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Development of Nanoporous Ni-Sn Alloy and Application for Chemoselective Hydrogenation of Furfural to Furfuryl Alcohol

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Abstract

A very simple synthetic procedure was developed for the preparation of Ni-Sn alloy catalysts that were utilised for chemoselective hydrogenation of furfural, producing furfuryl alcohol almost exclusively. The mixture of nickel nanoparticles supported on aluminum hydroxide (R-Ni/AlOH) and a solution containing tin was treated under hydrothermal condition, producing the as prepared nickel-tin alloy supported on aluminum hydroxide (Ni-Sn/AlOH). H_2 treatment at range of temperature of 673-873 K for 1.5 h to the as prepared Ni-Sn/AlOH produced nanoporous Ni-Sn alloy catalysts. XRD patterns and SEM images revealed that the formation of Ni-Sn alloy of Ni_3Sn and Ni_3Sn_2 phases and the transformation of crystalline gibbsite and bayerite into amorphous alumina were clearly observed after H_2 treatment at 873 K. The formation of the Ni-Sn alloy may have played a key role in the enhancement of the chemoselectivity. © 2014 BCREC UNDIP. All rights reserved

Keywords: nanoporous Ni-Sn alloy; chemoselective hydrogenation; furfural; furfuryl alcohol

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1. Introduction

The chemoselective hydrogenation of the C=O bond in α,β-unsaturated ketones/aldehydes has been extensively studied because the unsaturated alcohols that the reaction forms are important in the production of a variety of fine chemicals [1]. The group-9 and group-10 metals, such as Rh, Ir, Ni, Pd, and Pt, are well known to generally hydrogenate the C=C bond more easily than the C=O bond of α,β-unsaturated aldehydes [2]. Despite extensive research [3-5], only Ir-, Os-, and Pt-based catalysts have thus far produced unsaturated alcohols [6-8]. To improve the chemoselective hydrogenation of the C=O group, the modification of the previously mentioned metals is necessary, i.e., the addition of more electropositive metals [9] or the use of oxide supports that strongly interact with the active metals [10]. Although these modified catalyst systems have been effective, catalyst preparation critically depends on the precise control of the amounts of the second metal [11-13]. Recently, the tin alloying of the platinum group has been extensively studied and widely applied in various chemical transformations [14,15]. Pt-Sn/SiO_2 showed a higher selectivity towards

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furfuryl alcohol (FFalc) rather than Pt/SiO_2 in the hydrogenation of furfural (FFald) [16,17]. 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 C=O rather than the C=C bond to form unsaturated alcohols in the hydrogenation of α,β-unsaturated aldehydes [18,19]. 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 C=O group over C=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 C=O hydrogenation could be controlled by changing the additive amount of Sn [20,21]. In the present work, we continue to describe the catalytic performances of our Ni-Sn alloy catalysts that were obtained according to the previous reported [20] in the selective hydrogenation of FFald to FFalc. The as prepared nickel-tin alloy supported on aluminium hydroxide (Ni-Sn(1.0)/AlOH; 1.0 = Ni/Sn molar ratio) was intentionally treated by hydrogen gas at the range of temperature of 573-873 K to confirm the formation of Ni-Sn alloy phases. The effects of the formed Ni-Sn alloy phases on the activity and selectivity in hydrogenation of biomass-derived furfural at various reaction conditions were studied.

2. Materials and Methods

2.1. Materials

Raney Ni-Al alloy (50 %wt of Ni and 50 %wt of Al) Kanto Chemical Co. Inc.), NaOH (WAKO, 97%), and $SnCl_2 \cdot 2H_2O$ (WAKO, 99.9%) 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, 22, 23]: 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(1.0)/AlOH, 1.0 is Ni/Sn ratio) is described as the follows [20]. R-Ni/AlOH that was obtained from the above procedure (Section 2.2.1) was mixed with a solution that contained 3.96 mmol $SnCl_2 \cdot 2H_2O$ at room temperature and stirred for 2 h. The mixture was placed into a sealed-Teflon autoclave reactor for the hydrothermal treatment at 423 K for 2 h. The resulting precipitate was filtered, washed with distilled water, and dried under vacuum overnight. The as prepared nickel-tin alloy supported on aluminium hydroxide (Ni-Sn(1.0)/AlOH; 1.0 = Ni/Sn molar ratio) was intentionally treated by hydrogen at the range of temperature of 673-873 K and produced the H_2-treated Ni-Sn alloy (denoted as Ni-Sn(1.0); 1.0 = Ni/Sn molar ratio).

2.2.3. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were recorded on a Mac Science M18XHF instrument using monochromatic CuKα radiation (l = 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 (α1 = 0.154057 nm, α2 = 0.154433 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 [24]. Scanning electron microscopy (SEM) images of the synthesised catalysts were taken on a JEOL JSM-610 SEM after the samples were coated using a JEOL JTC-1600 autofine coater.

The 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 [25,26].

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(1.5) 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 characterization

The bulk compositions of the synthesised Ni-Sn(1.0) alloy catalysts before and after H2 treatment are summarised in Table 1. The loading amount of Sn in the as prepared Ni-Sn(1.0)/AlOH is 3.96 mmol g^{-1} which is almost equal to the amount of Ni metal (entry 1). No change of the amount metals both Ni and Sn was observed after H_2 treatment at 673 K for 1.5 h (entry 2).

Table 1. Chemical compositions of the synthesised Ni-Sn(1.0) alloy catalysts before and after H_2 treatment

Entry	Catalyst[a]	LA of Ni[b] (mmol g^{-1})	LA of Sn[b] (mmolg^{-1})	Ni/Al[c]	Sn/Al[c]
1	Ni-Sn(1.0)/ AlOH	3.78	3.96	0.69	0.72
2[d]	Ni-Sn(1.0)	3.78	3.96	0.69	0.72

[a] The value in the parenthesis is Ni/Sn molar ratio

[b] LA=loading amount of Ni or Sn, determined by ICP-AES

[c] Molar ratio, determined by ICP-AES. [d]after H_2 treatment at 673 K for 1.5 h

BET specific surface area, total pore volume, and average pore diameter are summarised in Table 2. With the increase of temperature of H_2 treatment from 673 K to 873 K, BET specific surface area increased drastically from 26 m^2 g^{-1} to 126 m^2 g^{-1} (entries 2 and 4) which was comparable to the previous results for Ni-Sn(1.5)/AlOH alloy catalyst [21]. Interestingly, total pore volume and pore diameter also increased that reflected the formation of nanosized pores during the elevated temperature under H_2 atmosphere.

H_2 uptake and the active surface of Ni (S_{Ni}) that were obtained from reversible H_2 chemisorption and the results are summarised in Table 3. As the increase of temperature from 673 K to 873 K, H_2 uptake decreased slightly from 66 mmol g^{-1} to 56 mmol g^{-1} (entries 2 and 4). Active surface of Ni (S_{Ni}) also decreased as the increase of temperature of H_2 treatment. The H_2 uptake and S_{Ni} of the synthesised Ni-Sn(1.0) alloy catalysts is much higher than that of the previous results for Ni-Sn(1.5) supported on the various inorganic supports and the bulk Ni-Sn(1.5) catalysts [21]. We suggested that the high H_2 uptake and S_{Ni} of the present Ni-Sn(1.0) alloy catalysts due to the high dispersion both Ni metal and Ni-Sn alloy species.

The XRD patterns of the as prepared Ni-Sn(1.0)/AlOH and H_2-treated Ni-Sn(1.0) catalysts are shown in Figure 1. Ni-Sn(1.0)/AlOH showed the sharp diffraction peaks at 2θ = 18.26°, 27.8°, and 40.54° that were recognised to bayerite and at 2θ = 18.7°, 20.36°, 36.66°, 37.76° and 53.18° which were assigned to gibbsite (Figure 1a) [27]. After H_2 treatment at 673 K, the evolution of Ni-Sn phase formation was

Table 2. BET surface area (S_{BET}), total pore volume (V_p), and average pore diameter (d_{pore}) for Ni-Sn(1.0) before and after H_2 treatment at 673-873 K

Entry	Catalyst[a]	Temp. of H_2 treatment (K)	S_{BET}[b] (m^2g^{-1})	V_p[b] (cm^3g^{-1})	d_{pore}[c] (nm)
1	Ni-Sn(1.0)/AlOH	as prepared	72	0.039	2.8
2	Ni-Sn(1.0)	673	26	0.040	4.9
3	Ni-Sn(1.0)	773	61	0.086	5.7
4	Ni-Sn(1.0)	873	126	0.079	5.6

[a] The value in the parenthesis is Ni/Sn molar ratio

[b] Determined by N_2 adsorption at 77 K

[c] Calculated according to BJH approach

observed at 2θ of 30.3°, 38.6°, 43.5°, 44.6° and 44.8° that recognised as Ni_3Sn_2(101), Ni3Sn(102), Ni_3Sn_2(110), and Ni_3Sn(201), respectively [27] (Figure 1b). On the other hand, the diffraction peaks of bayerite and gibbsite completely disappeared after H_2 treatment at 673 K indicating the transformation of crystalline bayerite or gibbsite into amorphous alumina which have no detectable peaks in XRD analysis [28,29]. In addition, the diffraction peaks of Ni metal at 2θ of 51.6° and 76.2° corresponding to Ni(200) and Ni(220) were also observed. The formation of Ni-Sn alloy phases such as Ni_3Sn and Ni_3Sn_2 was clearly observed and intensified after H_2 treatment at 773 K and 873 K for 1.5 h (Figure 1c and 1d).

Table 3. H_2 chemisorption results for Ni-Sn(1.0) alloy catalyst before and after H_2 treatment at 673-873 K

Entry	Catalyst[a]	Temp. of H_2 treatment (K)	H_2 uptake[b] (μmol g^{-1})	S_{Ni}[b] ($m^2 g^{-1}_{cat}$)
1	Ni-Sn(1.0)/AlOH	*as prepared*	73	48.0
2	Ni-Sn(1.0)	673	66	32.1
3	Ni-Sn(1.0)	773	59	24.4
4	Ni-Sn(1.0)	873	56	21.3

[a] The value in the parenthesis is Ni/Sn molar ratio.
[b] Based on total H_2 uptake at 273 K (noted after corrected for physical and chemical adsorption)

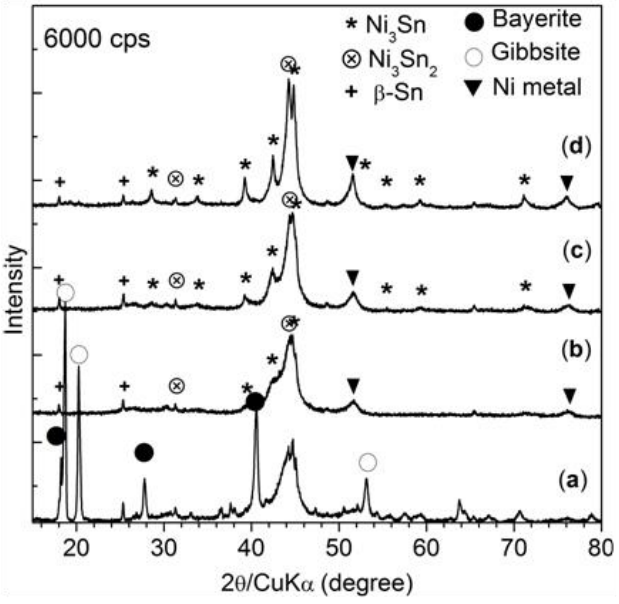


Figure 1. XRD patterns of Ni-Sn(1.0) before and after H_2 treatment; (a) as-prepared, (b) 673 K (c) 773, and (d) 873 K.

Scanning electron microscopy (SEM) images for Ni-Sn(1.0)/AlOH before and after H_2 treatment revealed that the morphological differences between the as-prepared and H_2-treated samples are readily visible in the Figure 2. The as-prepared Ni-Sn(1.0)/AlOH is constituted by Ni-rich angular particles and irregularly oriented Al-rich crystal-like particles. Besides the spongy morphology of Ni, the Al-rich region contains hexagonal prismatic rods and spiral crystals constructed by plates stacking perpendicular to the longitudinal axis, which are characteristic morphologies of gibbsite and bayerite, respectively (Figure 2a) [30-32]. The characteristic morphologies of Al-rich region were maintained and become more rigid after H_2 treatment at 873 K (Figure 2b).

3.2. Hydrogenation of furfural

Results of the selective hydrogenation of FFald using supported Ni-Sn(1.0) alloy catalysts are summarised in Table 4 and the reaction pathways are shown in Scheme 1. It can be observed that by using the as prepared Ni-Sn(1.0)/AlOH catalysts, FFalc yield was 91 % while tetrahydrofurfuryl alcohol (THFalc) yield was 6 %, respectively (entry 1). After H_2 treatment at 673 K for 1.5 h, Ni-Sn (1.0)/AlOH cata-

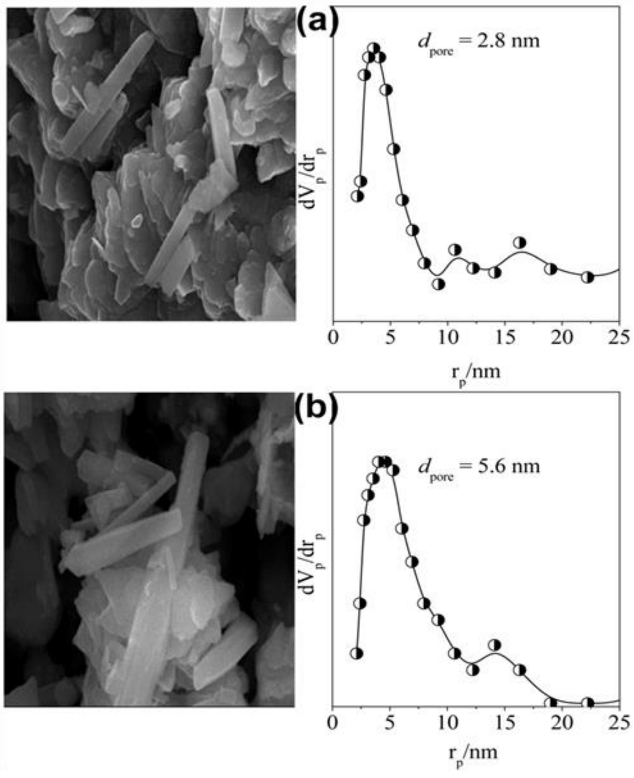
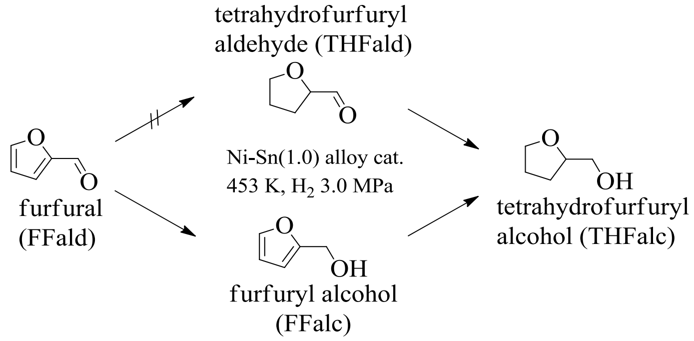


Figure 2. SEM images and average pore diameter of Ni-Sn(1.0) (a) as-prepared and after H_2 treatment at (b) 873 K for 1.5 h.



Scheme 1. Reaction pathways of FFald hydrogenation by supported Ni-Sn (1.0) alloy catalyst

Table 4. Results of FFald hydrogenation over various Ni-Sn alloy catalysts

Entry	Catalyst[a]	Temp. of H_2 treatment (K)	Conv. (%)	Yield[b] (%)	Select.[c] (%)	TOF s[d]/h
1	Ni-Sn(1.0)/AlOH	as prepared	97	97	91(6)	39
2	Ni-Sn(1.0)	673	>99	90	90(10)	39
3	R-Ni/AlOH	-	>99	0	0(100)	-
4	Sn/AlOH	673	0	0	0	-

[a] The value in the parenthesis is Ni/Sn molar ratio. Reaction conditions: FFald, 1.1 mmol (FFald/Ni ratio=15); iso-PrOH (3 mL); H_2, 3.0 MPa, 453 K, 75 min.

[b] Yield of FFalc, determined by GC using an internal standard technique.

[c] Selectivity to FFalc. The value in the parenthesis is the selectivity to THFalc.

[d] Turnover frequency, calculated based on the mole of FFalc to the amount of active Ni metal per hour

lyst gave 90 % and 10 % yields of FFalc and THFalc, respectively (entry 2). On the other hand, R-Ni/AlOH converted FFald to give >99% THFalc (entry 3), indicating that R-Ni/AlOH hydrogenated both C=C and C=O of FFald. Moreover, Sn/AlOH was not active as catalysts and did not produce the hydrogenated products under the same conditions (entry 4). Therefore, we conclude 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 FFalc rather than THFalc. These results 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)

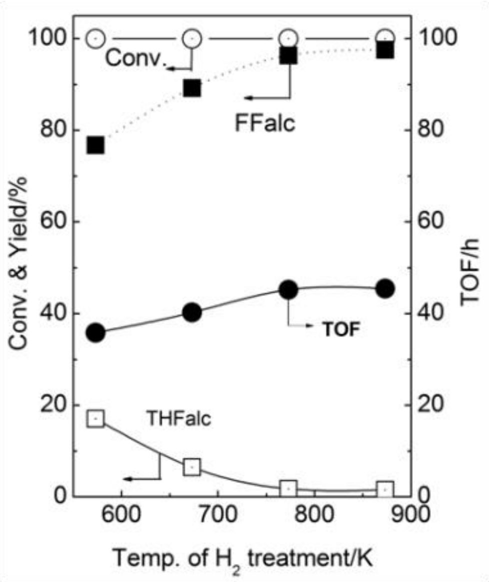


Figure 3. Effect of H_2 treatment on conversion, yield, and TOF. Reaction conditions: FFald, 1.1 mmol (FFald/Ni ratio = 15); iso-PrOH (3 ml); H_2, 3.0 MPa, 453 K, 75 min

The H_2-treatment of the as prepared Ni-Sn(1.0)/AlOH at various temperatures and evaluation of its catalytic performances in furfural hydrogenation were carried out. The conversion, yield, selectivity, and turn over frequency (TOF) as a function of temperature of H_2 treatment are shown in Figure 3.

FFald was completely converted into FFalc (>99 % yield) whereas THFalc was retained (~1.0 % yield) after H_2 treatment at 773 K. On the other hand, TOFs slightly increased as an increasing of temperature and retained at 45 h^{-1} at 773 K. These results are consistent with the previous works that the formation of alloy phases such as Ni_3Sn and Ni_3Sn_2 are believed to be responsible for the high chemoselectivity towards C=O bond [20,21].

4. Conclusions

Nanoporous Ni-Sn alloy catalysts have been successfully synthesised by simple procedure. The catalysts exhibited highly active and chemoselective for hydrogenation of furfural produced furfuryl alcohol almost exclusively. The formation of the Ni-Sn alloy possibly plays a key role in the enhancement of the chemoselectivity.

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