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Hydrogenation of Biomass-derived Furfural over Highly Dispersed-Aluminium Hydroxide Supported Ni-Sn(3.0) Alloy Catalysts

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Abstract

A novel method was applied for the preparation of highly dispersed nickel-tin (Ni-Sn) alloy catalyst supported on aluminium hydroxide using a simple method at a relatively low temperature. The addition of Sn (1.04mmol) on the Raney nickel supported on aluminium hydroxide (R-Ni/AlOH) to form Ni-Sn(3.0)/AlOH (3.0 is Ni/Sn ratio) alloy catalyst remarkably enhanced the selectivity towards hydrogenation of C=O rather than C=C in furfural giving high yield of furfuryl alcohol almost exclusively. The Ni-Sn(3.0)/AlOH (3.0 is Ni/Sn ratio) alloy was also found to be reusable without any significant loss of selectivity for at least six consecutive runs.

Keywords: hydrogenation, biomass-derived furfural, furfuryl alcohol, Ni-Sn alloy catalyst.

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Nomenclature

FFald	Furfuraldehyde	FFalc	Furfuryl alcohol
THFalc	Tetrahydrofurfuryl alcohol	R-Ni/AlOH	Raney nickel supported on aluminium hydroxide
Ni-Sn(3.0)/AlOH Nickel-tin alloy supported on aluminium hydroxide; 3.0= Ni/Sn molar ratio			

1 Introduction

Furfuryl alcohol (FFalc), unsaturated alcohol of furan derivative compounds and an important intermediate

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compound, was employed in the various industrial applications for production of various synthetic fibres, rubbers, resins, e.g., dark thermosetting resins resistant to acids, bases and resins used for strengthening ceramics. It is also used as a solvent for furan resin, pigment, varnish, and as rocket fuel and currently used for biobased nanomaterials [1-4]. Industrially, furfuryl alcohol was produced by liquid phase hydrogenation of furfural at the high temperature and pressure by using copper-chromite catalysts system which exhibits moderate selectivity towards furfural alcohol [5,6]. However, the main drawback of this catalyst system is toxicity and unrecyclable due to presence Cr^{+6} which may have important consequences for the environment.

Nickel based catalyst could be a good promising to substitute the classical catalyst system in production of furfuryl alcohol although the modification of nickel metal is necessary in order to improve its selectivity towards $\text{C}=\text{O}$ rather than $\text{C}=\text{C}$. There are two ways modification, i.e., the addition of more electropositive metals [7] or the use of oxide supports that strongly interact with the active metals [8]. Although these modified catalyst systems have been effective, catalyst preparation critically depends on the precise control of the amounts of the second metal [9-11]. Recently, the tin alloying of the platinum group has been extensively studied and widely applied in various chemical transformations [12-14]. Pt-Sn/ SiO_2 showed a higher selectivity towards furfuryl alcohol (FFalc) rather than Pt/ SiO_2 in the hydrogenation of furfural (FFald) [13]. Delbecq et al. suggested that an increase of the charge density of Pt metal by the addition of hyperelectronic metals or by the formation of a metal alloy could enhance the affinity towards $\text{C}=\text{O}$ rather than the $\text{C}=\text{C}$ bond to form unsaturated alcohols in the hydrogenation of α,β -unsaturated aldehydes [15, 16]. However, precious metals, such as Pt, were utilised in these catalyst systems. Therefore, alternative economical and eco-friendly heterogeneous catalysts that would ensure the preferred hydrogenation of the $\text{C}=\text{O}$ group over $\text{C}=\text{C}$ are highly desired.

We recently have reported the chemoselective hydrogenation of FFald and various unsaturated carbonyl compounds over Ni-Sn catalysts both bulk and supported. The chemoselectivity of Ni-Sn alloy catalysts in $\text{C}=\text{O}$ hydrogenation could be controlled by changing the amount of Sn [17-19]. In the present work, we continue to describe the catalytic performances of Ni-Sn alloy catalysts supported on aluminium hydroxide in the selective hydrogenation of FFald to FFalc.

2 Experimental

2.1 Materials

Raney Ni-Al alloy ((50%wt of Ni and 50%wt of Al) Kanto Chemical Co. Inc.), NaOH (97%, WAKO), and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (99.9%, WAKO) were purchased and used as received. All organic chemical compounds were purified using standard procedures prior to use.

2.2 Catalyst preparation

2.2.1 Synthesis of R-Ni/AlOH

Typical procedure of the synthesis of Raney nickel supported on aluminium hydroxide catalyst (denoted as R-Ni/AlOH) is described as follows [20]: Raney Ni-Al alloy powder (1.0 g) was slowly added to a dilute aqueous solution of NaOH (0.31 M, 8 mL) at room temperature. The temperature was raised to 363 K and 1 mL of 3.1 M NaOH solution was subsequently added and stirred for 30 min. The mixture was placed into a sealed-Teflon autoclave reactor for hydrothermal treatment at 423 K for 2 h. The resulting precipitate was filtered, washed with distilled water until filtrate was neutralized, and then stored in water. The catalyst was dried under vacuum before the catalytic reaction.

2.2.2 Synthesis of Ni-Sn/AlOH

Typical procedure of the syntheses of nickel-tin alloy supported on aluminium hydroxide (denoted as Ni-Sn(3.0)/AlOH, 3.0 is Ni/Sn ratio) is described as follows [17, 19]: R-Ni/AlOH that was obtained from the above procedure (Section 2.2.1) was mixed with a solution that contained 1.45 mmol $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ at room temperature and stirred for 2 h. The mixture was placed into a sealed-Teflon autoclave reactor for the hydrothermal treatment at 423 K for 2 h. The resulting precipitate was filtered, washed with distilled water, and dried under vacuum overnight.

2.3 Catalyst characterisations

Powder X-ray diffraction (XRD) measurements were recorded on a Mac Science M18XHF instrument using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). 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} ($\alpha_1 = 0.154057 \text{ nm}$, $\alpha_2 = 0.154433 \text{ nm}$). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements were performed on an SPS 1800H plasma spectrometer by Seiko Instruments Inc. Japan (Ni: 221.7162 nm and Sn:189.898 nm). The BET surface area (S_{BET}) and pore volume (V_p) were measured using N_2 physisorption at 77 K on a Belsorp Max (BEL Japan). The samples were degassed at 473 K for 2 h to remove physisorbed gases prior to the 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 [21].

The H_2 uptake was determined through irreversible H_2 chemisorption. After the catalyst was heated at 393 K under vacuum for 30 min, it was heated at 673 K under H_2 for 30 min. The catalysts were subsequently cooled to room temperature under vacuum for 30 min. The H_2 measurement was conducted at 273 K, and H_2 uptake was calculated according to the method described in the literature [22].

2.4 Catalytic reaction

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 453 K. After 75 min, the conversion of FFald and the yield of FFalc were determined via GC analysis. The Ni-Sn(3.0)/AlOH 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.

Analytical GLC was performed on a Shimadzu GC-8A equipped with a flame ionisation detector and with Thermo 3000 and Silicone OV-101 packing. A Shimadzu 14A with a flame ionisation detector equipped with a RT- β DEXsa capillary column was used for product analyses of the hydrogenations of α,β -unsaturated aldehydes and ketones. Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-17B equipped with a thermal conductivity detector and with an RT- β DEXsm 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.

3 Results and discussion

3.1 Catalyst characterisation

Ni-Sn alloy catalysts supported on aluminium hydroxide (denoted as Ni-Sn(3.0)/AlOH, 3.0 is Ni/Sn ratio) were prepared via the hydrothermal treatment of the mixture of R-Ni/AlOH and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solution. The physicochemical properties of Ni-Sn(3.0)/AlOH are summarised in Table 1.

Table 1 Physicochemical properties of the synthesised R-Ni/AlOH and Ni-Sn(3.0)/AlOH catalysts

Entry	Catalyst	Sn ^a (mmol/g)	Ni/Al ^a	H ₂ uptake ^b / mmol g ⁻¹	CO uptake ^c / mmol g ⁻¹	S _{BET} ^d / m ² g ⁻¹	D ^e /nm
1	R-Ni/AlOH	0	0.91	104	81	151	9.0
2	Ni-Sn(3.0)/AlOH	1.04	1.07	110	91	90	5.3

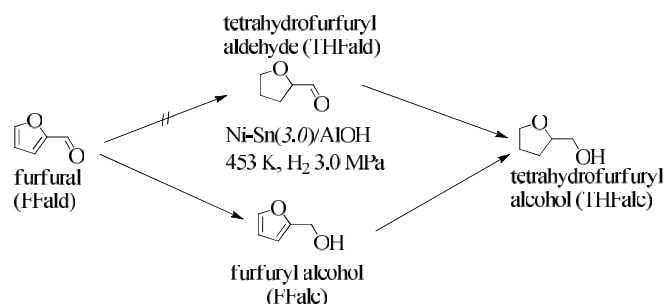
^a Determined by ICP-AES. ^b Based upon total H₂ uptake at 273 K (noted after corrected for physical and chemical adsorption). ^c Based upon total CO uptake at 273 K (noted after corrected for physical and chemical adsorption). ^d BET surface area, determined by N₂ adsorption at 77 K. ^e Average Ni particle sizes, calculated according to the method described in the literature [22].

Based on the ICP-AES analyses, the loading amount of Sn was 1.04 mmol which was reflected in the Ni/Sn ratio of 3.0. The Ni/Al ratio confirmed the presence of aluminium hydroxide that resulted from the alkali leaching of the Raney Ni-Al precursor in the form of gibbsite and bayerite as indicated by the XRD patterns as reported elsewhere previously [17, 23]. The H₂ and CO uptakes, BET surface area (S_{BET}), and the average Ni particle sizes of R-Ni/AlOH and Ni-Sn(3.0)/AlOH catalysts are summarised in Table 1.

3.2 Catalytic reaction

3.2.1 Hydrogenation of furfural

The results of the chemoselective hydrogenation of FFald by various catalysts are summarised in Table 2, and the reaction pathways are shown in Scheme 1.



Scheme 1 Reaction pathways of FFald hydrogenation by Ni-Sn(x)/AlOH catalysts.

Table 2 Catalytic reaction results of Ni-Sn(3.0)/AlOH catalysts in the hydrogenation of FFald

Entry	Catalyst ^a	Sn ^b /mmolg ⁻¹	Conv. ^c /%	Yield ^d /%
1	R-Ni/AlOH	0	>99	0(100)
2	Ni-Sn(3.0)/AlOH	1.04	98	94(4)
3	SnO	-	4	0(0)
4	SnO ₂	-	28	6(3)
5	SnCl ₂ ·2H ₂ O	-	72	3(1)

^aThe value in the parenthesis is Ni/Sn molar ratio. *Reaction conditions*: catalyst (0.05 g), FFald (1.1 mmol), *iso*-PrOH (3 mL), H₂ (3.0 MPa), 453 K, 1 h. ^bLoading amount of Sn, determined by ICP-AES. ^cConversion, determined by GC using an internal standard. ^dYield of FFald. The value in the parenthesis is yield of tetrahydrofurfuryl alcohol (THFald), determined by GC using an internal standard technique.

It can be observed that by using R-Ni/AlOH catalyst, >99% FFald was converted to give >99% THFald (entry 9), indicating that R-Ni/AlOH hydrogenated both C=C and C=O of FFald (entry 1). Interestingly, by addition of Sn to R-Ni/AlOH with the loading amount of 1.04 mmol, a remarkable increase of FFald yield was achieved (entry 2, 94%). This result suggests that further hydrogenation of the C=C furan ring in FFald did not proceed in the presence of the Ni-Sn(3.0)/AlOH catalyst. Moreover, SnO, SnO₂, and SnCl₂·2H₂O did not produce the hydrogenated products under the same conditions (entries 3-5). Furthermore, the hydrogenation of FFald using the Ni-Sn(3.0)/AlOH catalyst resulted in only an 8.7% THFald yield at 453 K and 3 MPa of H₂, even after 6 hrs. These results suggest that the addition of tin to nickel retards the C=C hydrogenation activity of nickel. Swift et al. 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 due to the change in the electron density of nickel metal [24]. 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 due to the higher affinity towards C=O rather than the C=C bond, as noted previously [15, 16]. Resasco et al. reported that the selective hydrogenation of C=O versus C=C in α,β -unsaturated aldehydes by a Pd-Cu alloy supported on silica was caused by the preferable η^2 -coordination of C=O to Pd [25]. Therefore, we propose that the formation of a Ni-Sn alloy may facilitate in the adsorption mode of the FFald molecule through the C=O group, giving rise to much higher yields and selectivity of FFald than THFald. These suggestions are consistent with the fact that no tetrahydrofurfuryl aldehyde (THFald) was observed in all the catalytic results. Therefore, we speculate that FFald hydrogenation by Ni-Sn/AlOH catalysts does not proceed via THFald due to the formation of the Ni-Sn alloy (Scheme 1).

3.2.2 Solvent screening

The results of solvent screening for FFald hydrogenation are summarised in Table 3. Alcohols, such as *iso*-propanol (*iso*-PrOH), 1-propanol, ethanol, and methanol, are superior to other solvents, giving quantitatively high FFald yields (entries 1-4). On the other hand, FFald hydrogenation did not proceed effectively in toluene, giving only a 36% FFald yield at the same conditions (entry 5). In H₂O, as the conversion of FFald was 96% and gave only 12% and 8% of hydrogenated product of FFald and THFald, respectively (entry 6). Another 76% yields were hydrogenolyzed products of 1,2-pentanediol (26%) and 1,5-pentanediol (50%).

Table 3 Results of solvent screening for FFald hydrogenation over Ni-Sn(3.0)/AlOH catalyst^a

Entry	Solvent	Conversion/% ^b	Yield/% ^b	
			FFalc	THFalc
1	<i>iso</i> -propanol	98	95	3
2	methanol	>99	98	2
3	ethanol	>99	95	5
4	1-propanol	92	85	5
5	toluene	62	36	0
6	H ₂ O	96	12	8

^aReaction conditions: catalyst (0.05 g), FFald (1.1 mmol), solvent (3 mL), H₂ (3 MPa), 453 K, 1 h. ^b Determined by GC using an internal standard technique.

3.2.3 Effect of reaction temperature

The influence of reaction temperature on the yield of FFalc over Ni-Sn(3.0)/AlOH alloy catalyst is shown in Fig. 1. The yield of FFalc gradually increased as temperature was increased, and complete conversion of FFald (~99%) was achieved at 453 K. Therefore, we conclude that the optimised reaction temperatures for FFald hydrogenation using Ni-Sn(3.0)/AlOH was 453 K.

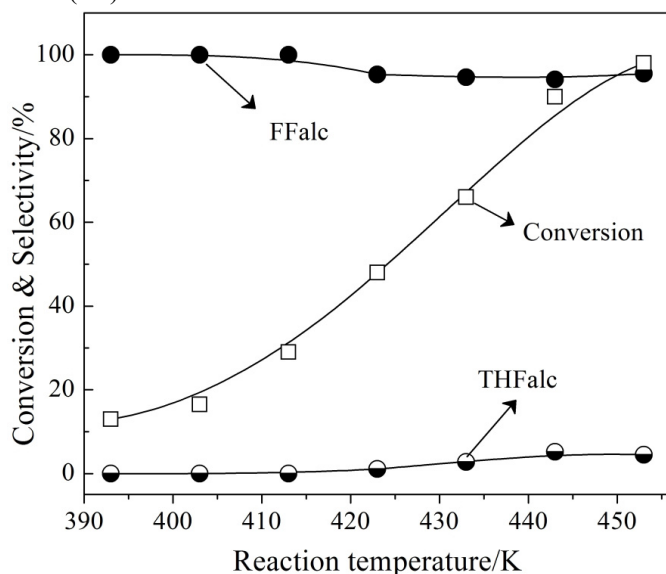


Fig.1 Effect of reaction temperature on the FFalc yield over Ni-Sn(3.0)/AlOH alloy catalysts. Reaction conditions: catalyst (0.05 g), FFald (1.1 mmol), *iso*-PrOH (3 mL), H₂ (3.0 MPa), 1 h.

3.2.4 Time profiles

The reaction profiles of FFald hydrogenation at 453 K on the Ni-Sn(3.0)/AlOH alloy catalysts are shown in Fig. 2. FFald conversion gradually increased as the increase of reaction time and the completed reaction was achieved after 75 min. On the other hand, FFalc selectivity slightly decreased to ~95% after reaction time 45 min due to further hydrogenation of C=C furan ring towards the formation of THFalc.

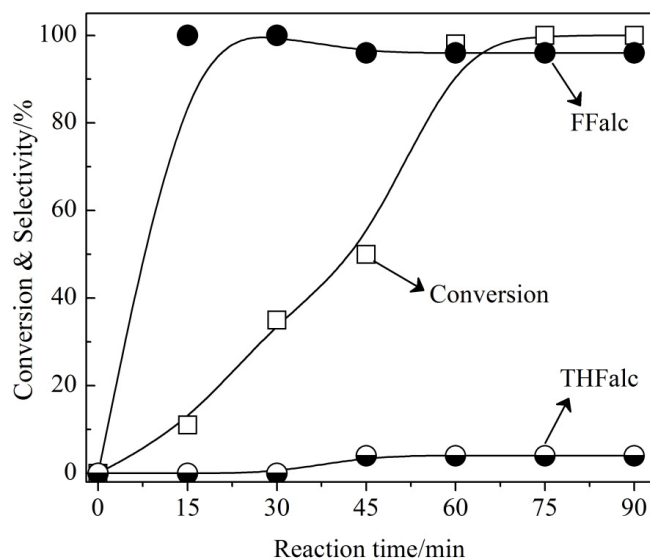


Fig.2 Time profiles of the hydrogenation of FFald over Ni-Sn(3.0)/AlOH alloy catalyst. *Reaction conditions:* catalyst (0.05 g), FFald (1.1 mmol), *iso*-PrOH (3 mL), H₂ (3.0 MPa), 453 K.

3.2.5 Reusability test

A reusability test was performed on the Ni-Sn(3.0)/AlOH catalyst, and the results are summarised in Table 4. The used Ni-Sn(3.0)/AlOH catalyst was easily separated by either simple centrifugation or filtration after the reaction. The activity of the catalyst slightly decreased while the high selectivity was maintained for at least six consecutive runs. The XRD patterns of the recovered Ni-Sn(3.0)/AlOH exhibited that the catalyst structure maintained (Figure 3). The amount of Ni, Sn, and Al that leached into the reaction solution was 0.96%, 4.8%, and 2.0% after the sixth run, respectively.

Table 4 Results of the reusability test for Ni-Sn(3.0)/AlOH in the hydrogenation of FFald

Run	1	2	3	4	5	6
Conversion (%)	98	97	94	94	93	91
Yield ^a (%)	94	93	90	90	89	90
Selectivity ^b (%)	96	96	96	96	96	99

Reaction conditions: Catalyst, 0.05 g; FFald, 1.1 mmol; *iso*-PrOH (3 mL); H₂, 3.0 MPa, 453 K, 60 min. ^a Yield of FFalc. ^b Selectivity to FFalc, determined by GC using an internal standard technique.

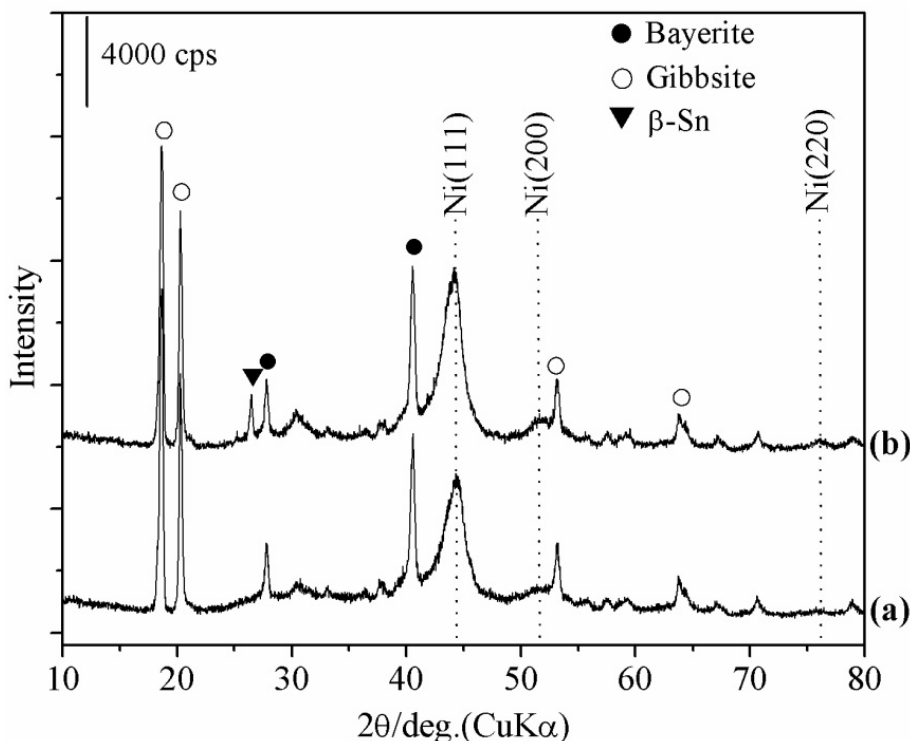


Fig. 3 XRD patterns of (a) fresh and (b) the recovered Ni-Sn(3.0)/AlOH catalyst. (●) bayerite; (○) gibbsite; (▼) β-Sn.

4 Conclusion

Ni-Sn alloy catalysts supported on aluminium hydroxide were successfully synthesised using a simple method at a relatively low temperature. The addition of Sn (1.04mmol) on the R-Ni/AlOH to form Ni-Sn(3.0)/AlOH; 3.0 is Ni/Sn molar ratio remarkably enhanced the selectivity towards hydrogenation of C=O rather than C=C giving high yield of unsaturated alcohols. The Ni-Sn(3.0)/AlOH alloy was also found to be reusable without any significant loss of selectivity for at least six consecutive runs.

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