Bimetallic Ru-Sn as Effective Catalysts for the Selective Hydrogenation of Biogenic Platform Chemicals at Room Temperature

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Abstract

Supported bimetallic ruthenium-tin (denoted as Ru-Sn(x); x = molar ratio of Ru/Sn) catalysts were examined for room temperature (RT) hydrogenation of biogenic platform chemicals of levulinic acid (LA) to γ-valerolactone (GVL). Six types of metal oxide support c.a. Nb₂O₅, TiO₂, ZnO, ZrO₂, γ-Al₂O₃, active charcoal (AC), were employed as the support for Ru-Sn(x). Ru-Sn(3.0)/Nb₂O₅ (Ru/Sn = 3.0) that reduced at 500 °C demonstrated the highest yield of GVL (98%) at 30 °C, 30 bar H₂ for 3 h. The increase in Sn loading amount (Ru/Sn = 1.5) resulted in decreasing of LA conversion (83%) under the same reaction conditions. Among the studied supported Ru-Sn catalysts, Nb₂O₅ and ZnO supports exhibited better catalytic performances than that other for RT hydrogenation of LA and various biogenic platform chemicals. The Ru-Sn(3.0)/Nb₂O₅ catalyst was characterized by means of various adsorption and spectroscopic techniques. The Ru-Sn(3.0)/Nb₂O₅ catalyst was found to be reusable without any significant loss of its activity.

Keywords: bimetallic ruthenium-tin; room temperature hydrogenation; biogenic platform chemicals; levulinic acid; γ-valerolactone


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1. Introduction

The dwindling supplies of fossil fuels supply and the increasing of the energy demand, ligno-cellulosic biomass possesses the promising feedstocks that can be converted into various chemicals and fuel platforms using acid catalyst [1,2]. For instance, a biomass consist of C5-C6 sugars can be transformed into oxygenates such as furfural (FFald), levulinic acid (LA), and various organic carboxylic acids [3–5].
Among those oxygenates, LA is perhaps the most interesting platform chemical as it can be made in relatively high yields from lignocellulosic by using diluted sulfuric acid catalyst [6], which could be turned out into various high-added value chemicals and fuels in the presence of heterogeneous bimetallic catalysts [7]. Under low temperature, the hydrogenation of LA leads to the formation of γ-hydroxyvaleric acid (GHVA) as an unstable intermediate then undergoes to ring closure by intermolecular esterification and loses a water molecule to form γ-valerolactone (GVL) [8] or dehydration to form α-angelica lactone (α-AGL), which is followed by hydrogenation to GVL [9]. GVL can be used as versatile feedstock for the synthesis of fuel additives/biofuels [10] (e.g., liquid hydrocarbon diesel [11], gasoline-like hydrocarbon [12], and valeric biofuels [13]), as a precursor of bulk chemicals (e.g., 1,4-pentanediol [14], aromatic hydrocarbon [15], and 4-hydroxyvaleric acid ionic liquids [16]). Furthermore, GVL has been demonstrated to be a renewable solvent for the Sonogashira reaction [17] and a green polar aprotic solvent for the improvement of biomass conversion [18].

Supported ruthenium-based catalysts, in the forms both monometallic and bimetallic systems, have been employed for the catalytic conversion of LA to GVL [19]. Although ruthenium-based catalysts are effective and frequently applied, harsh reaction conditions (at >140 °C and >40 bar of H2) are required to achieve complete reaction with >99% yield of GVL [20,21]. Only few reports have been published for the catalytic conversion of LA to GVL over Ru-based catalysts at near ambient or low temperature [22]. In the literature, the first established catalyst for the room temperature (RT) hydrogenation of LA to GVL was PtO2 under high H2 pressure (>50 bar) and long reaction time of 40 h with a slow reaction rate of GVL formation [23]. To circumvent these shortcomings, Tan et al. [24] developed the Ru/RGO (RGO = reduced graphene oxide) catalysts for RT hydrogenation of LA to GVL with high yield of 99.9% at 40 bar H2 for 8 h and the highest TOF of 2112 h⁻¹. They suggested that the high activity could be attributed to the formation of electron-rich state of Ru⁰ nanoparticles that are demonstrated to be highly active towards the activation of C=O bonds [24]. Consistent with the results of Ru/RGO catalysts, the Ru/FLG (FLG = few-layer graphene) catalysts demonstrated an improved activity, selectivity, and stability compared with Ru/AC and the average GVL production rate was 178 h⁻¹ at 40 bar H2 for 12 h [25]. Moreover, Ru/N-doped hierarchically porous carbon (NHPC) [26] and Ru@C-Al2O3 [27] catalysts were examined for RT hydrogenation of LA to GVL (25 °C, 10 bar H2 and 4-5 h) with the highest TOF of 398 h⁻¹ and 658 h⁻¹, respectively. They claimed that these high TOFs were attributed to the strong interaction between Ru⁰ and the defect sites of NHPC or C-Al2O3 composite which enhanced the activity and prevented the migration and aggregation of Ru nanoparticles. Recently, Ru/TiO2-nanosheet [28], and Ru/TiO2-nitrogen doped-carbon (NC) [29] catalysts were applied for RT hydrogenation of LA to GVL (30 °C, 30-60 bar, 8-12 h) with high GVL selectivity and the obtained TOFs were 41.5 h⁻¹ and 278 h⁻¹, respectively. The high activity and stability of these catalysts were due to a high dispersion of Ru nanoparticles on TiO2 nanosheet with exposed (001) facets on TiO2@CN support. Though both carbon and titania supported Ru-based catalysts were highly active for RT hydrogenation of LA to GVL, they hold the disadvantage of high price of precursors and difficulty in preparing catalyst materials or high initial H2 pressure used or longer reaction time, thus they may have shortcomings for industrial implementations.

Apart from the development of carbon or titania-supported Ru nanoparticles catalysts, the addition of second electronegative metals (e.g., Sn, In, or Fe) or direct modification of Ru nanoparticles with oxophilic metal oxide species (e.g., ReOx, WOx, or MoOx) have been investigated and applied for various catalytic systems [14,30–32]. Wettstein et al. [33] reported carbon supported bimetallic Ru-Sn (Ru-Sn/C) catalysts for selective hydrogenation of LA to GVL in 2-sec-butyl-phenol solvent at quite high pressure and temperature reaction (180 °C and 35 bar H2). The catalyst containing equal amounts of Ru and Sn had a lower activity for LA to GVL. The beneficial effect of Sn to Ru/C was the increase in activity and stability due to the formation of Ru2Sn3 and Ru3Sn4 alloy phases [33]. Vorotnikov et al. [34] developed an inverse bimetallic RuSn catalyst for selective reduction of carboxylic acids to alcohols. The authors suggested that the SnO2/Ru species was believed to be responsible for the C=OH scission (SnO2 cluster) and hydrogenation activation (Ru), led to high selectivity of 1-propanol in the hydrogenation of propionic acid at 160 °C, 100 bar H2 in a trickle bed flow reactor system [34]. Most recently, Ru-Sn/ZnO catalyst was employed for hydrogenation of octanoic acid to octanol in a fixed-bed continuous reactor system at elevated temperatures (300 °C) and 30 bar H2. The presence of Ru3Sn7 al-

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loy phase was the active site for the significant improvement of the hydrogenation activity and selectivity to octanol as well as the stability in long-term reactions [35].

Herein, we reported the synthesis of supported bimetallic ruthenium-tin (Ru-Sn) by using coprecipitation-hydrothermal method at 150 °C for 24 h, followed by reduction with H₂ at 400-500 °C for 2 h [14,31,32] and applied for the aqueous phase hydrogenation of LA to GVL at room temperature (RT) (Scheme 1). Various metal oxides such as niobium oxide (NbO₅), anatase titanium oxide (TiO₂), zinc oxide (ZnO), zirconia oxide (ZrO₂), and gamma-alumina (γ-Al₂O₃), and active charcoal (AC) were employed for the support of bimetallic ruthenium-tin (denoted as Ru-Sn(x)/support (x = molar ratio of Ru/Sn) catalysts. We found that the Ru-Sn(3.0/ NbO₅) exhibited the highest yield of GVL (98%) with tuneable high Turnover Frequency (TOF) (306 h⁻¹) at 30 °C, 30 bars H₂ after 3 h. The effect of Sn loading amount (Ru/Sn molar ratio), temperature of catalyst reduction, effect of solvent, simple kinetic studies, role of support and catalyst structure-activity relationship are systematically discussed.

2. Materials and Methods

2.1 Materials

Ruthenium(III) chloride (RuCl₃) and tin(II) chloride dihydrate (SnCl₂·2H₂O) were purchased from Sigma-Aldrich Co. The commercial Ru(5 wt%)/C catalyst was purchased and used as received from Tokyo Chemical Industries Co. The supports of NbO₅, ZnO, ZrO₂, TiO₂ (S BET = 51 m²·g⁻¹), and γ-Al₂O₃ (S BET = 100 m²·g⁻¹) were purchased from Japan Aerosil Co. The active charcoal (AC) (S BET = 600 m²·g⁻¹) was purchased from Merck Millipore Co. All organic chemical compounds were purified using standard procedures prior to use [36].

2.2 Methods

2.2.1 Catalyst preparation

The detail procedure for the synthesis of bimetallic ruthenium-tin supported on NbO₅ (denoted as Ru-Sn(x)/NbO₅ (x = Ru/Sn molar ratio)) is described as follows [14,31]. Typically, a 0.1025 g (0.494 mmol) RuCl₃ (Mr = 207.42; Sigma-Aldrich, 99.9%) was dissolved in deionised water (denoted as solution A) and an ethanol solution of SnCl₂·2H₂O (0.0163 mmol) was dissolved in ethanol (denoted as solution B). A 20 mL ethylene glycol, a 1.0 g NbO₅ (Wako Pure Chemical) and solution A and B were mixed in room temperature and the temperature was raised to 50 °C under gentle stirring for overnight. The mixture then transferred into a teflon with stainless cover of autoclave reactor for hydrothermal treatment at 150 °C for 24 h. A black solid was then calcined with N₂ (200 mL/min) at temperature 30-500 °C for 2 h (ramping 4 °C/min) followed by reduction with H₂ (200 mL/min) at 500 °C for 2 h and produced a reduced Ru-Sn(3.0)/NbO₅ catalyst (3.0 is molar ratio of Ru/Sn).

2.2.2 Catalyst characterizations

The powder X-ray diffraction (XRD) analysis was performed on a Miniflex II 600 Rigaku instrument with Cu as monochromatic source of CuKα radiation (λ = 0.1544 nm). The XRD was operated at 40 kV and 15 mA with a step width of 0.02°, a scan speed of 4°·min⁻¹ (α1 = 0.1540 nm, α2 = 0.1544 nm), solar slit 1.25°, and using a Ni Kβ filter.

The Brunauer–Emmett–Teller (BET) specific surface area (S BET) and pore volume (Vp) were measured using N₂ physisorption at -196 °C on a Belsorp Max (BEL Japan). The samples were degassed at 200 °C 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 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 [37].

The NH₃-TPD was carried out on a Belsorp Max (BEL Japan). The samples were degassed at elevated temperature of 100-200 °C for 2 h to remove physisorbed gases prior to the measurement. The temperature was then kept at 200 °C for 2 h while flushed with He gas. NH₃ gas (balanced NH₃, 80% and He, 20%) was introduced at 100 °C for 30 min, then evacuated

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Scheme 1. Reaction pathways for aqueous phase hydrogenation of LA to GVL over bimetallic ruthenium-tin catalysts at room temperature.
by helium gas to remove the physisorbed also for 30 min. Finally, temperature programmed desorption was carried out at temperature of 100 – 800 °C and the desorbed NH3 was monitored by TCD.

The H2-TPR was performed on a Chemisorb 2750, Micromeritics. The samples were heated at 110 °C for 2 h under N2 stream with flow rate of 40 ml/min, then cooled to room temperature. Before reduction processes, the line was purged with H2 (5% Ar gas v/v) for 30 min, then reduced with the same gas (H2 (5% Ar v/v)) at elevated temperature of 30-700 °C with ramping 10 °C/min. The H2 uptake was calculated by using calibration curve (H2 gas; 5% Ar gas v/v, and flow rate of 40 ml/min).

2.2.2 Hydrogenation of LA to GVL

A typical procedure for the catalytic reaction is described as follow: Catalyst (24 mg), LA (2.0 mmol), H2O (3 mL) as a solvent, and dodecane (0.2 mmol) as an internal standard were placed into a glass reaction tube, fitted inside a stainless-steel reactor of TAIATSU Techno, Japan. After H2 was introduced into the reactor with an initial H2 pressure of 30 bars at room temperature (30 °C). After 3 h (180 min), the conversion of LA and the yield of GVL were determined via GC analysis. For reusability test, the used Ru-Sn(3.0)/Nb2O5 catalyst was easily separated using either simple centrifugation or filtration in air and dried under vacuum at room temperature, then it was utilized repeatedly without any additional treatments.

2.2.3 Product analysis

Analysis of reactants (LA, aldehydes, ketones, carboxylic acids) and products (GVL, 2-MeTHF, 2-PeOH, and alcohols) was performed on a Perkin Elmer XL-Autosystem equipped with a flame ionization detector and with Restek Rtx® BAC Plus 1 capillary column (30 m, 0.32 mmID, 1.8 mdf). Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-17B equipped with a thermal conductivity detector and with an RT-8DEXsm capillary column. 1H and 13C NMR spectra were obtained on a JNM-AL400 spectrometer at 400 MHz; samples were dissolved in chloroform-d or D2O with TMS as an internal standard. The calibration curve was performed using known concentrations of internal standard, reactants, and products to determine the correct response factors. The conversion of levulinic acid and yield of the products were calculated according to the following equations (Equations (1) and (2)).

\[
\text{Conversion} = \frac{C_0 - C_i}{C_0} \times 100\% \quad (1)
\]
\[
\text{Yield} = \frac{\text{mol product}}{\text{introduced mol reactant}} \times 100\% \quad (2)
\]

where, \(C_0\) is the introduced mol reactant (levulinic acid) and \(C_i\) is the remaining mol reactant, which are all obtained from GC analysis using an internal standard technique.

The turnover frequency (TOF, mol-GVL.molRu⁻¹.h⁻¹) was calculated with high yield of GVL by using Equation (3).

\[
\text{TOF} (h^{-1}) = \frac{\text{Amount of GVL produced} (\text{mol}_{GVL})}{\text{Total metal Ru} (\text{mol}_{Ru}) \times \text{time} (h)} \quad (3)
\]

Table 1. Results of RT hydrogenation of LA to GVL over various supported ruthenium-based catalysts at low temperature.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversiona (%)</th>
<th>Yielda (%)</th>
<th>TOFb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ru-Sn(3.0)/Nb2O5 (unred.)</td>
<td>52</td>
<td>36</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>Ru-Sn(3.0)/Nb2O5 400 °C/H2</td>
<td>85</td>
<td>85</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Ru-Sn(3.0)/Nb2O5 500 °C/H2</td>
<td>98</td>
<td>98</td>
<td>0</td>
</tr>
<tr>
<td>4a</td>
<td>Sn/Nb2O5</td>
<td>71</td>
<td>71</td>
<td>0</td>
</tr>
<tr>
<td>5a</td>
<td>-</td>
<td>96</td>
<td>96</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Ru-Sn(1.5)/Nb2O5 500 °C/H2</td>
<td>83</td>
<td>83</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Ru (5 wt%)/Nb2O5</td>
<td>57</td>
<td>29</td>
<td>28</td>
</tr>
<tr>
<td>8</td>
<td>Sn/Nb2O5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>RuCl3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>None</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Reaction conditions: catalyst (2.4 mg), LA (2.0 mmol), H2O (3.0 mL), H2 (30 bar), 30 °C, 3 h. aConversion of LA and Yield of GVL were determined by GC using an internal standard technique. bTOF is turnover frequency of GVL formation (mmolGVL.molRu⁻¹.h⁻¹). cAt 10 bar H2. dThe second reaction run (the recovered catalyst was used without any treatment).

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3. Results and Discussion

3.1 Hydrogenation of LA over Ru-Sn(x)/Nb2O5 Catalyst

In the first set experiments, we conducted the aqueous phase hydrogenation of LA to GVL at low temperature using Ru-Sn/Nb2O5 catalysts at 30 °C, 30 bar H2 for 3 h and the results are summarised in Table 1. Unreduced Ru-Sn(3.0)/Nb2O5 catalyst converted 52% of LA to produce 36% GVL and 16% pseudo-levulinic acid (p-LA) (entry 1). Over pre-educed Ru-Sn(3.0)/Nb2O5 400 °C/H2 catalyst, a remarkably high yield of GVL (85%) was obtained at 85% conversion of LA with the average GVL productivity (TOF) of 133 mmolGVL.molSn−1.h−1 (entry 2). Further increase in the reduction temperature, Ru-Sn(3.0)/Nb2O5 500 °C/H2 catalyst exhibited the highest yield of GVL (98%) with the average GVL productivity (TOF) of 306 mmolGVL.molSn−1.h−1 under the same reaction conditions (entry 3). These results indicate that the reduction of catalyst with hydrogen is important to produce highly active and selective bimetallic Ru–Sn catalysts for hydrogenation of LA to GVL.

To clarify the effect of initial H2 pressure, the reaction was conducted at initial H2 pressure of 10 bar and LA conversion was significantly decreased to 71% without altering of GVL selectivity (entry 4). The reusability of Ru-Sn(3.0)/Nb2O5 500 °C/H2 was also evaluated and the conversion of LA, selectivity of GVL, and apparent reaction rate showed almost constant after the second reaction run (entry 5). Furthermore, when the amount of Sn was increased (Ru/Sn molar ration of 1.5), the conversion of LA significantly decreased to 83% without the change of GVL selectivity (entry 6). In contrast, the conversion of LA and yield of GVL were 29% and 28%, respectively over unmodified Ru (5wt%)/Nb2O5 catalyst (entry 7). This is consistent with the fact that the presence of tin metal in Ru-Sn(x)/Nb2O5 catalyst beneficially affected to the activity and selectivity of Ru nanoparticle in the hydrogenation of LA [34] and various carboxylic acids [38]. In addition, Sn/Nb2O5 and RuCl3 were inactive for hydrogenation of LA (entries 8–9) and no reaction was observed in absence of catalyst (entry 10).

3.2 Effect of Catalyst Support

To understand the role of support, various supported bimetallic Ru–Sn catalysts were prepared and tested for the hydrogenation of LA to GVL under the same reaction conditions and the results are summarised in Table 2. Five types of supports (e.g., ZrO2, TiO2, ZnO, γ-Al2O3, and activated charcoal (AC) were employed for the preparation of supported bimetallic Ru–Sn catalysts. Ru-Sn(3.0)/ZnO catalyst converted 96% LA to produce high yield of GVL (96%) (entry 1), which is comparable with the Ru-Sn/Nb2O5 catalysts. It has been reported that both Nb2O5 and ZnO are typical acidic supports that could play as the Bronsted acid sites, while Ru-Sn or SnOx could serve as the Lewis acid sites during the hydrogenation of carboxylic acids under aqueous phase reaction [39,40]. To confirm this suggestion, catalytic reaction over Ru-Sn(3.0)/γ-Al2O3 catalyst showed quiet high LA conversion (85%), however quite high remained yield of p-LA (24%) was observed indicating the effect of acidic support inhibit the reaction of GVL formation (entry 2). In fact, catalytic reaction over monometallic Ru/Nb2O5 gave only 57% LA conversion to produce 29% GVL and 28% p-LA (Table 1, entry 7). This result suggested that the high yield of GVL over Ru-Sn/Nb2O5 and Ru-Sn/ZnO was mainly due the synergistic action between Ru-Sn or SnOx species and acidic metal oxide support. Though the precise role of Nb2O5 or ZnO as support in is not yet clear, previous reports have showed that the domination of Sn-support and Ru-support are generally known [34]. Strong metal–support interactions in supported Ru–Sn catalysts may hinder the formation of Ru–Sn alloys. It is therefore assumed

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv. (%)</th>
<th>GVL (%)</th>
<th>p-LA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ru-Sn(3.0)/ZnO</td>
<td>96</td>
<td>96</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Ru-Sn(3.0)/γ-Al2O3</td>
<td>85</td>
<td>61</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>Ru-Sn(3.0)/TiO2</td>
<td>47</td>
<td>47</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Ru-Sn(3.0)/ZrO2</td>
<td>66</td>
<td>66</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Ru-Sn(3.0)/AC</td>
<td>73</td>
<td>73</td>
<td>0</td>
</tr>
</tbody>
</table>

Reaction conditions: catalyst (2.4 mg), LA (2.0 mmol), H2O (3.0 mL), H2 (30 bar), 30 °C, 3 h. aConversion of LA and Yield of GVL were determined by GC using an internal standard technique.

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that Nb₂O₅ or ZnO, as a support material, may provide moderate metal-support interactions to generate the Ru₃Sn₇ alloy, which is the robust and active phase for hydrogenation [41]. Likewise, the second role of Nb₂O₅ or ZnO is supposedly hydrogen supply through hydrogen dissociation on Nb₂O₅ or ZnO and hydrogen spillover from Nb₂O₅ or ZnO to Ru in the Ru–Sn alloy or on isolated ruthenium metal surfaces [42]. As the results, high conversion of LA and high yield of GVL were obtained even more under room temperature. Moreover, other supported Ru-Sn(3.0) catalysts (e.g., Ru-Sn(3.0)/TiO₂, Ru-Sn(3.0)/ZrO₂, and Ru-Sn(3.0)/AC) showed 47-73% conversion of LA (entries 2-5). These results suggest that the unmodified TiO₂, ZrO₂, or AC supported may require more time or temperature reaction to achieve the completed reaction compared to the their modified support as already described in the above introduction. Therefore, it can be concluded that supported Ru-Sn(3.0)/Nb₂O₅ and Ru-Sn(3.0)/ZnO catalysts were the highest activity and selectivity for RT hydrogenation of LA to GVL.

3.3 Role of Solvent

To assess the effect of solvent and initial H₂ pressure on the LA conversion and yield of GVL, the hydrogenation of LA was carried out in absence of solvent and in various solvents (e.g., 2-propanol, 1,4-dioxane, H₂O/2-propanol and H₂O/1,4-dioxane) the results are also shown in Table 3.

The reaction in the absence of solvent only afforded 19% conversion of LA (19% yield of GVL) even at high H₂ pressure (30 bar) and after 3 h (entry 11). It may be due to the saturation of active site of catalyst by the presence of high concentration of molecular reactant. The use of 2-propanol, 1,4-dioxane, H₂O/2-propanol, and H₂O/1,4-dioxane resulted in quiet low LA conversion of 25%, 29%, 52%, and 40%, respectively (entries 2-5) to yield low amount of GVL. The effectivity of solvents during the hydrogenation reaction is related to their dielectric constant (e). It is found that among the studied solvents, H₂O has the highest dielectric constant of 78.54, which may affect the miscibility of reaction system. Our previous results have also shown that hydrogenation of LA to GVL in the presence of bimetallic Ni-Sn alloy catalyst was effectively occurred in H₂O or its mixture solvents (e.g., H₂O/2-Propanol or H₂O/ethanol or H₂O/methanol) [43,44].

3.4 Substrate Scope

The substrate scope of the Ru-Sn(3.0)/Nb₂O₅ and Ru-Sn(3.0)/ZnO catalysts in the hydro-

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>ε&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Conv.&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>GVL</th>
<th>p-LA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Solvent-free</td>
<td>-</td>
<td>19</td>
<td>19</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2-Propanol</td>
<td>18.5</td>
<td>25</td>
<td>15</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1,4-Dioxane</td>
<td>2.21</td>
<td>29</td>
<td>19</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>H₂O/2-Propanol</td>
<td>-</td>
<td>52</td>
<td>38</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>H₂O/1,4-Dioxane</td>
<td>-</td>
<td>40</td>
<td>30</td>
<td>10</td>
<td></td>
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</table>

Table 3. Results of RT hydrogenation of LA to GVL over Ru-Sn(3.0)/Nb₂O₅ 500 °C/H₂ catalyst at RT.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Ru-Sn(3.0)/Nb₂O₅ &lt;br&gt;Conv.&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>Ru-Sn(3.0)/ZnO &lt;br&gt;Conv.&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Dodecanoic acid</td>
<td>n-Dodecanol</td>
<td>82</td>
<td>80</td>
<td>79</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>1-Pentenoic acid</td>
<td>1-Pentenol (1-Pentanol)</td>
<td>59</td>
<td>57(2)</td>
<td>61</td>
<td>59(2)</td>
</tr>
<tr>
<td>3</td>
<td>Methyl levulinate</td>
<td>γ-Valerolactone</td>
<td>76</td>
<td>76</td>
<td>81</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>2-Pentanone</td>
<td>2-Pentanol</td>
<td>83</td>
<td>83</td>
<td>79</td>
<td>79</td>
</tr>
<tr>
<td>5</td>
<td>Acetophenone</td>
<td>1-Phenyl ethanol</td>
<td>76</td>
<td>76</td>
<td>81</td>
<td>81</td>
</tr>
<tr>
<td>6</td>
<td>Cyclopentanone</td>
<td>Cyclopentanol</td>
<td>78</td>
<td>78</td>
<td>64</td>
<td>64</td>
</tr>
<tr>
<td>7&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Furfural</td>
<td>Furfuryl alcohol (THFalc)</td>
<td>98</td>
<td>96(2)</td>
<td>93</td>
<td>90(3)</td>
</tr>
<tr>
<td>8&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Furfuryl alcohol</td>
<td>THFalc</td>
<td>11</td>
<td>11</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>9&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2-Methylfuran</td>
<td>Tetrahydromethylfuran</td>
<td>17</td>
<td>17</td>
<td>13</td>
<td>13</td>
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</tbody>
</table>

Table 4. Results of catalytic hydrogenation of various carboxylic acids, ketones, and aldehydes over Ru-Sn(3.0)/Nb₂O₅ and Ru-Sn(3.0)/ZnO catalysts.

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genation of various carboxylic acids, aldehydes, and ketones was examined and the results are summarised in Table 4.

Hydrogenation of aliphatic carboxylic acids such as dodecanoic acid over Ru-Sn(3.0)/Nb₂O₅ catalyst produced 80% yield of n-dodecanol at 82% conversion, while Ru-Sn(3.0)/ZnO catalyst gave 78% yield at 79% conversion at 500 °C, 30 bar H₂ for 3 h, in 1,4-dioxane/H₂O (entry 1) [30,45]. Both Ru-Sn(3.0)/Nb₂O₅ and Ru-Sn(3.0)/ZnO catalysts exhibited high selectivity towards unsaturated alcohol (1-pentenol; ~93% selectivity) from hydrogenation of unsaturated 1-pentenoic acid at moderate conversion (59-61%) (entry 2). These results indicate that our Ru-Sn(3.0)/Nb₂O₅ and Ru-Sn(3.0)/ZnO catalysts are active and selective for hydrogenation both C=O and –COOH to corresponding alcohols even under low reaction temperature.

Moreover, hydrogenation of typical ketone 2-pentanone was also examined and afforded 83% 2-pentanol (Ru-Sn(3.0)/Nb₂O₅) and 79% 2-propanol (Ru-Sn(3.0)/ZnO) (entry 4). Acetophene, a typical and simplest aromatic ketone, was selectively hydrogenated to phenyl ethanol (76-81%) without hydrogenation of the C=C of aromatic ring under current conditions (entry 5). Typical cyclic ketone of cyclopentanone showed higher reactivity over these catalysts as indicated by the high conversion (64-78%) and high yield of cyclic alcohol (entry 6). In addition, hydrogenation of biomass-derived furfural selectively produced furfuryl alcohol and small amount of tetrahydrofurfuryl alcohol (THFalc) with yield of 96% (Ru-Sn(3.0)/Nb₂O₅) and 90% (Ru-Sn(3.0)/ZnO) under the same reaction conditions (entry 7). In contrast, hydrogenation of furfuryl alcohol, and 2-methylfuran in ethanol or H₂O [46,47] produced tetrahydrofurfuryl alcohol (9-11%) (entry 8) or tetrahydroxymethylfuran (13-17%) (entry 9). These results confirmed that Sn-modified Ru/Nb₂O₅ and Ru/ZnO catalysts showed higher activity towards the hydrogenation of C=O rather than C=C bond in ketones and aldehydes, thus much higher unsaturated alcohols were obtained.

3.5 Structure-Activity Relationship

To understand the structure-activity relationship both Ru-Sn(3.0)/Nb₂O₅ and Ru-Sn(3.0)/ZnO catalysts were characterized by means of ATR-IR, XRD, N₂ adsorption, H₂ chemisorption, and NH₃-TPD techniques. The physico-chemical properties of the catalysts are summarized in Table 5. Figure 1 shows the XRD patterns of representative supported Ru-Sn catalysts after reduction with H₂ at 500 °C for 1.5 h. The XRD patterns exhibited the main diffraction peaks of support, c.a. ZnO or Nb₂O₅, and the presence of ruthenium, tin, or Ru-Sn species are unable to detect by using XRD technique due to the extremely low amount of sample.

As expected, the specific surface area BET (S₅₇₅) both catalysts exhibited the low surface area of metal oxide support, indicating the ac-

![Figure 1. XRD patterns of supported Ru-Sn(3.0)/Nb₂O₅ and Ru-Sn(3.0)/ZnO after reduction with H₂ at 500 °C for 1.5 h.](image)

Table 5. Physico-chemical properties of the synthesised Ru-Sn(3.0)/Nb₂O₅ and Ru-Sn(3.0)/ZnO catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>S₅₇₅b (m²·g⁻¹)</th>
<th>H₂ uptaked (mmol·g⁻¹)</th>
<th>Acidic amounte (μmol NH₃·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Weak (100-600 °C)</td>
<td>Strong (&gt;600 °C)</td>
</tr>
<tr>
<td>1</td>
<td>Ru-Sn(3.0)/Nb₂O₅</td>
<td>58.5</td>
<td>1.56</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>Ru-Sn(3.0)/ZnO</td>
<td>68.8</td>
<td>1.42</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>Ru-Sn(3.0)/ZrO₂</td>
<td>63.4</td>
<td>na</td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td>Ru-Sn(3.0)/γ-Al₂O₃</td>
<td>132</td>
<td>na</td>
<td>174</td>
</tr>
</tbody>
</table>

aThe value in the parenthesis is the Ru/Sn molar ratio. bS₅₇₅ is specific surface areas, determined by N₂ physisorption at 77 K using BET method. cThe H₂ uptake was derived from H₂-TPR data. dAcidity was derived from NH₃-TPD spectra.
tive metal (Ru or Ru-Sn) would be dispersed on the outer surface of metal oxide support. It is found that the $S_{BET}$ of each sample was around 58-132 cm$^2$/g which reflected to the $S_{BET}$ of support. The representative of hydrogen-temperature programmed reduction (H$_2$-TPR) data of Ru-Sn(3.0)/Nb$_2$O$_5$ and Ru-Sn(3.0)/ZnO samples were also summarised in Table 5. The H$_2$ uptake of Ru-Sn(3.0)/Nb$_2$O$_5$ sample was 1.56 mmol.g$^{-1}$, while for Ru-Sn(3.0)/ZnO was 1.42 mmol.g$^{-1}$ (entries 1-2). The surface acidity was determined by using ammonia-temperature programmed desorption (NH$_3$-TPD) and representative NH$_3$-TPD spectra for Ru-Sn(3.0)/Nb$_2$O$_5$ and Ru-Sn(3.0)/ZnO samples are shown in Figure 2.

The NH$_3$-TPD profiles were formally divided into three desorption temperature regions to denote two types of acid sites [48,49]: (1) weak to moderate acid sites, ranging from 100 to 600 °C and (2) strong acid sites, ranging from >600 to 800 °C (Table 5). Ru-Sn(3.0)/ZnO sample has a peak at 235 °C and two peaks at 570 °C and 650 °C, which can be attributed to the weak and strong acid sites, respectively. In contrast, Ru-Sn(3.0)/ZnO has desorption peak at 600 °C indicating the presence of strong acid site. A small peak with low intensity was also observed at 475 °C over this sample, which can be attributed to the weak acid sites. The presence of both Lewis and Bronsted acids sites were clarified by using pyridine adsorption and the results are shown in Figure 2(b). The spectra of adsorbed species were obtained after introduction of 1-2 ml pyridine at room temperature, followed by purging with N$_2$ flow at 50 °C until the spectra were stable. According to the literatures of pyridine adsorption peaks on Sn-containing catalysts [50,51], the bands are assigned in the following way. Pyridinium ion (PyH$^+$) produced by the reaction of pyridine with Bronsted acid sites (B) shows bands around 1633 cm$^{-1}$ ($\nu_{8a}$). Coordinatively bound pyridines on Lewis acid sites (L) shows bands

![Figure 2. Representative of (a) NH$_3$-TPD profiles, (b) pyridine adsorption, and deconvoluted NH$_3$-TPD spectra of (b) Ru-Sn(3.0)/Nb$_2$O$_5$ and (c) Ru-Sn(3.0)/ZnO catalysts.](image-url)
around 1445 (u19b) and 1575 cm⁻¹. Physisorbed or hydrogen-bonded pyridine (H) shows bands around 1437 and 1599 cm⁻¹. The band around 1490 cm⁻¹ is common to vibrations due to PyH⁺ (B) and coordinatively bound pyridine (L) [52]. These results indicate that acid sites of Ru-Sn(3.0)/Nb₂O₅ and Ru-Sn(3.0)/ZnO are both Lewis and Brønsted acidic under the condition in Figure 2(b).

Furthermore, to understand the interaction between the molecular reactant of LA and surfaces of catalyst, the solvent-free reaction (the spectra were recorded according to reaction of entry 1, Table 3) was carried out in the range of 1-3 h and the evolution of two band types at 1700 cm⁻¹ (C=O band of LA), and ~1760 cm⁻¹ (C=O band of GVL) was monitored by using ATR-IR and the results are shown in Figure 3. A typical absorbance of −COOH of LA was clearly observed at wavenumber of 1700 cm⁻¹ after 1 h of reaction. The intensity of n(−COOH) gradually decreased and slightly shifted to higher wavenumber of 1708 cm⁻¹ after reaction time of 15 h. The spectra at t = 0 h are the results of LA adsorbed before the reaction at 30 °C after purging with nitrogen gas for 30 min. After hydrogen (30 bar, 30 °C) was introduced, the time-dependence IR spectra was recorded. The time course of the relative amount of the adsorbed LA (area of the C=O stretching band at 1700 cm⁻¹) and the relative amount of GVL formed (area of the C=O stretching band at 1757 cm⁻¹). As seen in Figure 3 shows the IR spectra of representative OH stretching band of H₂O generated from hydrogenation & cyclisation of LA to GVL. The time course of relative amount of generated H₂O intensified as the reaction time was prolonged up to 15 h.

The current results show that the precise design of bimetallic Ru-based catalysts (e.g., the type and amount of second metal (Sn), support) are still challenging to obtain highly active and selective catalyst for room temperature hydrogenation of LA to GVL. The required quite high initial H₂ pressure (30 bar) is challenging in the transformation of various bioogenic oxygenated compounds in term of the design of catalyst material. Though, the bimetallic Ru-Sn on ZnO or Nb₂O₅ or even on various studied support in this report showed a great potential for various reactions and further investigation on the fundamental aspect of reaction (kinetic studies, stability and reusability) of type of reaction system (batch of flow) will be a great challenging.

4. Conclusions

Supported bimetallic ruthenium-tin catalysts were examined for the selective hydrogenation of biogenic platform chemicals at low temperature (30-50 °C). Ru-Sn(3.0)/Nb₂O₅ (Ru/Sn = 3.0) that reduced at 500 °C demon-

Figure 3. Ex-situ ATR-FTIR of solvent free of LA hydrogenation over Ru-Sn(3.0)/Nb₂O₅ catalyst at room temperature. Reaction conditions: catalyst (2.4 mg), LA (4.0 mmol), H₂ (30 bar), 30 °C.
strated the highest 98% yield of γ-valerolactone at 30 °C, 30 bar H₂ for 3 h. The increase of Sn loading amount (Ru/Sn = 1.5) resulted in decreasing of LA conversion (83%) under the same reaction conditions. Among the studied supported Ru-Sn catalysts, Nb₂O₅ and ZnO supports exhibited better catalytic performances than that other for RT hydrogenation of LA and various biogenic platform chemicals. The high activity and selectivity of both catalysts can be attributed to the synergistic between high dispersion of Ru or Ru-Sn nanoparticles and the presence of Lewis/Bronsted acid sites of the catalyst system. Moreover, the Ru-Sn(3.0)/Nb₂O₅ catalyst was found to be reusable without any significant loss of its activity.

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CRediT Author Statement

A.S. Azzahra, H.P. Dewi: Formal Analysis, Investigation, ATR-IR study, and Experiment. R. Rodiansono, I.F. Nata: Conceptualization, Methodology, Writing-Original draft, Writing-Review & Editing, Supervision. G.K. Sunnardianto, K.C. Sembiring, J. Jayanuddin: Writing-Review & Editing, Supervision, Formal Analysis (XRD, NH₃-TPD, H₂-TPR, and N₂-adsorption analyses). All authors have read and agreed to the published version of the manuscript.

References


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