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Recent progress in the direct synthesis of γ-valerolactone from biomass-derived sugars catalyzed by RANEY® Ni–Sn alloy supported on aluminium hydroxide†

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The direct synthesis of γ-valerolactone (GVL) from biomass-derived sugars (e.g., cellobiose, sucrose, glucose, and fructose) using RANEY® nickel–tin alloy supported on aluminium hydroxide (RNi–Sn(x)/AlOH; x is the loading amount of Sn) catalysts has been investigated. A RNi–Sn(1.04)/AlOH (1.04 = loading amount of Sn (mmol)) catalyst exhibited the highest yield of GVL from cellobiose (37%), sucrose (67.3%), glucose (71.6%), and fructose (74.9%), whereas conventional RANEY® Ni and RNi/AlOH catalysts produced only C-6 sugar alcohols (sorbitol & mannitol) at 443 K, H_2 3.0 MPa for 12 h. The reduction of RNi–Sn(x)/AlOH with H_2 at 673–873 K for 1.5 h resulted in the formation of Ni–Sn alloy phases (e.g., Ni_3Sn and Ni_3Sn_2) and caused the transformation of aluminium hydroxide (AlOH) to amorphous alumina (AA). The RNi–Sn(2.14)/AA 873 K/H_2 catalyst contained a Ni_3Sn_2 alloy as the major phase, which exhibited the best yield of GVL from sucrose (65.3%) under the same reaction conditions. The RNi–Sn(1.04)/AlOH catalyst was reusable and stable for at least five consecutive reaction runs.

Introduction

Strategic development for the efficient production of γ-valerolactone (GVL), a versatile biomass-derived platform chemical, has grown very fast in the last two decades due to its enormous promising applications in the chemical industries.[1] For instance, GVL can be used as a versatile feedstock for the synthesis of fuel additives/biofuels[2–4] (e.g., liquid hydrocarbon diesel,[5] gasoline-like hydrocarbon,[6] and valeric biofuels[7]), as a precursor of bulk chemicals (e.g., 1,4-pentanediol,[8] aromatic hydrocarbon,[9] and 4-hydroxyvaleric acid ionic liquids[10]). Furthermore, GVL has been demonstrated to be a renewable solvent for the Sonogashira reaction[11] and a green polar aprotic solvent for the improvement of biomass conversion.[12,13]

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† Electronic supplementary information (ESI) available: Experimental sections, physico-chemical properties and XRD patterns of the as-prepared and H_2-reduced RNi–Sn(x)/AlOH, SEM and TEM images, TG-DTA data, and NH_3-TPD spectra. See DOI: 10.1039/d0cy01356k

A number of investigations on the utilization of heterogeneous catalysts in the synthesis of GVL through the hydrogenation of biomass-derived levulinic acid (LA) or its ester have been reported[14–18] and several reviewed-papers in these fields have also been published previously.[1,19–22] Among them, supported ruthenium-based catalysts, in the form of both monometallic and bimetallic systems, have been frequently employed and apparently have demonstrated a superior catalytic performance with high GVL yield (100%).[14,18,23–26] Although ruthenium-based catalysts are highly efficient catalysts, relatively harsh reaction conditions (at >413 K and >4.0 MPa of H_2) are required to achieve complete reaction with >99% yield of GVL.[15,18,27–31] Several significant efforts have successfully reduced the reaction temperatures to ambient temperature with a high conversion of LA and yield of GVL, whereas a relatively high initial H_2 pressure or longer reaction time is required for achieving complete reaction.[32,33]

Nowadays, great interest has arisen to obtain GVL not only from the catalytic hydrogenation of LA or its ester but also produced directly from available biomass-derived molecules (e.g., lignocellulosic materials or bulk carbohydrates (disaccharides or monosaccharides)) in a one-pot approach through the combined actions of Lewis and Brønsted acid site catalysts.[34–39] Heeres et al. have reported the synthesis of GVL from C6-sugar sources (glucose, fructose) using an acid

catalyst in combination with a hydrogenation catalyst (Ru/C) and either molecular hydrogen or formic acid as the hydrogen donor. They reported that the highest yield of GVL (52%) was obtained from fructose when formic acid was used as the hydrogen donor at 453 K after 16 h. When using molecular hydrogen as the hydrogen source, the highest yield of GVL (62 mol%) was obtained from fructose in combination with TFA and Ru/C in water (453 K, 9.4 MPa H_2, 8 h).[34] Ebitani *et al.* reported the dehydration/hydrogenation of fructose using an Au/ZrO_2 catalyst and formic acid as the source of hydrogen in a two-step reaction at 393 K for dehydration and 423 K for hydrogenation and 48% yield of GVL was obtained.[35] Hernández *et al.* reported the one-pot cascade conversion of xylose into GVL over Zr and Al containing bifunctional beta-zeolite catalysts, possessing both Lewis and Brønsted acid functionalities. A 35% yield of GVL was obtained at 463 K after 48 h.[36] Cui *et al.* combined $H_3PW_{12}O_{40}$ and Ru/TiO_2 catalysts for the conversion of fructose into GVL in various solvents and the highest yield of GVL (67%) was obtained from fructose in 20 vol% water/γ-butyrolactone at a temperature of 423 K, 4.0 MPa H_2 after 6 h.[37] Melero *et al.* reported the synthesis of GVL from xylose using Zr–Al-beta zeolite catalysts and the maximum yield of GVL (34%) was obtained under optimized reaction conditions of 463 K and 10 h.[38] Most recently, Ren *et al.* synthesized GVL from carbohydrates in a two-step reaction in the presence of heteropoly acid-based ionic liquid and Ru/ZrO_2 catalysts in water. The authors reported that a 63% yield of GVL (based on fructose) was obtained using 1-methyl-3-(3-sulfopropylimidazolium) silico-tungstate ([MIMPS]4SiW) and Ru/ZrO_2 catalysts at 453 K in a two-step reaction, the first step was in 0.1 MPa nitrogen (N_2) for 3 h (dehydration), and the second step was in 4.0 MPa H_2 for 10 h (hydrogenation). Under the same reaction conditions, the GVL yields were 68% (from glucose), 60% (from starch), and 60% (from cellulose).[39] Low to moderate (37–68%) yields of GVL were obtained from the direct conversion of biomass-derived sugars using noble metal Ru-based or Au-based catalysts. Therefore, the development of new transition metal-based heterogeneous catalyst systems for effective synthesis of GVL from carbohydrates, especially disaccharides (sucrose and cellobiose) or monosaccharides (fructose and glucose) in a

one-pot reaction without acidic co-catalyst addition is of great interest and is a great challenging work (Scheme 1).

In the present work, we report our extended investigation on the direct synthesis of γ-valerolactone (GVL) from biomass-derived cellobiose and sucrose (disaccharides) and C6-sugars glucose and fructose (monosaccharides) using RANEY® nickel-tin alloy supported on aluminium hydroxide (denoted as RNi–Sn(x)/AlOH; x is the loading amount of Sn) instead of ruthenium-based catalysts. Interestingly, the RNi–Sn(1.04)/AlOH catalyst produced GVL with high yields of 37% (from cellobiose), 67.3% (from sucrose), 71.6% (from glucose) and 74.9% (from fructose) under optimized reaction conditions of 443 K, H_2 3.0 MPa, and 12 h, whereas conventional RANEY® Ni and RNi/AlOH catalysts produced only C-6 sugar alcohols under the same reaction conditions. Therefore, the effects of various reaction conditions such as temperature, initial H_2 pressure, loading amount of Sn, time, and reusability test of catalysts in the direct conversion of sugars into GVL are systematically investigated.

Results and discussion

Catalyst characterization

A series of RANEY® nickel–tin alloy supported on aluminium hydroxide (denoted as RNi–Sn(x)/AlOH, x = Sn loading amount, mmol g^{-1}) catalysts with different Sn loading amounts (*ca.* 0.26 mmol; 0.45 mmol; 0.76 mmol; 1.04 mmol; 2.14 mmol; and 3.96 mmol g^{-1}) were prepared *via* the hydrothermal treatment of a mixture of RANEY® nickel supported on aluminium hydroxide (RNi/AlOH)[40–42] and a $SnCl_2·2H_2O$ solution in ethanol/H_2O at 423 K for 2 h and produced the as-prepared RNi–Sn(x)/AlOH. After reduction of the as-prepared RNi–Sn(x)/AlOH with H_2 gas at 673–873 K for 1.5 h, RNi–Sn(x) supported on amorphous alumina (RNi–Sn(x)/AA) catalysts were produced. The bulk compositions, the H_2 uptake and the amount of acid sites (derived from NH_3-TPD spectra), representative SEM and TEM images, TG-DTA data, and the XRD patterns of RANEY® Ni, RNi/AlOH and RNi–Sn(x)/AlOH catalysts have been described in previous reports[40,42–44] and the details are also provided in Table S1–S2 and Fig. S1–S6 in the ESI.†

Direct conversion of sucrose to GVL

Screening of catalysts. In the first experiment, the catalytic conversion of sucrose over various nickel-based catalysts was performed and the results are summarized in Table 1. We use the terms C6-sugars and C6-sugar alcohols in our report due to the difficulty in separation of the products using our HPLC columns. Even though two types of sugar columns (namely SH1821 and NH_2-Inertsil columns) were applied, the chromatogram of these products (sorbitol and mannitol or glucose and fructose) partially overlapped, therefore, the yields of glucose/fructose and sorbitol/mannitol are presented as C6-sugars and C6-sugar alcohols, respectively. Conventional RANEY® Ni (in a slurry prior to addition to prevent oxidation or pyrophoric reaction in air) exhibited a
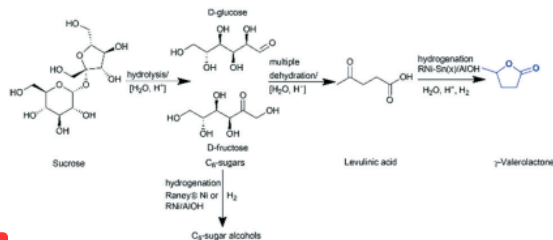
Scheme 1 Possible reaction pathways for the direct synthesis of γ-valerolactone (GVL) from biomass-derived sucrose in the presence of RNi–Sn(x)/AlOH catalysts.

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Table 1 Results of the direct one-pot conversion of sucrose over various nickel-based catalysts

Entry	Catalyst[a]	Composition[a] (mmol g⁻¹)			Conv.[b] (%)	Yield[b] (%)				
		Ni	Al	Sn		C6-sugars[c]	C6-sugar alcohols[d]	LA	GVL	Others[e]
1	RANEY® Ni	3.98	0.63	—	99.1	15.5	81.6	0.0	0.0	0.0
2	RANEY® Ni/AlOH	3.46	3.80	—	>99	0.0	99.0	0.0	0.0	0.6
3	RNi–Sn(0.26)/AlOH	3.82	3.66	0.26	>99	1.0	77.8	3.5	14.7	1.0
4[f]	RNi/AlOH + SnCl₂·2H₂O	3.46	3.80	1.15	>99	7.2	35.2	10.7	12.1	25.5
5[f]	RNi/AlOH + SnO	3.46	3.80	1.15	>99	9.0	58.7	4.7	9.2	17.8
6	Sn/AlOH	—	—	4.10[g]	91	79.0	0.0	9.0	0.0	3.0
7	SnCl₂·2H₂O	—	—	—	89	24.0	0.0	14.3	0.0	10.0
8	SnO	—	—	—	87	73.1	0.0	5.3	0.0	0.0
9[h]	No catalyst	—	—	—	71	70.6	0.0	0.0	0.0	0.0

Reaction conditions: substrate/Ni = 85; sucrose (0.35 mmol); solvent H₂O (5 ml); H₂ (3.0 MPa); temperature (443 K); reaction time (12 h). [a] The value in parentheses is the loading amount of Sn (mmol); the bulk compositions were determined by using ICP-AES analysis. AlOH = aluminium hydroxide (in the form of bayerite and gibbsite, based on the XRD analysis (Fig. S1, in the ESI†)). [b] Conversion and yield were determined by HPLC using an internal standard technique. [c] Glucose and fructose are included as C6-sugars. [d] Sorbitol and mannitol are included as C6-sugar alcohols. [e] Others include glucoside and furans (5-hydroxymethyl furfural and furfural). [f] The catalyst was prepared by physical mixing of RNi/AlOH and SnCl₂·2H₂O or SnO (the loading amount of Sn was 1.15 mmol g⁻¹ to keep the Ni/Sn molar ratio of approximately 3.0).[42] [g] Feeding amount of Sn, prepared by an impregnation method. [h] The products were glucose and fructose, no hydrogenated products were obtained.

99.1% conversion of sucrose and produced an 81.6% of C6-sugar alcohols (sorbitol and mannitol) (entry 1). As expected, the RANEY® Ni supported on aluminum hydroxide (RANEY® Ni/AlOH) catalyst completely converted sucrose to quantitatively produce a 98% yield of C6-sugar alcohols (sorbitol + mannitol) under the same reaction conditions (entry 2). The molar ratio of mannitol to sorbitol (M/S) was maintained at around of 0.4, suggesting that the isomerization of glucose-fructose as well as the further conversion of sorbitol or mannitol into glycerol, acetol, and ethylene glycol did not take place over RANEY® Ni, RANEY® Ni/AlOH, or supported RANEY® Ni catalysts.[40,45]

Interestingly, the addition of 0.26 mmol g⁻¹ Sn to RANEY® Ni/AlOH (RNi–Sn(0.26)/AlOH) remarkably shifted the reaction products toward LA and GVL with yields of 3.5% and 14.7%, respectively, whereas the yield of C6-sugar alcohols (sorbitol & mannitol) considerably decreased to 77.8% (entry 3). The differences in the obtained reaction products from the catalytic reaction of sucrose over RNi/AlOH and RNi–Sn(0.26)/AlOH catalysts were clearly observed, suggesting that the presence of tin in the RNi–Sn(0.26)/AlOH catalyst plays a prominent role in the selective synthesis of GVL or LA from sucrose. Therefore, further discussion on the effect of various Sn loading amounts on the conversion of sucrose and the yields of LA and GVL will be discussed later in this paper. The activity of RNi/AlOH and RNi–Sn(0.26)/AlOH catalysts was higher than that of conventional RANEY® Ni as indicated by the sucrose conversion. The activity of the catalysts can be attributed to the high dispersion of metallic Ni⁰ on the surface of aluminium hydroxide. The presence of aluminium hydroxide can also hinder the aggregation of Ni metal during the reaction in an aqueous environment. The dispersion of metallic nickel can be roughly estimated from the XRD patterns of RNi/AlOH and RNi–Sn(x)/AlOH. In fact, the broadened diffraction peaks of Ni (at 2θ = 44.6°) and the

presence of aluminium hydroxide were clearly observed (Fig. S1, in the ESI†).

The reaction mixture obtained from the RNi–Sn(0.26)/AlOH catalyst seems to be light brown (entry 3, Table 1), while from RNi/AlOH remained a clear solution (entry 2, Table 1). The UV-vis spectroscopy analysis results confirmed the presence of levulinic acid in the reaction mixtures of entry 3, Table 1 and entries 5 and 8, Table 2. In contrast, the reaction mixture of entry 2, Table 1 does not exhibit the absorption peak of LA as shown in Fig. S7, in the ESI.† Since LA and GVL were not observed over the RANEY® Ni/AlOH catalyst and to confirm the role of Sn addition, physical mixtures of RNi/AlOH and SnCl₂·2H₂O or SnO catalysts (the loading amount of Sn was 1.15 mmol g⁻¹ to keep the Ni/Sn molar ratio of approximately 3.0) were prepared and also used for the reaction. Over RNi/AlOH + SnCl₂·2H₂O, the conversion of sucrose was >99% and the products were distributed to C-6 sugars (7.2%), C6-sugars alcohols (35.2%), LA (10.7%), GVL (12.1%), and others (25.5%) (entry 4). A relatively high yield of others (25.5%) (mainly contain glucoside and furans (5-hydroxymethyl furfural and furfural)) was obtained, suggesting that SnCl₂·2H₂O promoted the further dehydration of C6-sugars to form glucoside or furans (entry 4). The RNi/AlOH + SnO catalyst was also active for the conversion of sucrose (>99% conversion) and the products were distributed to C6-sugars (9.0%), C6-sugar alcohols (58.7%), LA (4.7%), GVL (9.2%), and others (17.8%) (entry 5). The yield of others (mainly contain glucoside and furans (5-hydroxymethyl furfural and furfural) obtained over this catalyst was smaller than that of the RNi/AlOH + SnCl₂·2H₂O catalyst system. These results suggested that the presence of both Sn²⁺ and SnO showed a notable promotion effect on the LA and GVL formation, which are laterally different between with and without the addition of SnCl₂·2H₂O or SnO powder. It has been reported that SnCl₂·2H₂O and SnCl₄·5H₂O were

Table 2 Results of the catalytic reaction of various sugars over the RNi–Sn(1.04)/AlOH catalyst

Entry	Substrate	Reaction time (h)	Conversion[a] (%)	Yield[b] (%)			
				C-6 sugar alcohols	LA	GVL	Others[c]
1[d]	LA	3	>99	—	—	>99	0.0
2[d]	Ethyl-levulinate (EL)	3	>99	—	—	>99	0.0
3	Glucose	3	63	26.1	9.2	27.7	0.0
4	Glucose	7	>99	27.6	3.2	69.8	1.6
5	Glucose	12	>99	26.8	0.0	71.2	1.0
6	Fructose	3	72	24.3	11.7	36.0	0.0
7	Fructose	7	>99	21.7	2.7	74.6	1.0
8	Fructose	12	>99	23.1	0.0	74.9	2.0
9[e]	Cellobiose	10	48	29.6	8.4	10.0	0.0
10[e]	Cellobiose	24	98	53.9	3.7	37.4	3.0
11	Sorbitol	7	7.1	—	—	—	Trace
12	Mannitol	7	5.5	—	—	—	Trace

Reaction conditions: substrate/Ni = 85; H$_2$O, 5 mL; H$_2$, 3.0 MPa; temperature 443 K. [a] Conversion and yield were determined by HPLC using an internal standard technique. [b] Yields of liquid products were C6-sugars (glucose + fructose), C6-sugar alcohols (sorbitol + mannitol), LA = levulinic acid, and GVL = γ-valerolactone. [c] Others include glucoside and furans (5-hydroxymethyl furfural and furfural). [d] Subtrate/Ni = 100; the conversion and yield were determined by GC using an internal standard technique. The data were taken from the reference of Rodiansono et al.[43] [e] Temperature reaction was 453 K.

effective Lewis acid catalysts for the isomerization/ dehydration of glucose and xylose to furanic compounds in water then subsequently transformed into LA which is easily hydrogenated to GVL under a H$_2$ atmosphere.[46] Antunes et al. have shown that the presence of tin in Al-containing zeolite-beta catalyzed the conversion of furanic compounds to LA.[47] Moreover, by using the Sn/AlOH catalyst, mixtures of C-6 sugars (79%), LA (9.0%9, and others (3.0%) were obtained without the formation of hydrogenated products (e.g., C-6 sugar alcohols and GVL) (entry 6). A similar result was also obtained upon SnCl$_2$·2H$_2$O with a 24% yield of C6-sugars, 14.3% yield of LA, and 10% yield of others (entry 7). In addition, SnO was not an effective catalyst for the direct conversion of sucrose to GVL under the same reaction conditions, whereas the main products were C6-sugars (73.1%) and a small amount of LA (5.3%) (entry 8). Furthermore, the reaction in the absence of a catalyst under a H$_2$ atmosphere produced only C6-sugars (70.6% yield) as the result of the hydrolysis reaction of sucrose with a conversion of 71% (entry 9).

Effect of Sn loading amounts. The effect of Sn loading amounts on the product distributions in the direct conversion of sucrose to GVL in the presence of RNi–Sn(x)/ AlOH catalysts is shown in Fig. 1.

The total yields (consisting of C6-sugars, C6-sugar alcohols, LA, GVL, and others) were almost constant at approximately 97% alongside the change in Sn loading amounts. By using the RNi–Sn(0.26)/AlOH catalyst (a Sn loading amount of 0.26 mmol corresponding to a Ni/Sn molar ratio of 14.8), a remarkable difference was observed, whereas the products were distributed to LA (3.5%) and GVL (14.7%) (Table 1, entry 3 and Fig. 1). Obviously, the yield of GVL increased gradually as the Sn loading amounts were 0.26–1.04 mmol (the highest yield of GVL was 67.3%) then slightly decreased to 55% and 47% when the Sn loading amounts were 2.14 mmol and 3.96 mmol, respectively,

whereas the yield of C6-sugars, C6-sugar alcohols, and LA remained unchanged. At a high loading amount of Sn, the surface of Ni metal may be partially covered by Sn^{2+} or SnO during the preparation or due to the formation of bimetallic Ni–Sn alloy species.[44] The importance of Ni–Sn alloy formation and the formation of oxidic tin during the catalytic conversion of biomass-derived cellulose or sugars have been investigated by Ma and co-workers.[48,49] They proposed that catalytic conversion of cellulose or sugars was mainly propelled by the synergistic actions between the oxidic tin (in the form of Sn^{2+}, Sn(OH), SnO$_x$) which serves as Brønsted acid for the sugar dehydration reaction and the metallic Ni in the Ni–Sn alloy for the hydrogenation reaction to C6-sugar alcohols, LA, and GVL. The formation of oxidic tin in the form of SnO$_x$ was observed as the active species during the catalytic conversion of cellulose to hydroxy-acetone and
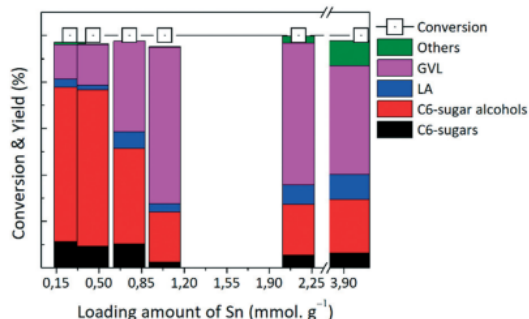

Fig. 1 Results of product distribution from the one-pot conversion of sucrose to GVL over RNi–Sn(x)/AlOH catalysts (x = 0.26, 0.45, 0.76, 1.04, 2.14, and 3.96 mmol g^{-1}). Reaction conditions: substrate/Ni = 85; sucrose (0.35 mmol); solvent H$_2$O (5 ml); H$_2$ (3.0 MPa); temperature (443 K); reaction time (12 h). C6-Sugars include glucose and fructose; C6-sugar alcohols include sorbitol and mannitol; others include glucoside and furans (5-hydroxymethyl furfural and furfural). LA = levulinic acid, GVL = γ-valerolactone.

1-hydroxy-2-butanone[48] and the formation of SnO_x in Ni_3Sn_4 alloy catalyzed the catalytic conversion of cellulose to acetol *via* glucose-fructose isomerization and retro-aldol condensation.[49]

To confirm the importance of catalyst acidity, ammonia-temperature programmed desorption (NH_3-TPD) was performed and the results are summarised in Table S1, in the ESI.† RANEY® Ni,[50] RNi/AlOH, and commercial γ-Al_2O_3 (ref. 51) have a total acidity of 195 μmol g^{-1}, 474 μmol g^{-1}, and 180 μmol g^{-1}, respectively, which mainly consisted of weak acidity (entries 1 and 2). After introducing Sn (loading amount of 0.26–3.96 mmol g^{-1}) to RNi/AlOH, the total acidity of RNi–Sn(x)/AlOH slightly increased to around 477–491 μmol g^{-1} (entries 3–7). There was no significant difference in the total acidity of RNi–Sn(x)/AlOH with different Sn loading amounts, suggesting that the effect of total acidity may be negligible during the one-pot conversion of sucrose to GVL under the current operating conditions. Therefore, it can be concluded that the effective direct conversion of sucrose to high yields of GVL can be achieved over the RNi–Sn(1.04)/AlOH catalyst, which was used as the best catalyst for the subsequent catalytic reactions.

Effect of reaction temperature. The influence of reaction temperature on the product distributions in the direct conversion of sucrose over the RNi–Sn(1.04)/AlOH catalyst is shown in Fig. 2.

It could be expected that sucrose was converted easily to C6-sugars (27.4% yield) and C6-sugar alcohols (58.4% yield) without the formation of LA and GVL at the lowest reaction temperature of 383 K. As the temperature increased to 423 K, a remarkable yield of GVL was obtained (54.5% yield), while the remaining C6-sugars formed C6-sugar alcohols, LA, and others, which are also observed. The yield of GVL increased smoothly as the reaction temperatures were increased to

reach the maximum yield of GVL (67.3%) at 443 K, then the yield of GVL slightly decreased to 63.3% at 463 K. These results indicate that the optimized reaction temperature for the one-pot conversion of sucrose to GVL over the RNi–Sn(1.04)/AlOH catalyst is 443 K. Therefore, the optimized reaction temperature of 443 K will be applied for the subsequent catalytic reactions.

Effect of H_2 initial pressure. The influence of the initial H_2 pressure on the product distributions in the direct conversion of sucrose over RNi–Sn(1.04)/AlOH is shown in Fig. 3.

At an initial H_2 pressure of 1.0 MPa, the main product was C6 sugars, followed by C6-sugar alcohols, LA, GVL, and a small amount of others at 83% conversion of sucrose. As the initial H_2 pressure increased to 2.0 MPa, the yields of C6-sugars and LA significantly decreased while that of others remained unchanged, thus a remarkably high yield of GVL (55%) was obtained. In this case, the hydrogenation of C6-sugars to C6-sugar alcohols and the multiple dehydrations of C6-sugars to form LA which rapidly hydrogenated to GVL in the presence of the RNi–Sn(1.04)/AlOH catalyst may occur simultaneously. In fact, the yield of C6-sugars drastically decreased to 7.5%, while the yield of C6-sugar alcohols significantly increased. The maximum yield of GVL (67.3%) was achieved at an initial H_2 pressure of 3.0 MPa, which then remained unchanged (66.7%) at 4.0 MPa. Therefore, it can be concluded that the effective direct conversion of sucrose to GVL can be achieved at an initial H_2 pressure of 3.0 MPa, which was used as the optimized initial H_2 pressure for further investigations in the subsequent catalytic reactions for time profiles and the catalytic reaction of various sugars.
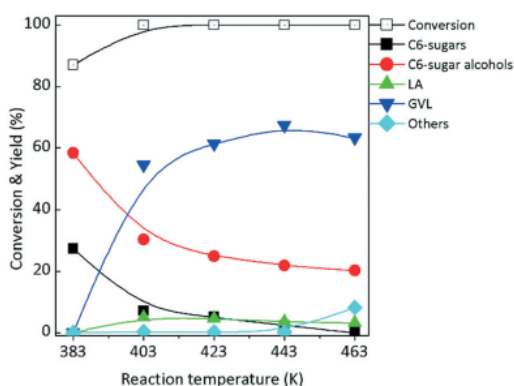

Fig. 2 Effect of reaction temperature on the conversion and yield in the one-pot conversion of sucrose to GVL over the RNi–Sn(1.04)/AlOH catalyst. Reaction conditions: substrate/Ni = 85; sucrose (0.35 mmol); solvent H_2O (5 ml); H_2 (3.0 MPa); reaction time (12 h). C6-sugars include glucose and fructose; C6-sugar alcohols include sorbitol and mannitol; others include glucoside and furans (5-hydroxymethyl furfural and furfural). LA = levulinic acid, GVL = γ-valerolactone.
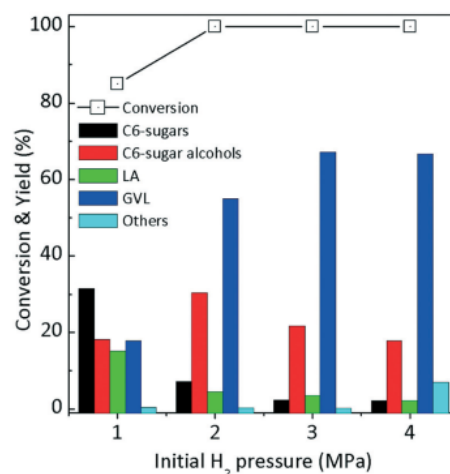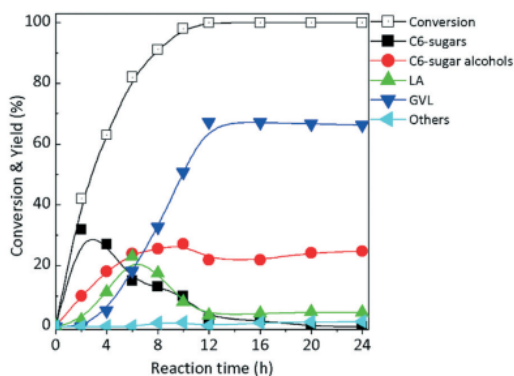

Fig. 3 Effect of initial H_2 pressure on the conversion and yield in the one-pot conversion of sucrose to GVL over the RNi–Sn(1.04)/AlOH catalyst. Reaction conditions: substrate/Ni = 85; sucrose (0.35 mmol); solvent H_2O (5 ml); temperature (443 K); reaction time (12 h). C6-sugars include glucose and fructose; C6-sugar alcohols include sorbitol and mannitol; others include glucoside and furans (5-hydroxymethyl furfural and furfural). LA = levulinic acid, GVL = γ-valerolactone.

Fig. 4 Time profiles of the one-pot conversion of sucrose to GVL over the RNi–Sn(1.04)/AlOH catalyst. Reaction conditions: substrate/Ni = 85; sucrose (0.35 mmol); solvent H_2O (5 ml); H_2 (3.0 MPa); temperature (443 K). C6-sugars include glucose and fructose; C6-sugar alcohols include sorbitol and mannitol; others include glucoside and furans (5-hydroxymethyl furfural and furfural). LA = levulinic acid, GVL = γ-valerolactone.

Time profiles. The kinetic profiles of the direct conversion of sucrose in the presence of the RNi–Sn(1.04)/AlOH catalyst at 443 K, an initial H_2 pressure of 3.0 MPa, and reaction times of 0–24 h were studied and the plot is shown in Fig. 4.

At a short reaction time of 2 h, the yield of C6-sugars was 32%, accompanied by C6-sugar alcohols, and LA with yields of 10%, and 2%, respectively; no formation of GVL was observed at 42% conversion of sucrose. The conversion of sucrose gradually increased as the reaction time was prolonged and reached complete reaction (100% conversion) after 12 h. GVL (5% yield) was firstly observed after a reaction time of 4 h and increased smoothly to reach the maximum yield of 67.3% after 12 h, then remained unchanged after the reaction time was extended to 24 h. A similar result was also observed upon the yield of C6-sugar alcohols which gradually increased to reach the maximum yield of 27.2% at 10 h and then was almost constant after the prescribed reaction time. A significant difference in the reaction profile was observed after a reaction time of 4 h. In this case, the yield of C6-sugars gradually decreased to reach nearly 0% after 12 h, while the yield of LA reached maximum (23%) after 6 h, and then decreased smoothly to almost constant (4%) after 12 h. The decrease in the yield of C6-sugars with the prolonged reaction time suggests that the formed C6-sugars (fructose & glucose) *via* the hydrolysis of the 1,2-β-glycosidic bond in the presence of H_2O and H_2 subsequently hydrogenated to C6-sugar alcohols or *via* multiple dehydrations to form LA then rapidly hydrogenated to GVL.[52] In fact, the amounts of C6-sugars and C6-sugar alcohols were quantitatively obtained at a short reaction time. On further prolonging the reaction time over 12 h, the yields of GVL, C6-sugar alcohols, and LA remained unchanged. As sucrose contains 2 molecules of C6-sugars (glucose and fructose), the molar ratio of GVL and LA to C6-sugar alcohols was around 1.6, suggesting that the competitive hydrogenation of C6-sugars to C6-sugar alcohols

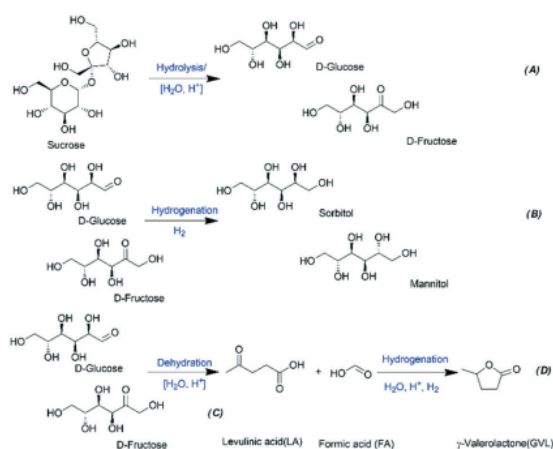or transformation into LA and GVL becomes reliable under the current reaction conditions.

Direct conversion of various sugars. To complete our investigation, the catalytic reaction of various sugars such as cellobiose, glucose, and fructose in the presence of the RNi–Sn(1.04)/AlOH catalyst at 443 K and an initial H_2 pressure of 3.0 MPa for 3 h, 7 h, 10 h, 12 h or 24 h was also carried out, and the results are summarized in Table 2.

Firstly, the catalytic reactions of LA and its ester (EL) were performed and as expected the conversion and yield of GVL were >99% (entries 1 and 2) and these results show very good consistency with the previous report.[43] Only 27.7% yield of GVL was obtained, followed by C6-sugar alcohols (sorbitol) (26.1%), and LA (9.2%) at 63% conversion of glucose after 3 h, suggesting that the catalyst required more time to activate the molecular reactant and then the reaction proceeded continuously to form the products (entry 3). Gratifyingly, the yield of GVL remarkably increased by approximately 2.5 times (from 27.7% to 69.8% and 71.2%) when the reaction times were prolonged to 7 h and 12 h, respectively, while the amount of sorbitol remained unchanged (entries 4 and 5). The increase in GVL yield from glucose as the reaction time was prolonged (entries 3–5) may be the result of glucose–fructose isomerization in the presence of H_2O and the oxidized tin. Previous reports have noticed that Sn^{2+}, Sn^{4+}, Sn, Sn-β or SnO species possessed both Lewis and Brønsted acid sites in an aqueous system. Those tin species catalyzed the glucose–fructose isomerization followed by dehydration, and then produced 5-hydroxymethyl furfural (HMF) in the presence of a tin/MCM-41 catalyst[53] or a zeolite Sn-beta (Sn-β) catalyst.[54] Alternatively, the oxidized tin (Sn^{n+}) slowly formed from metallic tin (Sn^0) or Sn^{2+} will come into contact with H_2O to form SnO or Sn(OH). The SnO or Sn(OH) in the Ni–Sn alloy catalyst may serve as Brønsted acid sites similar to the Sn–OH species observed in Sn–OH/SBA15.[55] The catalytic reactions of fructose were also performed under the same reaction conditions. The yields of GVL (36.0%) and LA (11.7%) from fructose were slightly higher than that of glucose at the same reaction time of 3 h (entry 6). When the reaction time was prolonged to 7 h, the yield of GVL increased by approximately two times (from 36.0% to 74.6%) while the yield of LA drastically decreased to 2.7% at 100% conversion of fructose (entry 7). Although the reaction time was extended to 12 h, the yields of GVL (74.9%) and C6-sugar alcohols (23.1%) remained unchanged. On the other hand, LA completely disappeared, suggesting that the formed LA was completely hydrogenated to GVL in the presence of RNi–Sn(1.04)/AlOH under the current reaction conditions (entry 8). The results of catalytic conversion of cellobiose over the RNi–Sn(1.04)/AlOH catalyst at 453 K and 3.0 MPa H_2 for 10 h and 24 h are also summarized in Table 2. Only 10% yield of GVL and 29.6% yield of C6-sugar alcohols were obtained at 48% conversion of cellobiose after 10 h (entry 9). The yields of GVL and C6-sugar alcohols significantly increased to 37.4% and 53.9%, respectively, at 98% conversion of cellobiose when the reaction time was extended to 24 h (entry

Catalysis Science & Technology

10). In addition, the catalytic reaction of sorbitol and mannitol did not take place in the presence of the RNi–Sn(1.04)/AlOH catalyst (entries 11 and 12).

Possible reaction pathways. Because the reaction of sucrose in the absence of a catalyst produced only C6-sugars (glucose and fructose) (data presented in Table 2, entry 1), it can be reasoned that the first step of the reaction was hydrolysis of the 1,4-β-glycosidic bond of molecular sucrose in the presence of water (Scheme 2A). The reactions of sucrose, glucose, and fructose in the presence of conventional RANEY® Ni and RANEY® Ni/AlOH catalysts resulted in C6-sugar alcohols as the main products and no small molecular products (*e.g.*, acetol, glycerol, ethylene glycol) were observed even though the reaction time was extended to 24 h (Scheme 2B).[40] These results suggest that the Ni catalyst was only able to hydrogenate the C=O group of the sugars to sugar alcohols. Additional acidic co-catalysts are needed for the further conversion of C6-sugar alcohols into glycerol or ethylene glycol to proceed as previously reported.[45] However, in our catalytic reaction system, the addition of acidic co-catalysts such as acetic acid or formic acid is unnecessary and potentially caused the leaching out of nickel metal species into the reaction mixture.

The product distribution obtained from conversion of glucose, fructose, or cellobiose as presented in Table 2 suggested that the competitive reaction between hydrogenation of C6-sugars to C6-sugar alcohols and dehydration of C6-sugars to LA and GVL over the RNi–Sn(1.04)/AlOH catalyst may occur. At a short reaction time (3 h), the glucose conversion was only 63% while the yields of C6-sugar alcohols and GVL were almost equal, *ca.* 26.1% and 27.7%, respectively (Table 3, entry 3). The yield of GVL increased progressively as the reaction time was prolonged

Table 3 The identified Ni–Sn alloy phases for Ni–Sn(x)/AA after reduction with H_2 at 673–873 K for 1.5 h

Entry	Catalyst[a]	Identified Ni–Sn alloy phases[b]	
		Major	Minor
1	RNi–Sn(1.04)/AA (673 K)	n.d	N_3Sn_2, Ni(0)
2	RNi–Sn(1.04)/AA (773 K)	Ni_3Sn	Ni_3Sn_2, Ni(0)
3	RNi–Sn(1.04)/AA (873 K)	Ni_3Sn	Ni_3Sn_2, Ni(0)
4	RNi–Sn(2.14)/AA (673 K)	Ni_3Sn_2 (88%)[c]	Ni_3Sn
5	RNi–Sn(2.14)/AA (773 K)	Ni_3Sn_2 (85%)[c]	Ni_3Sn
6	RNi–Sn(2.14)/AA (873 K)	Ni_3Sn_2	Ni_3Sn

[a] Values in parentheses is the loading amount of Sn, determined by ICP-AES analysis. [b] Based on the crystallographic databases.[58] [c] The % mol of the alloy component was estimated by the Multi-Rietveld Analysis Program LH-Riet 7.00 method on the Rietica software. n.d = not detected.

up to 12 h and the complete conversion of glucose was achieved, whereas the yield of C6-sugar alcohols remained unchanged (entries 3–5). Similarly, the results of the fructose reaction were also observed under the same reaction conditions (entries 6–8). These results confirmed that the reactions in Scheme 2C and D were predominant in the presence of the RNi–Sn(1.04)/AlOH catalyst, producing high yields of LA or GVL. It is well-known that the reaction in Scheme 2C required Lewis or Brønsted acid sites for the successive dehydration of sugar to furanic compounds or levulinic acid which subsequently hydrogenated to GVL (Scheme 2D) to proceed.[56] Reaction results of sorbitol or mannitol as mentioned above in Table 2, entries 11–12, also confirmed that the RNi–Sn(1.04)/AlOH catalyst was unable to catalyze the hydrogenolysis of C–C or C–O bonds in C6-sugar alcohols into glycerol or ethylene glycol under the current reaction conditions. These results confirmed the reaction route of LA and GVL formation through the transformation of glucose or fructose over synergistic actions between the nickel metal and co-metal tin with the surface acidity of aluminium hydroxide (AlOH). In addition, during the multiple dehydrations of sugar, molecular formic acid was also generated which may serve as Brønsted acid sites for the reactions or as a hydrogen donor under the operating reaction conditions as described previously.[34,35]

Catalytic reusability test. A reusability test was performed on the as prepared RNi–Sn(1.04)/AlOH catalyst; the results are shown in Fig. 5. The used RNi–Sn(1.04)/AlOH catalyst was recovered by either simple filtration or centrifugation. The recovered RNi–Sn(1.04)/AlOH catalyst was washed with absolute ethanol and dried *in vacuo* at room temperature without any further thermal treatment before the next reaction run.

We studied the catalytic reusability and deactivation during the direct conversion of glucose to GVL at lower conversions to obtain insight into understanding the rates and mechanisms of deactivation processes, as well as the tolerance (sensitivity) of catalysts.[57] The activity of the RNi–Sn(1.04)/AlOH catalyst is maintained, whereas the decrease in the conversion of glucose was negligible (from 63% (the first
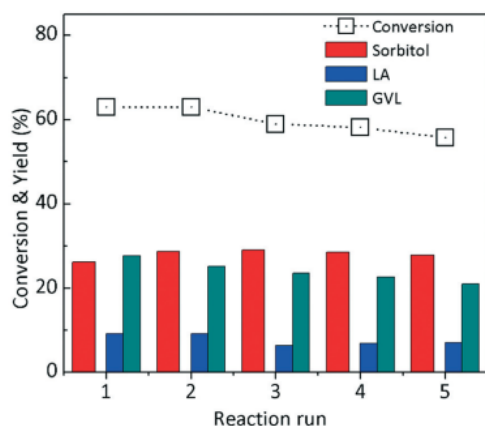

Scheme 2 Reaction scheme for the direct conversion of sugars into γ-valerolactone (GVL) in the presence of RNi–Sn(x)/AlOH catalysts. (A) Hydrolysis of sucrose, (B) hydrogenation of C6-sugars to C6-sugar alcohols, (C) multiple dehydrations of C6-sugars to levulinic acid and formic acid (FA), and (D) hydrogenation of levulinic acid to γ-valerolactone.

Fig. 5 Results of the reusability tests for the RNi–Sn(1.04)/AlOH catalyst in the direct conversion of glucose to GVL. Reaction conditions: substrate/Ni = 85; glucose (0.35 mmol); solvent H$_2$O (5 ml); H$_2$ (3.0 MPa); temperature (443 K); reaction time 3 h. Yields of liquid products were sorbitol, LA = levulinic acid, and GVL = γ-valerolactone.

Fig. 6 XRD patterns of the as-prepared and after reduction with H$_2$ at 673–873 K for 1.5 h of RNi–Sn(x)/AlOH catalysts with different Sn loading amounts; (A) **1.04** mmol and (B) **2.14** mmol. AlOH = aluminium hydroxide, contains bayerite (B) and gibbsite (G); AA = amorphous alumina.

run) to 56% (the fifth run) with a GVL yield of around 22–27% at a reaction time of 3 h. Considering the catalyst productivity, the yield of GVL might be kept high (around triplet ~65%) at much higher glucose conversion when the reaction time was extended up to 7 h or 12 h (Table 2, entries 4 and 5). A slight increase of sorbitol GVL may be attributed to the growth of Ni metal species and the Ni metal coverage on the surface of RNi–Sn(1.04)/AlOH.[43] The amounts of metal leaching into the reaction solution were analyzed by ICP-AES and were found to be 1.3 mol% (Ni), 5.7 mol% (Sn), and 6.9 mol% (Al) after the fifth run. The XRD patterns of the recovered RNi–Sn(1.04)/AlOH catalyst after the fifth reaction run revealed that a slightly intensified nickel reflection peak at 2θ = 44.6° and 51.3° was observed as shown in Fig. S9, in the ESI.†

Structure–activity relationship. On the basis of spectroscopic characterization results, we discuss the structure of active Ni, Sn and bimetallic Ni–Sn alloy species in both as-prepared and pre-reduced RNi–Sn(x)/AlOH catalysts (x = 1.04 and 2.14 mmol which correspond to Ni/Sn molar ratios of 3.0 and 1.4, respectively). Both RNi–Sn(1.04)/AlOH and RNi–Sn(2.14)/AlOH catalysts demonstrated higher yields of GVL than the other RNi–Sn(x)/AlOH catalysts.

Fig. 6A shows the XRD patterns of RNi–Sn(1.04) before and after reduction with H$_2$ at 673–873 K for 1.5 h. In the case of the as-prepared RNi–Sn(1.04)/AlOH catalysts, the broadened diffraction peaks at 2θ = 44.44° was clearly observed, which can be attributed to the formation of Ni–Sn alloys, i.e., Ni$_3$Sn and Ni$_3$Sn$_2$.[42,58] After reduction with H$_2$ at a temperature of 673 K, the diffraction peaks of aluminium hydroxides (e.g., bayerite and gibbsite) totally disappeared, and the broadened peaks at 2θ = 42–44.5° were hardly distinguished due to the overlap of the bimetallic alloy Ni–Sn phases and Ni metal diffraction peaks. Peak formations of a
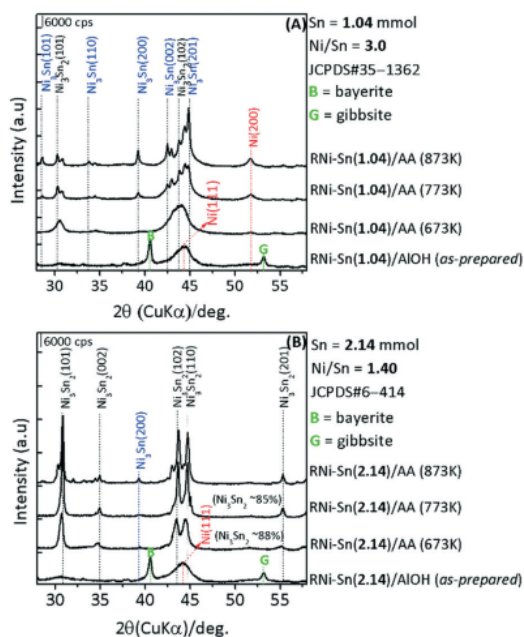
series of Ni$_3$Sn alloy phases (PDF#35-1362) at 2θ = 28.6, 39.3, 42.5, and 44.8° and the remaining metallic nickel (Ni^0) (PDF#04-0850) at 2θ = 51.6° corresponding to Ni(200) were clearly observed when the temperature was increased to 773–873 K. The remaining metallic nickel (Ni^0) in the RNi–Sn(1.04)/AA system may significantly contribute to the relatively high H$_2$ uptake (Table S3, entries 1–2, in the ESI†). Fig. 6B shows the XRD patterns of RNi–Sn(2.14) before and after reduction with H$_2$ at 673–873 K for 1.5 h. A similar result was also observed upon the as-prepared RNi–Sn(2.14)/AlOH catalyst, whereas the broadened diffraction peaks at 2θ = 44.44° was clearly observed. After reduction with H$_2$ at a temperature of 673 K, peak formations of a series of Ni$_3$Sn$_2$ alloys (PDF#06-414) at 2θ = 30.7, 34.8, 43.5, 44.4, and 55.2° were clearly observed, and the peaks intensified at temperatures of 773–873 K (Fig. 6B). The estimated proportions of Ni$_3$Sn$_2$ as the major alloy components were approximately 85% mol and 88% mol after reduction with H$_2$ at temperatures of 773 K and 873 K, respectively (Table 3, entries 4 and 5). These results show very good consistency with the previous results of the bulk Ni–Sn and supported Ni–Sn alloy systems, which were synthesized from the NiCl$_2$·6H2O precursor instead of RNi/AlOH.[58,59]

Fig. 7 shows the differences in the yields of C6-sugar alcohols and GVL obtained from direct conversion of sucrose using RNi–Sn(1.04)/AA and RNi–Sn(2.14)/AA catalysts after reduction with H$_2$ at 673–873 K for 1.5 h. By using the RNi–
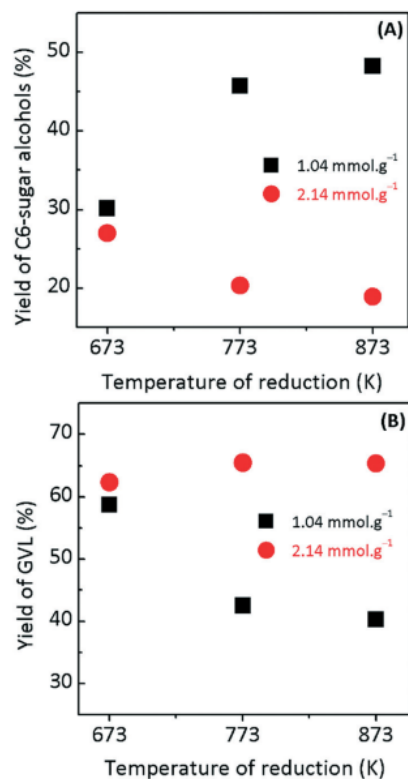
Fig. 7 Yield of (A) C6-sugar alcohols and (B) GVL obtained from the one-pot conversion of sucrose over RNi–Sn(1.04)/AA and RNi–Sn(2.14)/AA catalysts after reduction with H_2 at 673–873 K for 1.5 h.

Sn(1.04)/AA 673/H_2 catalyst, C6-sugar alcohols yield increased to 30.1% (higher than that of the as-prepared RNi–Sn(1.04)/AlOH (Fig. 1) and the yield of C6-sugar alcohols slightly increased as the temperature of reduction with H_2 was increased to 773 K and 873 K (Fig. 7(A)). This was consistent with the RNi–Sn(0.45)/AA results (Table S4, entries 1–3, in the ESI†), suggesting that Ni₃Sn in both RNi–Sn(0.45)/AA and RNi–Sn(1.04)/AA catalysts has high hydrogenation activity (as roughly depicted by the H_2 uptake of the catalysts as summarized in Table S2, entries 1–6, in the ESI†) as well as the metallic Ni(0) species on the surface of bimetallic Ni–Sn particles for the hydrogenation of C6-sugars in sucrose and therefore less activity to catalyze the formation of levulinic acid and GVL. Consequently, the hydrogenation of C6-sugars will take place rapidly, leading to high yields of C6-sugar alcohols, on the other hand, yields of GVL oppositely decrease (Fig. 7B). Moreover, both the RNi–Sn(0.45)/AA and RNi–Sn(1.04)/AA catalysts have a Ni/Sn molar ratio ≫1, which means that they contain a higher metallic Ni concentration on the outer surface. The XRD patterns of the as-prepared and H_2-reduced for both RNi–Sn(1.04)/AA and RNi–Sn (0.45)/AA confirmed the presence of metallic nickel as Ni(111) or Ni(200) as shown in Fig. 6A and S2, in the ESI,† respectively.

Over RNi–Sn(2.14)/AA catalysts, the yield of C6-sugar alcohols gradually decreased as the temperature of reduction with H_2 was increased (Fig. 7(A), on the other hand, the GVL yield increased smoothly as the temperature of reduction with H_2 was increased (Fig. 7(B). In the case of RNi–Sn(3.96)/AA catalysts with a molar ratio of Ni/Sn = 1.0 contained the mixture of Ni₃Sn, Ni₃Sn₂, Ni₃Sn₄, metallic Ni(0), and Sn (Sn(0) and SnO$_x$) phases both in the as-prepared and H_2-reduced at 673–873 K for 1.5 h (Fig. S1 and S3, in the ESI†). Although the GVL yield increased (42.7–55.5% mol) as the temperature reduction was increased, considerable amounts of other products (such as glucoside and furans (5-hydroxymethyl furfural and furfural) were also observed (Table S4, entries 4–6, in the ESI†).

To further confirm the presence of Ni₃Sn and Ni₃Sn₂ alloys in RNi–Sn(x)/AlOH catalysts which are the catalytically active phases in the direct conversion of sucrose, the supported Ni₃Sn/γ-Al₂O₃, Ni₃Sn₂/γ-Al₂O₃, and Ni₃Sn₂/AC catalysts were successfully synthesised using the procedure of supported Ni–Sn alloy as reported previously.[59,60] The XRD patterns of these supported Ni₃Sn and Ni₃Sn₂ catalysts are shown in Fig. S9, in the ESI† and the results of the direct conversion of sucrose under same reaction conditions are summarized in Table S4, entries 7–9, in the ESI.† Over the Ni₃Sn/γ-Al₂O₃ catalyst, at full conversion of sucrose produced 63.9% GVL, 26.4% C6-sugar alcohols, and 9.7% others (entry 7). Obviously, the amount of C6-sugar alcohols over the Ni₃Sn/γ-Al₂O₃ catalyst was higher than those of Ni₃Sn₂/γ-Al₂O₃ and Ni₃Sn₂/AC catalysts. This is consistent with RNi–Sn(1.04)/AA results (Fig. 7B), confirming that Ni₃Sn alloy has high hydrogenation activity towards the C=O bond in C6-sugars and produce relatively high yield of C6-sugar alcohols. Furthermore, over Ni₃Sn₂/γ-Al₂O₃ and Ni₃Sn₂/AC catalysts, the high yields of GVL of 67.1%, and 59.8%, respectively, were obtained at the complete conversion of sucrose (entries 8 and 9). These results suggest that the formation of Ni₃Sn and Ni₃Sn₂ alloy phases play a prominent role in the selective production of γ-valerolactone from sugars as a part of the sustainable catalysis system in the transformation of biomass-derived compounds into high value-added chemicals and fuels.

Conclusions

We have described the direct synthesis of γ-valerolactone (GVL) from biomass-derived sugars (e.g., cellobiose, sucrose, glucose, and fructose using RANEY® nickel–tin alloy supported on aluminium hydroxide (denoted as RNi–Sn(x)/AlOH) catalysts. Over conventional RANEY® Ni and RNi/AlOH catalysts, the main products were C6-sugar alcohols (sorbitol and mannitol) as the results of the hydrogenation reaction. Remarkable differences in product distributions were obtained from the catalytic reaction of cellobiose, sucrose, glucose, and fructose in the presence of the RNi–Sn(x)/AlOH catalysts. The highest yields of GVL were 37% (cellobiose), 67.3% (sucrose), 71.6% (glucose), and 74.9% (fructose) obtained using the RNi–Sn(1.04)/AlOH catalyst at 443 K, H_2

3.0 MPa after 12 h. Further treatment of RNi–Sn(x)/AlOH with H$_2$ at 673–873 K for 1.5 resulted in the formation of Ni–Sn alloy phases (e.g., Ni$_3$Sn and Ni$_3$Sn$_2$) and caused the transformation of aluminium hydroxide (AlOH) to amorphous alumina (AA). The highest yield of GVL (65.3%) was obtained over the RNi–Sn(2.14)/AA 873 K/H$_2$ catalyst, which contained a Ni$_3$Sn$_2$ alloy as the major phase. The reusability test results showed that the RNi–Sn(1.04)/AlOH catalyst was reusable and stable for at least five consecutive reaction runs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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