(1.4)/AlOH catalyst and the results are summarised in Table 1.

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_2O	>99	0	>99	0
6[c]	Methanol/H_2O	81	6	75	0
7[c]	Ethanol/H_2O	>99	3	96	1
8[c]	2-propanol/H_2O	>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]Volume ratio of alcohol/H_2O was 1.0/1.0.

In the alcohol solvents such as methanol, ethanol, 2-propanol, and 1-propanol, the LA conversions were 14%, 20%, 10%, and 15%, giving levulinic ester without GVL formation (entries 1-4), respectively. Surprisingly, nearly 100% LA conversion and 100% GVL yield were achieved when H_2O was used as a solvent (entry 5). The high conversion of LA and the high selectivity of GVL in water solvent can be attributed to the presence of H-bonded water molecule 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 of surface concentration in hydrogen atom due to dissociated water and strong interaction between water with substrate by 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 was originally come from D2O during LA hydrogenation in D2O solvent.[31] Moreover, we also intentionally carried out the reaction in D2O solvent at the same reaction conditions (^{13}C 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 H_2O on the LA conversion and GVL yield was clearly observed when alcohol/H_2O (1:1 volume ratio) was used as a solvent. The conversion of LA and the yield of GVL remarkably increased to 81% and 75%, respectively and levulinic ester (methyl 4-oxopentanoate) yield was diminished to 6%

in methanol/H_2O (entry 6). In ethanol/H_2O 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/H_2O, >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 results showed that LA conversion was only 35%, 15%, and 21%, respectively (entries 9-11). We believe that the reaction mechanism of LA hydrogenation over Ni-Sn(*x*)/AlOH alloy catalysts via hydrogenation of C=O of the carbon C5 of LA then hydrogenated to form HVA and without the formation of ester. The formation of HVA would prevent to esterification or hydrolysis while in presence of high pressure of H_2 or due to the main reaction was carried out in water or water/alcohol.[30a] It can be clearly observed that the reaction did not occur effectively when the alcohols or other aprotic solvents were used as solvent or even the reaction time was extended until 720 min at 393 K, 4.0 MPa of H_2 (Fig. 4). Therefore, it can be concluded that the hydrogenation of LA into GVL over Ni-Sn alloy catalyst proceeded efficiently in H_2O solvent system. For further investigation, the H_2O solvent will be used for the examination of various Ni-Sn(*x*)/AlOH catalysts and the effect of various reaction conditions such as time profiles, initial H_2 pressure, temperature, and reusability test.

Effect of Sn loading amount

Results of LA hydrogenation in H_2O using supported Ni-Sn/AlOH alloy catalysts are summarized in Table 2.

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

Entry	Catalyst[a]	Ni[b]/ mmolg^{-1}	Al[b]/ mmolg^{-1}	Sn[b]/ mmolg^{-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	$SnCl_2.2H_2O$				0	0
15	None				0	0

[a] Value in the parenthesis is Ni/Sn molar ratio. *Reaction conditions:* catalyst (0.05 g), LA (2 mmol), H_2O (3.0 mL), H_2 (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 H_2 at 673 K for 1.5 h. [f] After H_2 treatement at 773 K for 1.5 h. [g] After H_2 treatement at 873 K for 1.5 h. [h] Feeding amount of Sn. Prepared by impregnation method.

By using Ni-Sn(*7.9*)/AlOH and Ni-Sn(*3.7*)/AlOH catalysts, GVL yields were 97% and 98%, respectively (entries 1 and 2). By increasing the Sn loading amount from 0.45 mmolg^{-1} to 1.04 mmolg^{-1} (Ni/Sn = 3.0), GVL yield was >99% (entry 3) and the high yield of GVL was maintained up to 2.14 mmolg^{-1} of Sn loading amount (Ni/Sn = 1.4). In contrast, Ni-Sn(*1.0*)/AlOH (Sn = 3.96 mmolg^{-1}) gave 64% LA conversion with 100% selectivity to GVL (entry 5). After H_2 treatment at 673 K for 1 h, Ni-Sn (*3.0*)/AlOH catalyst gave 87% yield of GVL (entry 6). In contrast, H_2-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 H_2 treatment may play important role for the effective Ni-Sn species that can be rationally speculated as Ni_3Sn_2, while in Ni-Sn(*3.0*)/AlOH, Ni_3Sn, Ni_3Sn_4, and β-Sn were formed which were readily detected by XRD.[24] We found that the reaction rate of LA hydrogenation over as prepared Ni-Sn(1.4)/AlOH was 0.26 mmol/g_{cat}.min (conversion 71%), while over H_2-treated Ni-Sn(1.4)/AlOH and Ni-Sn(3.0)/AlOH are 0.28 mmol/g_{cat}.min (conversion 81%) and 0.18 mmol/g_{cat}.min (conversion 47%), respectively, after 60 min reaction time at 393 K, and 4.0 MPa of H_2. 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, SnO_2, and $SnCl_2 \cdot 2H_2O$ were not active for LA transformation under the same conditions (entries 11-14). In addition, the transformation of LA into GVL did not proceed without 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) and showed low in conversion of LA.[33]

Effect of reaction temperatures

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

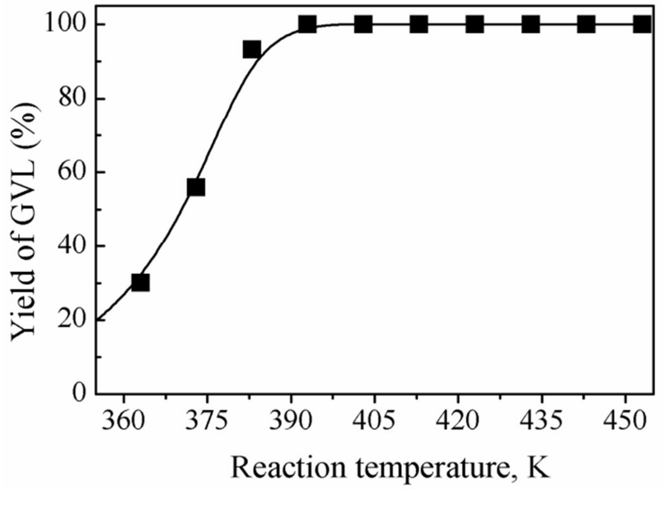

Fig. 2 Effect of reaction temperatures on the GVL yield in transformation of LA over Ni-Sn(*1.4*)/AlOH catalyst. *Reaction conditions:* catalyst (0.05 g), LA (2 mmol), H_2O (3 mL), H_2 (4.0 MPa), 180 min.

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

Effect of initial H_2 pressure

The effect of initial H_2 pressure on the yield of GVL in transformation of LA over Ni-Sn(*1.4*)/AlOH catalyst is shown in Fig. 3. As increasing initial H_2 pressure, GVL yield increased smoothly to reach nearly 100% up to 3.5 MPa within 180 min. Therefore, the initial H_2 pressure of 3.5-4.0 MPa was used as the optimised condition for LA transformation over Ni-Sn alloy catalysts.

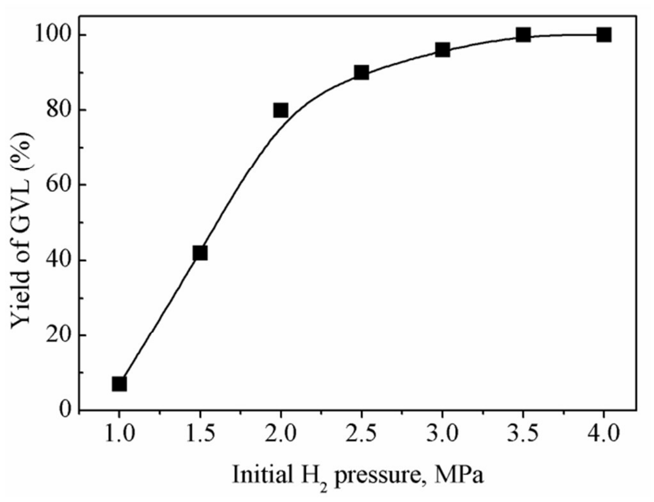

Fig. 3 Effect of initial H_2 pressure on the GVL yield in transformation of LA over Ni-Sn(*1.4*)/AlOH catalyst. *Reaction conditions:* catalyst (0.05 g), LA (2 mmol), H_2O (3 mL), 393 K, 120 min.

Time profiles

Time profiles of LA transformation over Ni-Sn(*1.4*)/AlOH catalyst in different solvents used are shown in Fig. 4. In H_2O and ethanol/H_2O, 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, a high yield of GVL was retained (>99%) even though 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.

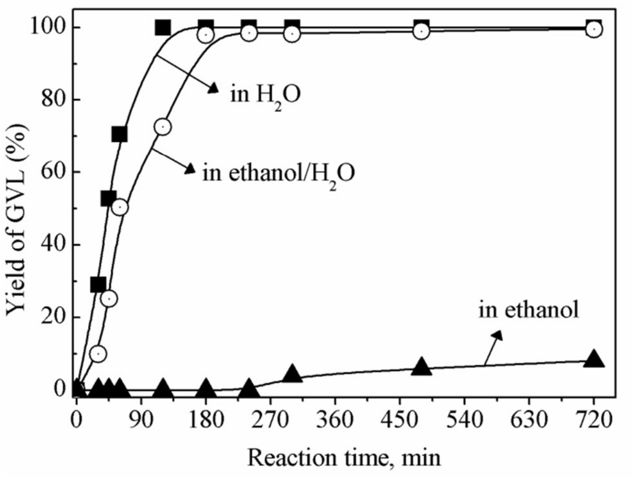

Fig. 4 Time profiles of LA transformation over Ni-Sn(*1.4*)/AlOH catalyst in different solvent used. *Reaction conditions:* catalyst (0.05 g), LA (2 mmol), solvent (3 mL), H_2 (4.0 MPa), 393 K.

Reusability test

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

Table 3 Reusability test of Ni-Sn(*1.4*)/AlOH catalyst in 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), H_2O (3 mL), H_2 (4.0 MPa), 393 K, 120 min. [a]Yield and selectivity to GVL, determined by GC using an internal standard technique.

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 then dried under vacuum without any further treatments. The activity and selectivity maintained for at least six consecutive runs. The amounts of metal leaching into the reaction solution was 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 no significant change from the fresh Ni-Sn(*1.4*)/AlOH even after six consecutive runs (Fig. S6, ESI†).

Experimental

Materials

Raney Ni-Al alloy ((50%wt of Ni and 50%wt of Al) Kanto Chemical Co. Inc.), NaOH (WAKO), and $SnCl_2 \cdot 2H_2O$ (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

Typical procedure of the synthesis of Raney nickel supported on 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 filtrate was neutralized, and then stored in water. The catalyst was dried under vacuum before the catalytic reaction.

Synthesis of Ni-Sn/AlOH

Typical procedure of the synthesis of nickel-tin alloy supported on aluminium hydroxide (denoted as Ni-Sn(*7.9*)/AlOH, 7.9 is Ni/Sn molar ratio) is described as the follows.[24,25] R-Ni/AlOH that was obtained from the above procedure was mixed with a solution that contained 0.45 mmol $SnCl_2\cdot 2H_2O$ at room temperature and stirred for 2 h. The mixture was placed into a sealed-Teflon autoclave reactor for the 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 Ni-Sn alloy, H_2 treatment at 773 K for 1 h was carried out for Ni-Sn(*3.0*)/AlOH and Ni-Sn(*1.4*)/AlOH samples. The XRD patterns of the H_2-treated had been reported previously.[24]

Catalyst characterisastion

Powder X-ray diffraction (XRD) measurements were recorded on a Mac Science M18XHF instrument using monochromatic Cu Kα 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} ($\alpha1$ = 0.154057 nm, $\alpha2$ = 0.154433 nm). ICP measurements were performed on an SPS 1800H plasma spectrometer by 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 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 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] 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 JEOL JEM1400. Raman spectra were taken on JASCO NRS-2100 Laser-Raman Spectrophotometer with Ar beam lamp of 488 nm and 514.5 nm.

The H_2 uptake was determined through irreversible 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. The catalysts were subsequently cooled to room temperature under vacuum for 30 min. The H_2 measurement was conducted at 273 K, and H_2 uptake was calculated according to the method described in the literature.[36]

Temperature-programmed reduction (TPR) was carried out on Micrometrics AutoChem II Chemisorption Analyser Instrument according to procedure previously reported.[37] The catalyst samples were outgassed at 423 K for 1 h and then cooled to 313 K under Ar flow of 70 ml/min. TPR profiles were registered while heating the samples from 313 K to 1073 K by 283 K/min heating rate under 50 ml/min flow of 10% H_2-Ar mixture.

General procedure for the transformation of LA

Catalyst (0.05 g), LA (2.0 mmol), H_2O (3 mL) as a solvent, and 1,8-octandiol (0.2 mmol) as an internal standard were placed into a glass reaction tube, fitted inside a stainless steel reactor. After H_2 was introduced into the reactor with an initial H_2 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 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 H_2O was performed on a Shimadzu GC-8A equipped with a flame ionisation detector and with 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/H_2O solvents. Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-17B equipped with a thermal conductivity detector and with an RT-βDEXsm capillary column. ^1H and ^{13}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 D_2O with TMS as an internal standard. Products were identified by GC-MS, ^1H, and ^{13}C NMR spectra (Fig. S7 and S8, ESI†).

Conclusions

Efficient transformation of levulinic acid (LA) into γ-valerolactone (GVL) using Ni-Sn(x)/AlOH (x = Ni/Sn ratio) was studied. Increasing the amount of Sn up to 2.14 $mmolg^{-1}$ enhanced the GVL yield which slightly decreased with 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. Ni-Sn(*1.4*)/AlOH catalyst was reusable for at least six consecutive runs without any significant loss of activity and selectivity.

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Notes and references

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