

Research Article

Selective Hydrogenation of Biomass-derived Furfural over Supported Ni₃Sn₂ Alloy: Role of Supports

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Abstract

A highly active and selective hydrogenation of biomass-derived furfural into furfuryl alcohol was achieved using supported single phase Ni₃Sn₂ alloy catalysts. Various supports such as active carbon (AC), γ -Al₂O₃, Al(OH)₃, ZnO, TiO₂, ZrO₂, MgO, Li-TN, and SiO₂ have been employed in order to understand the role of the support on the formation of Ni₃Sn₂ alloy phase and its catalytic performance. Supported Ni₃Sn₂ alloy catalysts were synthesised via a simple hydrothermal treatment of the mixture of aqueous solution of nickel chloride hexahydrate and ethanol solution of tin(II) chloride dihydrate in presence of ethylene glycol at 423 K for 24 h followed by H₂ treatment at 673 K for 1.5 h, then characterised by using ICP-AES, XRD, H₂- and N₂-adsorption. XRD profiles of samples showed that the Ni₃Sn₂ alloy phases are readily formed during hydrothermal processes and become clearly observed at $2\theta = 43$ - 44° after H₂ treatment. The presence of Ni₃Sn₂ alloy species that dispersed on the supports is believed to play a key role in highly active and selective hydrogenation of biomass-derived furfural towards furfuryl alcohol. Ni₃Sn₂ on TiO₂ and ZnO supports exhibited much lower reaction temperature to achieved >99% yield of furfuryl alcohol product compared with other supports. The effects of loading amount of Ni-Sn, reaction conditions (temperature and time profile) on the activity and selectivity towards the desired product are systematically discussed. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: selective hydrogenation; furfural; furfuryl alcohol; supported Ni₃Sn₂ alloy catalysts

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1. Introduction

Selective hydrogenation of furfural (FFald) to furfuryl alcohol (FFalc) is great industrial interest since it widely use in various applica-

tions [1]. Industrially, furfuryl alcohol was produced by liquid hydrogenation of furfural at the high temperature and H₂ pressure by using copper-chromite (Cu-Cr) catalysts which exhibits moderate in activity and selectivity. The main drawbacks of this catalyst system are toxicity and unrecyclable due to generated Cr₂O₃ and severe leaching of the metal into product

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[2, 3]. Therefore, several attempts have been reported in order to replace Cu-Cr catalysts or to develop a new metallic catalyst system which have more efficient catalytic process and less severe of environmental problem.

Among developed metal catalysts, nickel-based catalyst with metal co-promotor or modified supports has been studied intensively due to its high activity for hydrogenation both of C=C and C=O. Several metal co-promoters were applied to nickel such as Cu [4, 5], Fe, Ce [6, 7], and Sn [8] in order to improve its chemoselectivity towards C=O rather than to C=C. In this advantage, system based on Ni modified with Fe, Ce or heteropolyacids have been proved to be successful, reaching 98% selectivity to FFalc at almost total conversion [4-8]. However, in some cases these modified nickel catalysts cannot reuse [4] and also showed moderate in activity or selectivity [8]. Recently, Merlo *et al.* reported that tin modified of Pt/SiO₂ catalyst showed 96% selectivity to furfuryl alcohol and required 6 h to reach a complete reaction [9]. Moreover, the employing of noble metal catalyst is less favorable in economical advantageous. Therefore, the design less expensive the active and selective catalyst system for production furfuryl alcohol is an issue of interest, which still presents great challenges.

We have reported the preparation of Ni-Sn alloy catalysts supported on various inorganic compounds such as Al₂O₃, aluminium hydroxide (AlOH), active carbon (AC), SiO₂, and TiO₂. The supported Ni-Sn alloy catalysts were prepared via the hydrothermal treatment of a solution that contained Ni and Sn species at 423 K for 24 h followed by H₂ treatment at 573-873 K for 90 min. We found that the catalyst that consisted of Ni-Sn alloy (as Ni₃Sn₂ species) dispersed on TiO₂ allowed a remarkable reduction of the reaction temperature to 383 K. Our previous results have shown that the high conversion of FFald and the high selectivity of FFalc was achieved over Ni-Sn(1.5)/TiO₂ catalyst that can be attributed to the relatively high dispersion of Ni-Sn alloy on TiO₂ giving rise to active sites with a significantly higher catalytic activity [10]. The formation of Ni₃Sn₂ or Ni₃Sn alloy phases after H₂ treatment of Ni-Sn alloy catalysts supported on aluminium hydroxide are believed to play a key role in the enhancement of the chemoselectivity [11, 12].

In the present report, we have extended our study to the investigation of catalytic behaviour of Ni₃Sn₂ alloy catalysts supported on various inorganic compounds, such as: Al₂O₃, alumin-

ium hydroxide (AlOH), active carbon (AC), ZnO, SiO₂, Li-taeniolite (Li-TN), MgO, ZrO₂, and TiO₂. The supported Ni-Sn alloy catalysts were prepared with similar way to our previous report [10]. The catalytic performance of the synthesised catalysts was evaluated selective hydrogenation of biomass-derived furfural (FFald) to furfuryl alcohol (FFalc) and tetrahydrofurfuryl alcohol (THFalc).

2. Experimentals

2.1. Materials

Nickel(II) chloride hexahydrate (NiCl₂.6H₂O), tin(II) chloride dihydrate (SnCl₂.2H₂O), TiO₂, active carbon (S_{BET} = 815 m²g⁻¹), ZnO, MgO, ZrO₂, and aluminium hydroxide were purchased and used as received from WAKO Pure Chemical Industries, Ltd. unless otherwise stated. SiO₂ (S_{BET} = 200 m²g⁻¹) and Al₂O₃ (Al₂O₃, S_{BET} = 100 m²g⁻¹) were purchased from Japan Aerosil Co. Li-taeniolite (Li-TN) was donated by Kunimine Industries Co. Ltd. Furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol, iso-propanol, ethanol were purchased from Tokyo Chemical Industries Co. (TCI). All organic chemical compounds were purified using standard procedures prior to use.

2.2. Catalyst preparation

A typical procedure of the synthesis of γ -Al₂O₃ supported Ni-Sn (1.5 feeding ratio) alloy catalyst is described as follows [10]. NiCl₂.6H₂O (7.2 mmol) was dissolved in deionised water (denoted as solution A), and SnCl₂.2H₂O (4.8 mmol) was dissolved in ethanol/2-methoxy ethanol (2:1) (denoted as solution B) at room temperature. Solutions A, B, and γ -Al₂O₃ (1 g) were mixed at room temperature; the temperature was subsequently raised to 323 K and the mixture was stirred for 12 h. The pH of the mixture was adjusted to 12 through the dropwise addition of an aqueous solution of NaOH (3.1 M). The mixture was then placed into a sealed-Teflon autoclave for the hydrothermal reaction at 423 K for 24 h. The resulting black precipitate was filtered, washed with distilled water, and then dried under vacuum overnight. Prior to the catalytic reaction, the obtained black powder was treated under hydrogen at 673 K for 90 min. A similar procedure was also applied for the synthesis of supported Ni-Sn(1.5) alloy on SiO₂, ZrO₂, ZnO, MgO, and Li-TN.

2.3. Characterisations

Gas chromatography (GC) analyses were performed on a Shimadzu GC-8A equipped with a flame ionisation detector and with Thermo 3000 and Silicone OV-101 packing. GC-MS was performed on a Shimadzu GC-17B equipped with a thermal conductivity detector and with an RT-8DEXsm capillary column. ^1H and ^{13}C NMR spectra were obtained on a JNM-AL400 spectrometer at 400 MHz; samples for NMR were dissolved in chloroform- d_1 with TMS as an internal standard. Products were confirmed by the comparison of their GC retention time, mass, ^1H and ^{13}C NMR spectra with those of authentic samples. XRD measurements were recorded on a Mac Science M18XHF instrument using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm). The XRD was operated at 40 kV and 200 mA with a step width of 0.02° and a scan speed of 4°min^{-1} ($\alpha_1 = 0.154057$ nm, $\alpha_2 = 0.154433$ nm). ICP measurements were performed on an SPS 1800H plasma spectrometer of Seiko Instruments Inc. (Ni: 221.7162 nm and Sn: 189.898 nm).

The BET surface area (S_{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 measurement. The amount of nitrogen adsorbed onto the samples was used to calculate the BET surface area via the BET equation. The pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of approximately 0.995 according to the Barrett–Joyner–Halenda (BJH) approach based on desorption data [13]. SEM images of the synthesised catalysts were taken on a JEOL JSM-610SEM after the samples were coated using a JEOL JTC-1600 autofine coater.

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 treated 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 [14]

2.4. Typical procedure for hydrogenation of furfural

Catalyst (0.05 g), FFald (1.1 mmol), and iso-PrOH (3 mL) as solvent were placed into a glass reaction tube, which fitted inside a stainless steel reactor. After H_2 was introduced into the reactor with an initial H_2 pressure of

3.0 MPa at room temperature, the temperature of the reactor was increased to 383 K. After 75 min, the conversion of FFald and the yield of FFalc were determined via GC analysis. The $\text{Ni}_3\text{Sn}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst was easily separated using either simple centrifugation or filtration. The solvent was removed in vacuo, and the residue was purified via silica-gel column chromatography.

3. Results and Discussion

3.1. Catalyst characterisation

Ten types of supports (carbon (AC), $\gamma\text{-Al}_2\text{O}_3$, $\text{Al}(\text{OH})_3$, ZnO, ZrO_2 , MgO, Li-TN, TiO_2 , and SiO_2) were employed for the preparation of the supported Ni_3Sn_2 alloy catalysts and the physicochemical properties of the supported Ni_3Sn_2 alloy catalysts have been reported previously [10]. Among of the selected supports, we highlighted the XRD patterns of synthesised supported Ni_3Sn_2 alloy catalysts on general support ($\gamma\text{-Al}_2\text{O}_3$) and strong metal support interaction (SMSI) supports (TiO_2) as a function of loading amount of Ni_3Sn_2 . In the case of $\text{Ni}_3\text{Sn}_2/\gamma\text{-Al}_2\text{O}_3$, the XRD patterns revealed that Ni_3Sn_2 , a major alloy phase was formed on the Al_2O_3 and the diffraction peak of Ni_3Sn_2 alloy phase at $2\theta = 43\text{--}44^\circ$ become intensified with the increase of the loading amount of Ni-Sn (Figure 1a-d). The crystallite sizes of $\text{Ni}_3\text{Sn}_2(101)$ in $\text{Ni}_3\text{Sn}_2/\gamma\text{-Al}_2\text{O}_3$ increased as the increase of loading amount whereas 6 nm, 9 nm, 14 nm, and 16 nm, respectively.

In contrast with the $\text{Ni}_3\text{Sn}_2/\gamma\text{-Al}_2\text{O}_3$, supported $\text{Ni}_3\text{Sn}_2/\text{TiO}_2$ exhibited broadened peaks at $2\theta = 30.8^\circ$, 42.5° , and 44.2° , which correspond to the $\text{Ni}_3\text{Sn}_2(101)$, $\text{Ni}_3\text{Sn}_2(102)$, and $\text{Ni}_3\text{Sn}_2(110)$ diffraction peaks, respectively (Figure 2a-d). These results suggest that the higher dispersions of Ni-Sn alloy on the TiO_2 were formed as roughly depicted in the average $\text{Ni}_3\text{Sn}_2(101)$ crystallite sizes (Table 1).

We also are intentionally evaluated the formation of Ni_3Sn_2 alloy phase on another supports rather than $\gamma\text{-Al}_2\text{O}_3$ and TiO_2 as comparison and the XRD patterns of various supported Ni_3Sn_2 are showed in Figure 3. Unlike on the $\gamma\text{-Al}_2\text{O}_3$ and TiO_2 supports, $\text{Ni}_3\text{Sn}_2(101)$ alloy phase was formed and overlapped with the diffraction peaks of the supports. In the case of $\text{Ni}_3\text{Sn}_2/\text{SiO}_2$, the diffraction peak of Ni_3Sn_2 alloy phases are broadened and hardly observed that indicating a high dispersion of Ni-Sn alloy species on the support (Figure 3a). On ZrO_2 , ZnO, MgO, and Li-TN supports, the diffraction peaks at 2θ of 43.28° and 44.28° which characteristic peak for $\text{Ni}_3\text{Sn}_2(102)$ and $\text{Ni}_3\text{Sn}_2(110)$ alloy

phases as well as at 2θ of 30.8° for $\text{Ni}_3\text{Sn}_2(101)$ phase (Figure 3b-e).

The catalytic reaction results of each the synthesized supported Ni_3Sn_2 alloy in the hydrogenation of biomass-derived furfural into furfuryl alcohol are summarized in Table 1. For catalysts supported on Al_2O_3 , AlOH , SiO_2 , and AC, relatively high FFald conversions and yields of FFalc were obtained (Table 1, entries 1-4). For the $\text{Ni}_3\text{Sn}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst, FFald conversion was 85% with a FFalc yield of 84% (Table 1, entry 1), whereas the $\text{Ni}_3\text{Sn}_2/\text{AlOH}$,

$\text{Ni}_3\text{Sn}_2/\text{AC}$, and $\text{Ni}_3\text{Sn}_2/\text{SiO}_2$ catalysts produced FFalc yields of 67%, 72%, and 62%, respectively (Table 1, entries 2-4). A remarkably high FFald conversion ($>99\%$) and FFalc selectivity (100%) were obtained when $\text{Ni}_3\text{Sn}_2/\text{TiO}_2$ was used under the same conditions (Table 1, entry 5). The high conversion of FFald and the high selectivity of FFalc over $\text{Ni}_3\text{Sn}_2/\text{TiO}_2$ can be attributed to the relatively high dispersion of Ni-Sn alloy on TiO_2 giving rise to active sites with a significantly higher catalytic activity. Alternatively, the high conversion and selectivity may be a result of the strong interactions between the active metals and TiO_2 generating significant interactions between C=O groups and Ni-TiO_x sites and leading to high selectivity to unsaturated alcohols [15]. As comparison, Kijenski et al. have reported that Pt catalysts supported on TiO_2 gave higher selectivity to FFalc in the hydrogenation of FFald than did Pt supported on SiO_2 , ZrO_2 or MgO [16]. Our results also showed that Ni_3Sn_2 alloy catalysts supported on ZrO_2 , MgO , and Li-TN only gave 32%, 0%, and 20% yield of FFalc, respectively (Table 1, entries 7, 8, and 9). In the case of Ni_3Sn_2 supported on ZnO , the conversion of FFald was 89% with selectivity of FFalc and THFalc of 99% and 1%, respectively (entry 6). Recently, Corma *et al.* studied the chemoselectivity of Ni supported on TiO_2 in the hydrogenation of substituted nitro aromatics [17]. Moreover, the monometallic R-Ni/AlOH catalyst converted FFald to give $>99\%$ THFalc, which indicates that R-Ni/AlOH hydrogenated both C=C and C=O of FFald (entry 10), whereas

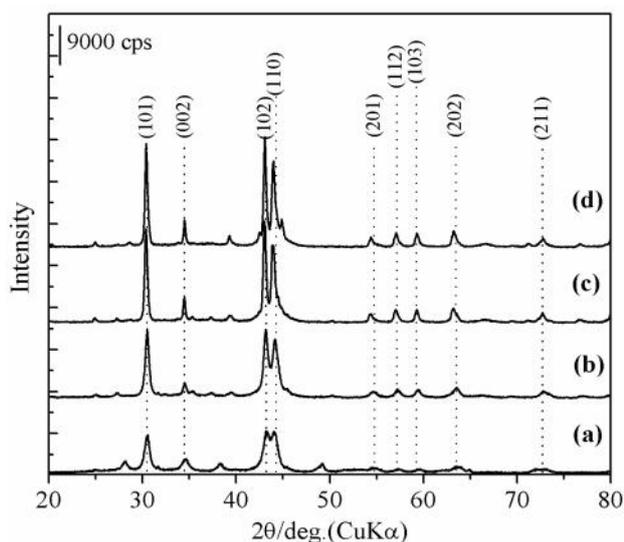


Figure 1. XRD patterns of supported Ni_3Sn_2 on $\gamma\text{-Al}_2\text{O}_3$ with different loading amount of (a) 4 mmol, (b) 8 mmol, (c) 12 mmol, and (d) 16 mmol.

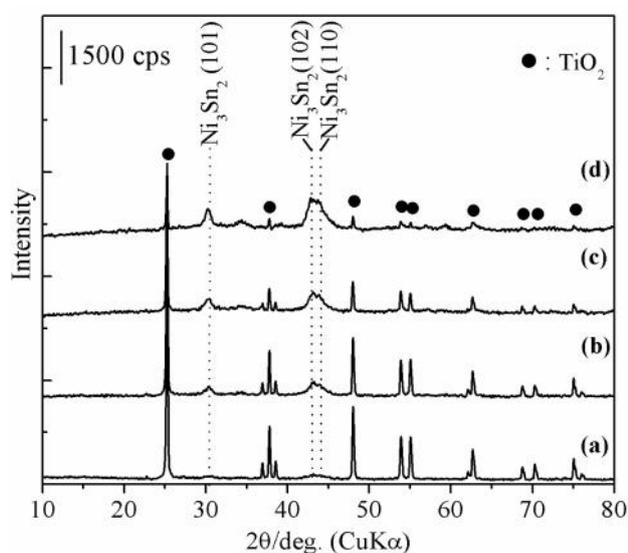


Figure 2. XRD patterns of supported Ni_3Sn_2 on TiO_2 with different loading amount of (a) 4 mmol, (b) 8 mmol, (c) 12 mmol, and (d) 16 mmol.

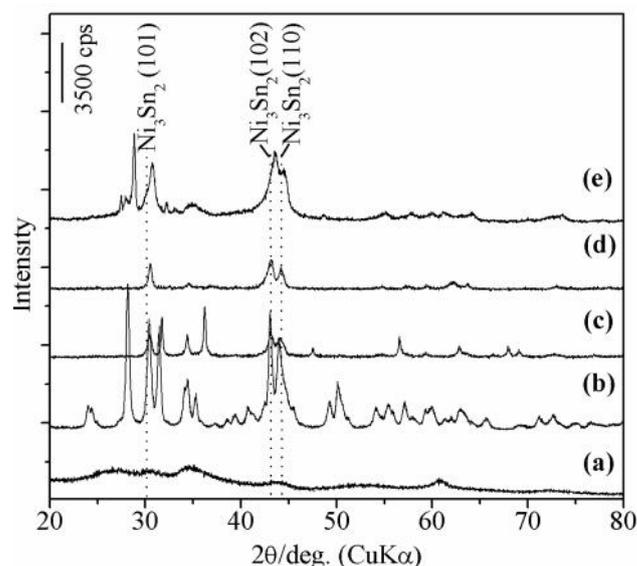


Figure 3. XRD patterns of Ni_3Sn_2 on various supports of (a) SiO_2 , (b) ZrO_2 , (c) ZnO , (d) MgO , and (e) Li-TN.

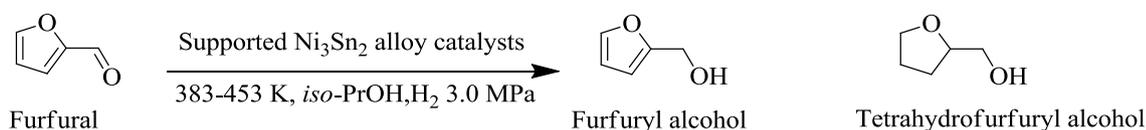
Sn/AlOH was not active for the hydrogenation of FFald under the same conditions (entry 11). These results suggest that the addition of tin to form Ni-Sn alloy retards the C=C hydrogenation activity of nickel. Swift *et al.* have reported that the formation of a Ni-Sn alloy by the addition of tin to a Ni/SiO₂ catalyst remarkably changed the reactivity of Ni/SiO₂ because of the change in the electron density of nickel metal [18]. Delbecq *et al.* indicated that the C=O hydrogenation selectivity in the hydrogenation of α,β -unsaturated aldehydes could be enhanced

by the formation of a Pt-Sn alloy because of the higher affinity of the alloy towards C=O rather than towards C=C bonds, as noted previously [19]. Resasco *et al.* have reported that the selective hydrogenation of C=O versus C=C in α,β -unsaturated aldehydes by Pd-Cu alloy supported on silica was caused by the preferential η^2 -coordination of C=O to Pd [20]. In addition, the catalytic reaction over supports (carbon (AC), γ -Al₂O₃, Al(OH)₃, ZnO, ZrO₂, MgO, Li-TN, TiO₂, and SiO₂) was also carried out under the same reaction condi-

Table 1. Comparison of catalytic activity of various supported Ni₃Sn₂ alloy catalysts for selective hydrogenation of biomass-derived furfural

Entry	Catalyst	LA ^a / mmolg ⁻¹	H ₂ ^b / mmolg ⁻¹	S _{BET} ^c / m ² g ⁻¹	D ^d / nm	Conv./ %	Yield ^e / %	Selectivity ^f /% FFalc THFalc
1 ^g	Ni ₃ Sn ₂ / γ -Al ₂ O ₃	6	9.1	94	16 ^h	85	84	99 1
2 ^g	Ni ₃ Sn ₂ /AlOH	6	9.0	120	15 ^h	67	67	100 0
3	Ni ₃ Sn ₂ /AC	6	13.0	676	17 ^h	72	72	100 0
4	Ni ₃ Sn ₂ /SiO ₂	12	13.5	234	10 ^h	62	62	99 1
5	Ni ₃ Sn ₂ /TiO ₂	6	13.0	52	6 ^h	>99	>99	100 0
6	Ni ₃ Sn ₂ /ZnO	6	nd	Nd	nd	89	88	99 1
7	Ni ₃ Sn ₂ /ZrO ₂	6	nd	Nd	nd	32	32	100 0
8	Ni ₃ Sn ₂ /MgO	12	nd	Nd	nd	8	0	0 0
9	Ni ₃ Sn ₂ /Li-TN	12	nd	323	nd	20	20	100 0
10 ⁱ	R-Ni/AlOH	9	104	151	11 ^j	>99	>99	0 100
11	Sn/AlOH	4.1	nd	nd	nd	0	0	0 0
12	γ -Al ₂ O ₃	-	-	100	-	5	0	0 0
13	TiO ₂	-	-	52	-	5	0	0 0
14	ZnO	-	-	-	-	3	0	0 0
15	ZrO ₂	-	-	-	-	4	0	0 0
16	SiO ₂	-	-	200	-	0	0	0 0
17	MgO	-	-	-	-	0	0	0 0
18	Li-TN	-	-	-	-	2	0	0 0

^aDetermined by ICP-AES. ^bH₂ uptake at 273 K (noted after corrected for physical and chemical adsorption). ^cBET specific surface areas, determined by N₂ physisorption at 77 K. ^dThe average Ni-Sn crystallite sizes derived from the Scherrer's equation. Reaction conditions: FFald, 1.1 mmol (FFald/Ni ratio = 15); iso-PrOH (3 mL); H₂, 3.0 MPa, 383 K, 75 min. ^eYield of FFalc, determined by GC using an internal standard technique. ^fSelectivity to FFalc and THFalc, determined by GC using an internal standard technique. ^gAt 433 K. ^hNi₃Sn₂(101). ⁱAt 403 K. ^jNi(111).



tions. The conversion of FFald was around 2-5% without the formation either FFalc or THFalc (entries 12-18) indicating the main active site of the catalysts (Ni_3Sn_2 alloy species) plays important role in the activity and selectivity.

In order to get insight into the role of support, the catalytic performance of three types of supported $\text{Ni}_3\text{Sn}_2/\text{TiO}_2$, $\text{Ni}_3\text{Sn}_2/\text{ZnO}$, and $\text{Ni}_3\text{Sn}_2/\gamma\text{-Al}_2\text{O}_3$ alloy catalysts have been evaluated at different reaction temperature, time profile, and loading amount of Ni_3Sn_2 and the results are shown in Figure 4, 5, and 6, respectively. Differences in the activity of each catalyst were clearly observed. On the supported $\text{Ni}_3\text{Sn}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst, the yield of FFalc gradually increased as temperature was in-

creased, and completed conversion of FFald (~99%) was achieved at 413 K. In the case of $\text{Ni}_3\text{Sn}_2/\text{ZnO}$, FFald was converted completely at 403 K. Surprisingly, $\text{Ni}_3\text{Sn}_2/\text{TiO}_2$ demonstrated a remarkably high FFald conversion of >99% (>99% FFalc yield) at a significantly lower temperature of 383 K.

The reaction profiles of FFald hydrogenation at 383 K on supported $\text{Ni}_3\text{Sn}_2/\text{TiO}_2$, $\text{Ni}_3\text{Sn}_2/\text{ZnO}$, and $\text{Ni}_3\text{Sn}_2/\gamma\text{-Al}_2\text{O}_3$ alloy catalysts are shown in Figure 5. When the supported $\text{Ni}_3\text{Sn}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst was used, 100% FFald conversion (>99% FFalc yield) was achieved after 120 min. The induction periods could be associated to the slow formation of oxidic tin (Sn^{IV}) from metallic tin (Sn^0) as reported by Sordelli *et al.* (Rh-Sn) [21] and Margitfalvi *et*

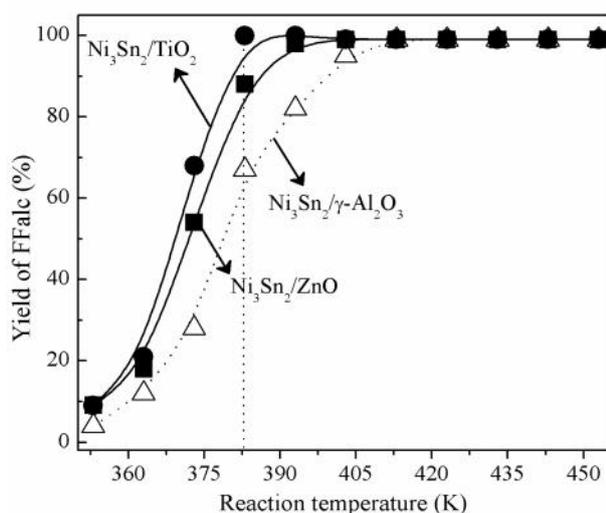


Figure 4. Effect of reaction temperature on the FFalc yield over the supported Ni_3Sn_2 alloy catalysts. Reaction conditions: catalyst, 0.05 g; FFald, 1.1 mmol; iso-PrOH, 3 mL; H_2 , 3.0 MPa, 75 min.

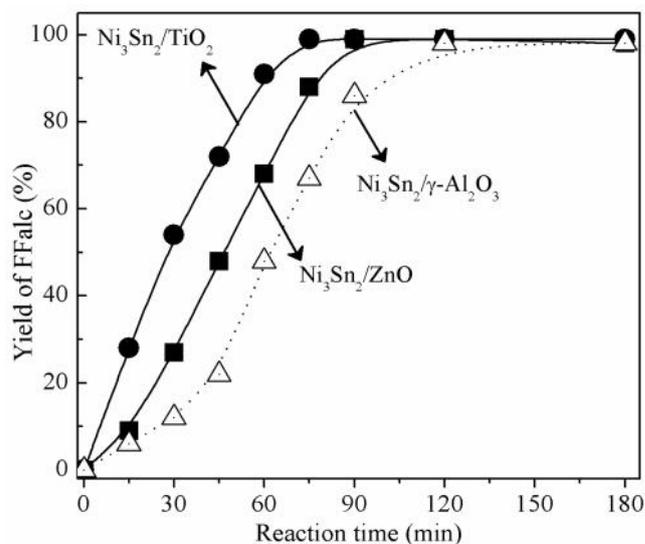


Figure 5. Time profile of the hydrogenation of FFald over the supported Ni_3Sn_2 alloy catalysts. Reaction conditions: catalyst, 0.05 g; FFald, 1.1 mmol; iso-PrOH, 3 mL; H_2 , 3.0 MPa, 383 K.

Table 2. Results of the reusability test for $\text{Ni}_3\text{Sn}_2/\gamma\text{-Al}_2\text{O}_3$ and $\text{Ni}_3\text{Sn}_2/\text{ZnO}$ alloy catalysts in the hydrogenation of FFald. Reaction conditions: FFald, 1.1 mmol (FFald/Ni ratio = 15); iso-PrOH (3 mL); H_2 , 3.0 MPa, 383 K, 75 min. ^aSelectivity to FFalc, determined by GC using an internal standard technique. ^bThe recovered $\text{Ni}_3\text{Sn}_2/\text{ZnO}$ catalyst was treated by H_2 at 673 K for 1 h.

Run	1	2	3	4	5	6
$\text{Ni}_3\text{Sn}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst						
Conversion (%)	85	82	78	78	70	65
Selectivity ^a (%)	99	99	98	99	99	99
$\text{Ni}_3\text{Sn}_2/\text{ZnO}$ catalyst						
Conversion (%)	89	63	60	55	50	93 ^b
Selectivity ^a (%)	99	99	99	99	99	99

al. (Pt-Sn) [22]. Since the crystallite size or dispersion of Ni-Sn alloy could affect the length of induction period, Ni₃Sn₂/TiO₂ showed a high activity at lower temperature (Figure 4) without an induction period (Figure 5). Notably, the supported Ni₃Sn₂/TiO₂, demonstrated a conversion of FFald 1.5 times greater than that of the Ni₃Sn₂/γ-Al₂O₃ and Ni₃Sn₂/ZnO catalysts.

The effect of loading amount of Ni₃Sn₂ (1.5-16 mmol g⁻¹) on supports of γ-Al₂O₃ and TiO₂ are also evaluated and the results are shown in Figure 6A and 6B, respectively. On Ni₃Sn₂/γ-Al₂O₃ system, the conversion of FFald gradually increased from loading amount of 1.5 to 6.0 mmol g⁻¹ then decreased at loading amount of 8.0-16.0 mmol g⁻¹. The highest conversion of FFald (74%) was achieved when loading amount of 6.0 mmol g⁻¹ and gave 70% yield of FFalc. On the other hand, the highest conversion of FFald (>99%) was achieved over 6.0 mmol g⁻¹ Ni₃Sn₂/TiO₂ catalyst with yield and selectivity towards FFalc of >99% at the same reaction conditions. These results revealed that supported Ni₃Sn₂/TiO₂ catalysts are superior to the supported Ni₃Sn₂/γ-Al₂O₃ and other that can be attributed due to high dispersion of Ni₃Sn₂ alloy species as well as the induction period did not occur on the Ni₃Sn₂/TiO₂ catalyst system [10, 21, 22].

A reusability test was performed on the Ni₃Sn₂/γ-Al₂O₃ and Ni₃Sn₂/ZnO catalysts, and the results are summarized in Table 2. In the case of reusability test of Ni₃Sn₂/TiO₂ have been reported elsewhere [10]. The used

Ni₃Sn₂/γ-Al₂O₃ and Ni₃Sn₂/ZnO catalysts were easily separated by either simple centrifugation or filtration after the reaction. The activity of the catalyst decreased while the high selectivity was maintained for at least six consecutive runs. The amount of Ni and Sn that leached into the reaction solution was 0.38% and 1.2% after four runs, respectively.

4. Conclusion

Catalytic performance of various supported Ni₃Sn₂ alloy catalysts have been evaluated in hydrogenation of biomass-derived furfural into furfuryl alcohol. Supported Ni₃Sn₂ alloy on TiO₂ and ZnO showed the higher yield and selectivity towards furfuryl alcohol product compared to the activity of other supports. Supported Ni₃Sn₂/γ-Al₂O₃ was also found to be reusable without any significant loss of selectivity even after six consecutive reactions run.

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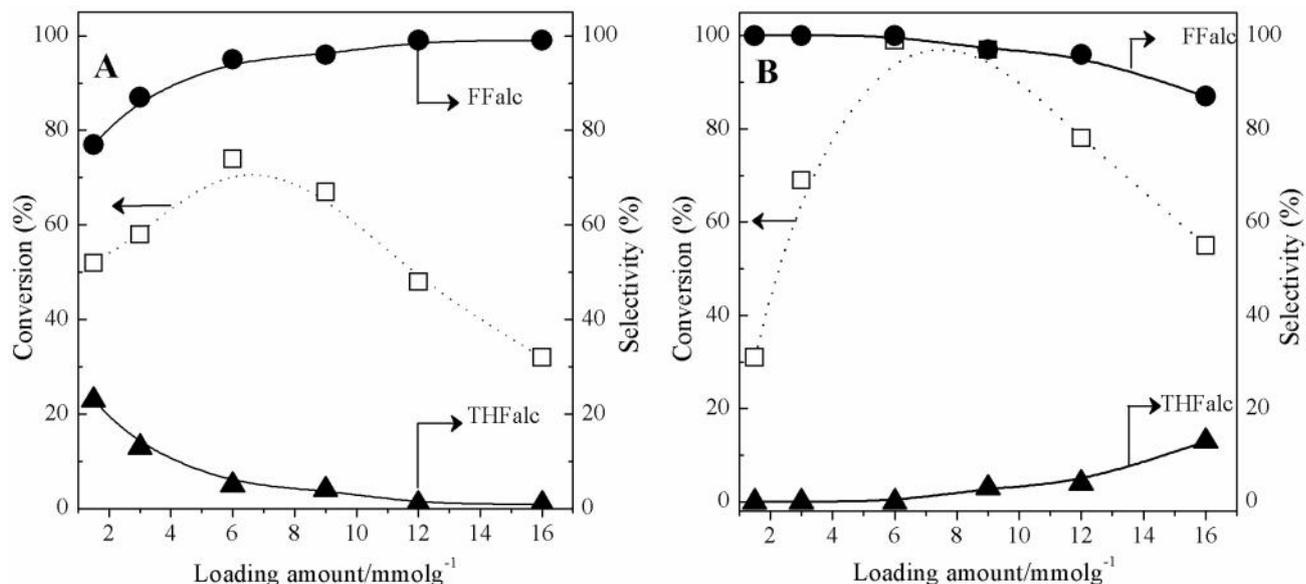


Figure 6. Conversion FFald, yield and selectivity of FFalc and THFalc as function of loading amount of Ni₃Sn₂ supported on (A) γ-Al₂O₃ and (B) TiO₂. Reaction conditions: catalyst loading, 0.05 g; FFald, 1.1 mmol; iso-PrOH, 3 mL; H₂, 3.0 MPa, 383 K, 75 min.

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